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Yield of intermediate products in the drought process of wheat milling

Yevgen Kharchenko[1], Andrii Sharan[1], Olena Yeremeeva[2], Larysa Novak[2]

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Abstract

Introduction. In order to determine the yield of intermediate milled products, the process of crop formation during the milling of wheat into varietal flour has been investigated.

Materials and methods. On the first three break systems, intermediate milling products under the rollers were selected and sifted to determine the mode of operation of the systems, and then pass fractions were sieved on sieves to determine the yield of individual product fractions. The results of the research were presented as a dependence of "general product – yield fraction".

Results and discussion. The output of all milling products on the first break system, depending on the milling mode, is nonlinear. On the second break system, the only dependence on the yield of small middlings and superfine flour is linear, and the yield of large and medium middlings, as well as flour has a nonlinear character. On the third break system, the large dependence of the yield of products on their milling regimes, all milling products except the yield of the small middlingshave a nonlinear character. On the third break system, the small linear dependencies of the yield of products from the milling regime are only superfine flour and flour, the remaining products are nonlinear in nature.

With an increase in the total product of intermediate shredding products from 29,4% to 56,6%, on the 1st system there was an extremum of the output of large grains at 40,0%. On the second tread system, with an increase in the total product of intermediate shredding products from 46,5% to 72,0%, an extreme average yield of cereals at 60,0% was observed. At the third trench system, an extreme release of superfine flour at 35,5% was observed at a general level of 11,9% to 40,6% of intermediate products. With an increase in the total product of intermediate milling products on the third trench system from 22,6% to 47,9%, an extremum of the output of small middlings was observed at 46,4%. Determined extremums are optimal values of intermediate products yield of three break systems.

Conclusions. The given dependences of the output of separate fractions of wheat grain milling products are recommended for calculations of quantitative balances of varietal mills.

Introduction

Investigation of wheat grain milling is an actual scientific problem, in connection with the fact that the grain milling function has not been invented due to its complexity [1–5, 8–14, 16, 19].

The function of grain milling is important from the practical point of view, and also necessary for calculating the quantitative balance of the technological process, on the basis of which the calculation of technological equipment of the milling unit and pneumatic transport [6]. Many researchers investigated milling of grain in rollers Campbell G.M., Fistes A., O.Vereschinskii and other researchers. Campbell G.M., Fang C., Muhamad I.I., Webb C., Bunn P.J., Hook S.C.W., Sadhukhan J., Mateos-Salvador F. [1-4, 8, 9, 16, 17] suggested the function of milling wheat grain for the I drowning system, which relates the size of the gap between rollers of the roller machine, the moisture content of the grain and its strength. A. Fistes, G. Tanovic, J. Mastilovic, M. Bardar, A. Takaci, D. Rakic [10-13] proposed a matrix method for calculating granulometric composition of milling products. The function of milling wheat grain on each separate technological system remains unknown [19].

In order to solve the problems of calculating the quantitative balance of grain milling in wheat flour, it is proposed to use dependencies that connect the output of individual fractions of intermediate products from their total product for the first three break systems. These dependencies have a rectilinear form [15, 18]. In practice, grain milling in rollers is known to reduce the distance between the rollers by shredding large products into small ones.

Linear dependencies between the output of cereals and dunes and the general product of these products are contrary to the phenomenon of grain milling [19].

Taking into account the above, it is relevant to carry out research into the establishment of the output of individual fractions of intermediate products and their total product in the first three break systems.

This will allow the calculation of the output of individual classes of intermediate shredding products when compiling the quantitative balance of milling grain of wheat into varietal flour.

The object of the study is a quantitative assessment of the process of crushing low-viscid grain wheat in the wheat miller.

The output of individual fractions of intermediate shredding products from their general product was investigated.

Materials and methods

Materials

During the research wheat grain was processed with the following quality indices: grain weight – 791 g/l, grain moisture content on the I drought system – 16,2%, vitreousness – 38%, garbage impurity – 0,4%, grain impurity – 2,3%.

Methods

Milling of grain. The milling of wheat grain was carried out in the production conditions in rollers, and the technical characteristics of the rollers are given in table. 1. The technological process was carried out according to the scheme shown in Fig.1

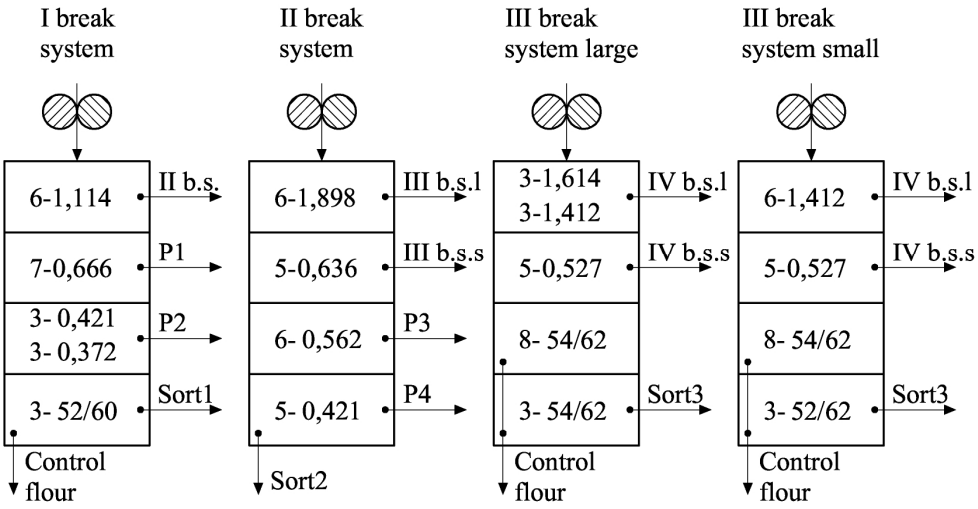

Figure 1. Scheme of tedious process

The formation of intermediate shredding products is carried out according to the following scheme: the technological process of crop formation in wheat mills includes three break systems, and the third break system is divided into large and small ones. The grain is fed to the I system, is crushed and transmitted by pneumo transport to the raiser, which sifted on the sieves.

The first east is sent to the roller mill of the second trample system. The second east in the form of a large gravy goes to the sieve system №1 for enrichment. The third step in the form of an average grits is directed to the sieve system №2 for enrichment. The third approach in the form of a mixture of small grains and dunes is directed to sorting system №1 for division into separate products. The first pass is high quality flour, which is sent to the collecting conveyor.

The crushed product in the roller II of the tidal system is pneumatically transported to the raiser. The first east is fed into a roller mill of the third large system. The second east is fed into a roller mill of the third tiny system of small. The third step in the form of large grains and shells is fed to the sieve system №3 for enrichment. The fourth east as a medium miller is fed to the sieve system №4 for enrichment. A passage in the form of a mixture of small grains, dunes and flour is fed into the raiser of the sorting system number 2 for division into separate products.

The crushed product in the roller II of the tidal system is pneumatically transported to the raiser. The first east is fed into a roller mill of the third large system. The second east is fed into a roller mill of the third tiny system of small. The third step in the form of large grains and shells is fed to the sieve system №3 for enrichment. The fourth east as a medium miller is fed to the sieve system №4 for enrichment. A passage in the form of a mixture of

small grains, dunes and flour is fed into the raiser of the sorting system number 2 for division into separate products.

The crushed products in the roller system of the third trench of the small system are fed pneumatic transport in the raiser for sorting. The first east is fed into the rolling machine IV of the break system of the large, and the second east is fed into the roller system IV of the break system of fine crushing. The third step in the form of a mixture of medium and small grains, as well as dunts, is fed into the raiser of the sorting system number 3. The passage gives off flour, which is fed to the control.

The selection of samples of milling products was carried out directly in the technological process as soon as the products passed through the rollers of the rollers.

Table 1

Kinematical and geometrical parameters of roller work

System	Number of rifts on I cm of roller coil, R, pc.	Slope of the rifts, Y,%	Coincidence of rotation speeds of rollers, K.	Speed of rotation of the speed roll, V, m / s	Mutual arrangement of riffles	Angles of inclination of rifts, deg.	Roller size
I b.s.	4	6	2,5	6	dull to dull	30°/65°	1000×250
II b.s.	5,4	6	2,5	6		30°/65°	1000×250
III b.s.l	6,5	6	2,5	6		30°/65°	1000×250
III b.s.s	7,5	6	2,5	6		30°/65°	1000×250

Sampling and determination of the general product of shredding products. Changing the milling regimes and sampling were carried out as follows: during the work of the milling unit on each tread system, the entire length of the roller was selected with the help of a tray product in quantities up to 300 g. After the product was selected with a helmet, which is equipped with rollers, they changed the distance between the rollers and repeatedly carried out the selection of the product along the entire length of the roller.

After selecting the shredding products, all selected and weighed samples were sieved on the control sieves to determine the total product of the intermediate products. The selection of milling products was carried out from the third trunks system to the first to avoid the effects of shredding regimes on the next system. For the 1st and 2nd trench systems, sifting of the milling products was carried out on a control metal sheet with the dimensions of the apertures of 1000 μm, for the third trench of large and small sieving carried out on the control sieve 560 μm.

The total product of intermediate products of crushing, which characterized the operating mode of the roller was calculated by the formula:

$$B_o = (\frac{m_n}{m_g} - N) \cdot 100 \quad (1)$$

where B_o – total product of intermediate shredding products,%; m_n – is the total mass of the sample after the roller, g; m_g – mass of the passage of the control sieve, g; N – shortcomings, g.

The shortcomings were determined by taking the chopping products before they arrived on the rolls of the roller. The product after sifting was screened on control sieves, was converted into interest and taken into account when calculating the yield of individual fractions of milling products. In the event that lack of attention was not observed during calculations were not taken into account. The following sieves were used to determine the underdevelopment: for I and II break systems – 1000 μm, for the third break system – 560 μm.

Quantitative evaluation and classification of milling products. The passage fraction was weighed after sifting and then scattered on sieves with apertures of 560 μm, 390 μm, 250 μm, 160 μm, and 132 μm. The 132 μm sieve was extracted with flour. The yield of individual fractions of crushing products was characterized as the passage and the east of the screen, the dimensions of which holes are shown in table 2

Table 2

Classification of wheat grain milling products in roller mills

№	Product name	Particle size range, μm	
		Pass sieve	East sieve
1	Large middlings	1000	600
2	Medium middlings	600	390
3	Small middlings	390	250
4	Superfine flour	250	160
5	Flour	132	–

After sifting, each passing fraction of the product was weighed and converted to a percentage by the formula 2:

$$B_i = (\frac{m_i}{m_g} - N) \cdot 100 \quad (2)$$

where, B_i – yield of the i-th faction,%; m_g – is the total mass of the sample after the roller, g; m_i – mass of the i-th product obtained after sieving, g; N – shortcomings.

Mathematical and statistical processing. On the basis of the obtained values, the dependencies in coordinates were constructed "the total product of the intermediate shredding products – the yield of the fraction of the product". On the basis of experimental data, using the least squares method, the yield equation of each individual product was

calculated (large middlings, medium middlings, small middlings, superfine flour, flour) from general products.

Method of determination of quality indices of processed wheat grain. The moisture content of the grain was determined by drying the weight of the crushed product weighing 5 g for 40 minutes in the drying cabinet of SESH-3M at 130 °C [7, 20].

Humidity of grain W was calculated by the formula:

$$W = \frac{m_0 - m_1}{m_0} \cdot 100 \quad (3)$$

where, m_0 – weight of weight loss before drying, g.; m_1 – weight of weight loss after drying, g.

The grain weight was determined on a litter purity by weighing 1 liter of grain.

The total vitreousness was determined by means of a diaphragm, by means of a sight-glass eyepiece of a diaphanoscope of 100 grains. To completely glassy grains were counted such that they were completely luminous, and to the mealy – completely not enlightened grains. Grains with partially translucent or partially non-translucent endosperm were attributed to partially glassy grains. General vitality was determined by the formula:

$$V = C + \frac{P}{2} \quad (4)$$

where C – number of fully glassy seeds, pcs.; P – the number of partially glassy seeds, pcs.

The common glasswidth was calculated with rounding to an integer.

Smear and grain impurities were determined by sieving weights of 50 g from the average sample in laboratory sieves of 1,7×20 mm and 1,0. After sifting, all ladders were individually dismantled on a collapsible board, separating whole grains, garbage impurities and grain additives separately. Passage was attributed to garbage impurity [19].

Results and discussion

Yield of the intermediate product and the milling on the 1st drowning system

Investigations of the outflow of droplets, dunsters and flour on the I-droplet system have shown that with an increase in the total product of intermediate products (1000 μm sieve) from 29,4% to 56,6%, the yield of these products has a curvilinear polynomial character that is different from those data, which are presented by a number of researchers.

With an increase in total product of intermediate products from 29,4% to 56,6%, the yield of large grains decreased by 2,6% from 12,9% to 10,3%. The research also found that the dependence of the yield of large grains on the total product of intermediate products has an extremum and achieves a maximum value within the limits of 37,0–45,0%, with the yield of large grains respectively ranging from 15,5–15,6%.

The results of the research are shown in Figure 2. The yield of medium, small grains, dunes and flour has a growing nonlinear character with an increase in the total.

With an increase in the total production of milling products on the I drowning system from 29,4% to 56,6%, the average grain yield increased by 10,1% from 7,9% to 18,0%; the yield of small grains increased by 3,8% from 2,4% to 6,2%; the yield of dunstids increased by 8,7% from 3,9% to 12,6%, and yield of flour increased by 7,3% from 2,2% to 9,5%.

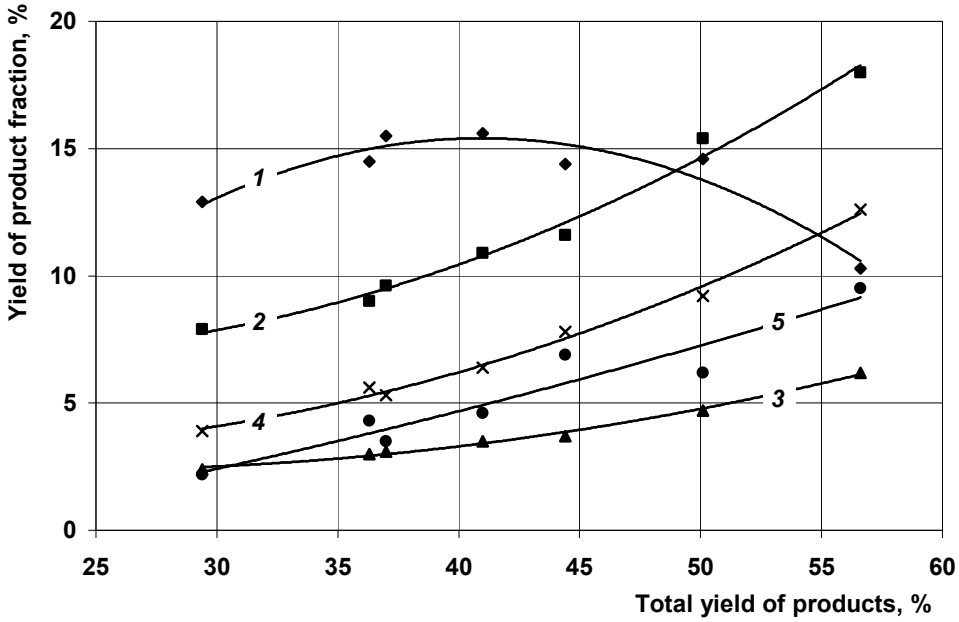

Figure 2. Yield middlings, superfine flour and flour depending on the mode of operation of the first break system:
1 – large middlings; 2 – medium middlings; 3 – small middlings; 4 – superfine flour; 5 – flour.

The presence of the extremum of the curve of the exit of the large middlings has the following explanation: an increase in the yield of the medium middlings, small middlings, superfine flour and flour is due to the redistribution of large grains into smaller milling products with an increase in the total product of the products on the 1st droplet system, as evidenced by the declining nature of the curve of the exit of the large grains with the general product of milling products more than 40% and the growing nature of the curves, which describe the yield of all other grain milling products of wheat on the I-ration system.

The mathematical processing of the experimental data obtained from the yield of intermediate shredding products on the I-droplet system made it possible to establish equations that describe the yield of individual product fractions from their total product:

Yield of large middlings:

$$B_{lm} = -0,0196B^2 + 1,605B - 17,45 \quad (5)$$

Yield medium middlings:

$$B_{mm} = 0,00805B^2 - 0,305B + 9,79 \quad (6)$$

Yield of small middlings:

$$B_{sm} = 0,0034B^2 - 0,163B + 4,3 \quad (7)$$

Yield of superfine flour:

$$B_{sf} = 0,0061B^2 - 0,215B + 5,05 \quad (8)$$

Yield of flour:

$$B_f = 0,0016B^2 + 0,113B - 2,44 \quad (9)$$

where, B_{lm} – yield of large middlings,%; B_{mm} – yield of the medium middlings,%; B_{sm} – yield of small middlings,%; B_{sf} – yield of the superfine flour,%; B_f – yield of flour,%; B – is the total product on the system (1000 μm sieve passage),%.

The same kind of dependence was obtained by Vereshchinsky O.P. [19] when milling wheat grain in a laboratory roller mill with a roller diameter of 185 mm (Figure 3), which confirms the objectivity of the research.

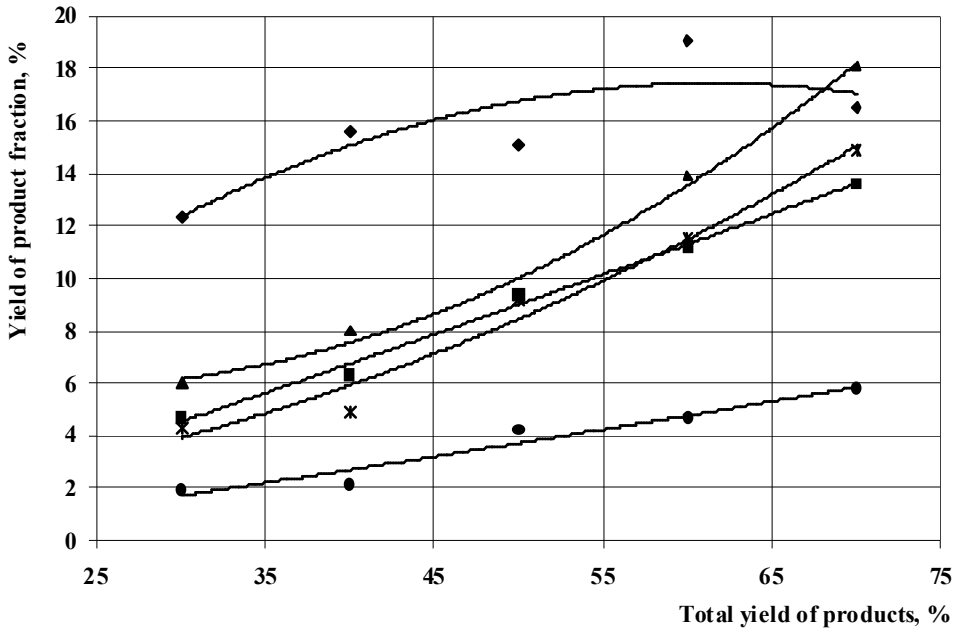

Figure 3. Yield of intermediate shredding products in a laboratory roller mill [19]: 1 – large middlings; 2 – medium middlings; 3 – small middlings; 4 – superfine flour; 5 – flour.

Figure 2 and 3 indicate the nonlinear nature of the dependence of the yield of individual intermediate shredding products on their overall product when chopping in a roller machine on the 1st droplet system.

Yield of intermediate products and milling on the second tread system

Investigations of the operating regime of the II tram system have established that with an increase in the total product of intermediate products from 46,5% to 72,0%, the yield of large, medium grains and flour is nonlinearly increasing, while the yield of small middlings and superfine flour is increased with increasing production of total products on II from 46,5% to 72,0%. The results of the research are shown in Figure 4.

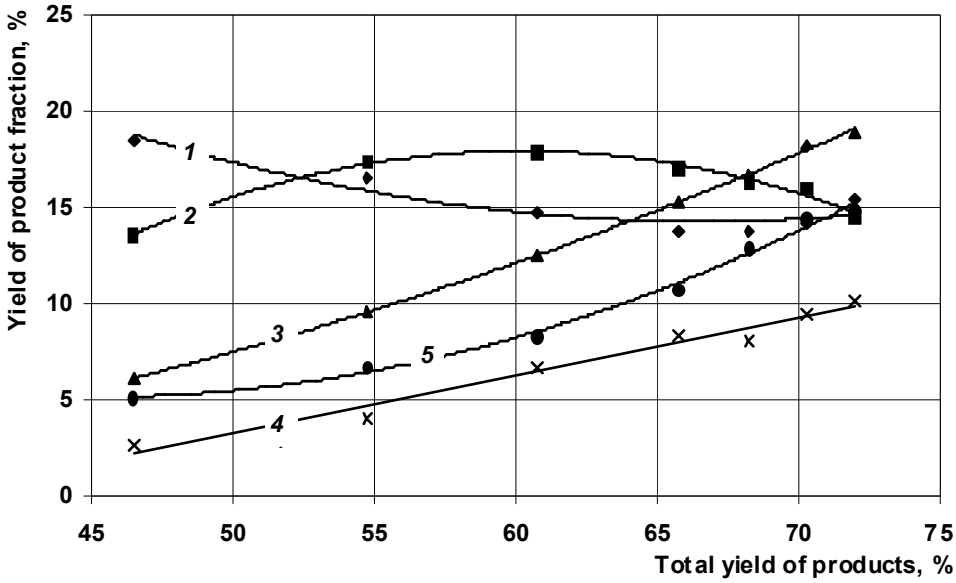

Figure 4. Yield middlings, superfine flour and flour depending on the milling mode of the second break system:
1 – large middlings; 2 – medium middlings; 3 – small middlings; 4 – superfine flour; 5 – flour.

With the increase in the total product of shredding products from 46,5% to 72,0% (1000 μm sieve) on the second trench system, the yield of large middlings decreased by 3,0%, from 18,5% to 15,5%. From the given Figure 4, it can be seen that with the increase in the total product of milling products on the second trench system, the yield of large grains decreases steadily, and the yield of small middlings, superfine flour and flour is constantly increasing.

The yield of the medium middlings with the increase in the total product of intermediate milling products in the specified limits varied from 13,6% to 14,6%, while the dependence of the yield of the average middlings has an extremum, which allows to determine the milling mode, which achieves the largest yield of the average middlings. The presence of an extremum within the overall value of 60% suggests that the increase in the total product of milling products above 60% leads to the redistribution of not only large grains into smaller products (small middlings, superfine middlings and flour) but also the medium middlings.

The yield of small middlings with an increase in the total product of intermediate shredding products from 46,5% to 72,0% increased by 12,8% from 6,2% to 18,9%, and the yield of superfine flour increased by 7,5%, namely from 2,7% to 10,2%.

With an increase in the total product of intermediate shredding products from 46,5% to 72,0%, the flour yield increased by 9,7% from 5,2% to 14,9%.

In studies of the mode of operation of the II system, the operating mode of the I system was 37,9% on average.

On the basis of experimental data, dependences were obtained that describe the yield of individual fractions of the milling products of the II tram system from their total product:

Yield of large middlings:

$$B_{lm} = 0,0111B^2 - 1,48B + 63,66 \quad (10)$$

Yield medium middlings:

$$B_{mm} = -0,0228B^2 + 2,7501B - 64,91 \quad (11)$$

Yield of small middlings:

$$B_{sm} = 0,508B - 17,9 \quad (12)$$

Yield of superfine flour:

$$B_{sf} = 0,298B - 11,6 \quad (13)$$

Yield of flour:

$$B_f = 0,014B^2 - 1,27B + 34,09 \quad (14)$$

where B_{lm} – yield of large middlings,%; B_{mm} – yield of the medium middlings,%; B_{sm} – yield of small middlings,%; B_{sf} – yield of the superfine flour,%; B_f – yield of flour,%; B – is the total product on the system (1000 μm sieve passage),%.

Yield of intermediate products and milling on the third trench system

On the third break system, the first east of the second trench system, which contains a significant amount of endosperm, is crushed. The crushed product consists of medium middlings, small middlings, superfine flour and flour. Large middlings were not found in shredding products. The research has established that with an increase in total product (560 μm sieve passage) from 11,9% to 40,6%, the yield of the product, which was classified as an average grains, increased by an average of 15,5% from 1,9% to 17,4% , the yield of small middlings decreased by 3,1% from 2,6% to 5,7%, the yield of superfine flour increased by an average of 2,4% from 1,7% to 4,1%, and the yield of flour increased by an average of 7,4% from 5,4% to 12,8%.

From the given Figure 5 it can be seen that the yield of the medium middlings, superfine flour and flour, depending on the general product of the milling products on the third break system, is of a nonlinear nature, and the yield of small middlings is linear. From

the given Figure 5 it can be seen that with an increase in total production from 11,9% to 40,6%, the yield of superfine flour has an extremum with a total product of crushing products 35,5%.

During investigations of the operating modes of the III tidal system of large and small, the average product of intermediate products of crushing II tram system was 64,3%.

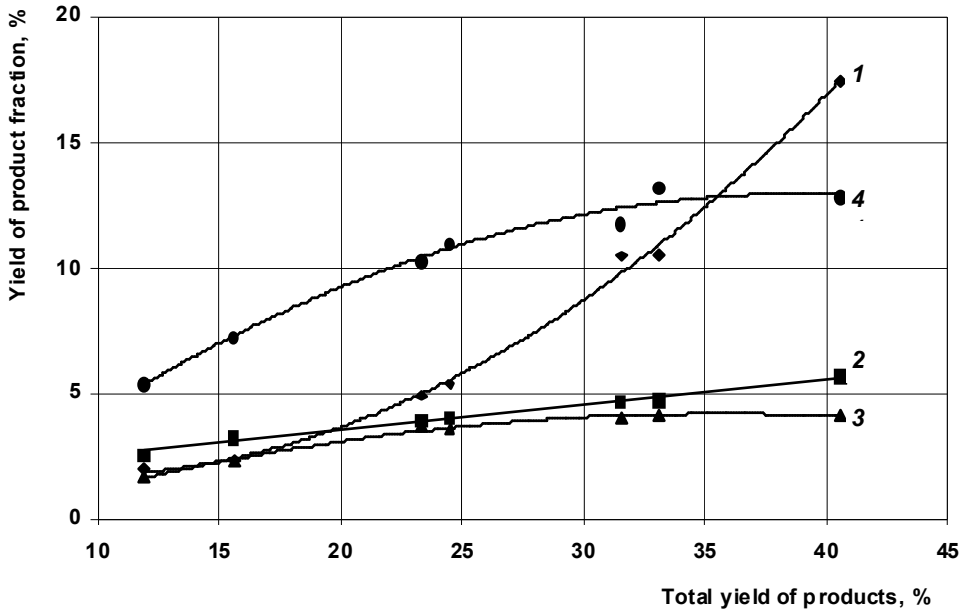

Figure 5. Yield middlings, superfine flour and flour depending on the milling mode of the third break system of large:
1 – medium middlings; 2 – small middlings; 3 – superfine flour; 4 – flour

On the basis of experimental data the dependences of yield of separate fractions of milling products of the third break system of large of their general product were obtained:

Yield medium middlings:

$$B_{mm} = 0,0154B^2 - 0,26B + 2,74 \quad (15)$$

Yield of small middlings:

$$B_{sm} = 0,101B + 1,51 \quad (16)$$

Yield of superfine flour:

$$B_{sf} = -0,0045B^2 + 0,32B - 1,54 \quad (17)$$

Yield of flour:

$$B_f = -0,0104B^2 + 0,81B - 2,77 \quad (18)$$

where B_{mm} – yield of the medium middlings,%; B_{sm} – yield of small middlings,%; B_{sf} – yield of the superfine flour,%; B_f – yield of flour,%; B – is the total product on the system (560 μm sieve passage),%.

Investigations of the milling regimes of products on the third trench system of small ones showed that with an increase in the total product of intermediate shredding products from 22,6% to 47,9%, the yield of the average grits increased by 2,3% from 14,0% to 16,3%, and in the general product of 33,1% there is an extremum of the function with a minimum value at which the yield of the average cream was 13,6%. The yield of small middlings increased by 8,0% from 3,3% to 11,3%, the yield of superfine flour increased by 7,2% from 1,4% to 8,6%, while the yield of flour increased by 8,2% from 3,8% to 12,0%. The results of the study of the yield of circular dendrobates and flour during the milling of stair products on the 3rd drowning system are given in Figure 6.

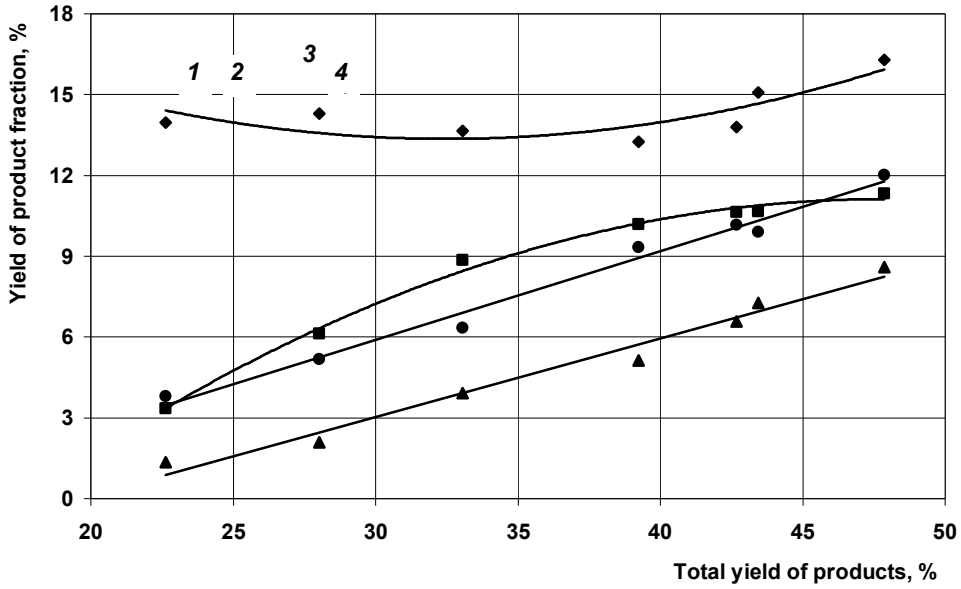

Figure 6. Yield middlings, superfine flour and flour depending on the milling mode of the third break system of small:
1 – medium middlings; 2 – small middlings; 3 – superfine flour; 4 – flour.

With an increase in the total product of intermediate products and milling from 22,6% to 47,9%, the yield of small middlings had an extreme of 46,4%.

From the given Figure 6 it can be seen that the dependence of the yield of medium and small middlings, depending on the general product of the products on the third trench system, is of a nonlinear nature, and the dependence of the yield of superfine flour and flour is linear in nature.

The processing of experimental data allowed us to obtain equations that describe the yield of individual fractions of milling products on the third trench system of small ones from their total product:

Yield medium middlings:

$$B_{mm} = 0,0112B^2 - 0,73B + 25,31 \quad (19)$$

Yield of small middlings:

$$B_{sm} = -0,0128B^2 + 1,19B - 17,25 \quad (20)$$

Yield of superfine flour:

$$B_{sf} = 0,29B - 5,68 \quad (21)$$

Yield of flour:

$$B_f = 0,32B - 3,91 \quad (22)$$

where, B_{mm} – yield of the medium middlings,%; B_{sm} – yield of small middlings,%; B_{sf} – yield of the superfine flour,%; B_f – yield of flour,%; B – is the total product on the system (560 μm sieve passage),%.

Comparing the results of studies with similar data from other researchers [15, 18], it can be seen that the yield of intermediate shredding products of the first three break systems has a nonlinear character for most middlings products, which confirms the crushing of large particles in the finer ones in the process of milling grain in flour.

Conclusions

The yield of intermediate milling products from their total product for many products of the first three break systems has a nonlinear character. The mathematical dependences of the yield of individual fractions of the milling products of the first three break systems from their total product are obtained. It is recommended to use them for the development of quantitative balances of milling of low-viscid grain wheat.

The scientific novelty consists in deepening the theory of milling of low-viscid grain of wheat in the case of varieties of wheat mills, as well as substantiation of the change of the yield of separate fractions of intermediate products of milling from the general product of these products on the first three break systems according to the curvilinear law.

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Application of sago pith waste and nanosilica from rice husk ash as hybrid bio-nanofiller composite for food plastic packaging

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Abstract

Introduction. Agricultural wastes such as Rice Husk Ash from rice (Oryza sativa) (RHA) and Sago Pith (Metroxylon sago sp.) (SP) wasted in thousand ton every harvest season. Both waste contain relatively high in silica and cellulose accordingly that can be utilized as bio-composites for degradable plastic.

Materials and methods. Nanosilica from RHA was obtained through sol-gel method and SP was refined through acid washing method. The experiment performed through pressure test, water immersion and heat absorbtion through microwave.

Results and discussion. The formulated sample has crosslinking of the hybrid filler with the PLA (Polylactic Acid) matrix which effectively improves hardness and density properties in PLA (amount 61%). This is found in combination of nanosilica, SPW fibre and PLA (60:20:20). In the water absorbtion test, the modified samples indicates insignificant water-resistant behaviour with effective combination silica : SPW fiber amount 20:10. This combination has complex barrier that inhibiting water molecule to infiltrate into the matrix compound. During heat exposure test, all modified biocomposites sample shown higher temperature than standart PLA yet the value is less significant. However, this might have been caused by the nanosilica composite exhibited an excellent thermal insulation and slow thermal desorption during thermal exposure that be accumulated in the polymer matrix and distributes higher temperature in modified biocomposites than pure PLA.

Conclusions. Although still need further research for safety aspect, this found shows high potential possibility of agricultural wastes generated as eco-friendly food and beverages packaging. Furthermore, this hybrid composite is able to reduce the usage of common plastics and styrofoam as container due to similarity shared by this composite in terms of common plastic physical and chemical characteristics.

Introduction

Substitutions for plastic composite have been the subject of rapid expansion in the development and application of food packaging recently [1-3]. However, the primary drawback of using fillers or composites as the reinforcement lies in the poor interfacial adhesion between hydrophilic composite materials and hydrophobic plastics, which results in poor mechanical properties of the final composites. Improvement of bonding interaction between matrix and composites can be achieved by modifying the filler-plastics surface.

Globally, 480 million metric tons of milled rice is produced each year, which contain 96 million metric tons of husks (20%) [4, 5]. After completely burning these husks at 700 °C for 6 h Rice Husk Ash (RHA) contains more than 90% of silica [6, 7]. Silica exists as a polymer in the form of SiO_2 then joining together to form the complex compound (SiO_4). Silica is widely used as a catalyst, filler, adsorbents, and gases separator. To increase the mechanical properties such as strength, durability and thermal stability, silica is converted to nano size that also make silica particle evenly distributed. Several techniques have been founded to prepare nanosilica yet the most common method is through sol-gel method [8,9].

The research of renewable resource has been developed and continues to emerge the making of bio-plastic material especially for production organic-inorganic hybrids types driven by petroleum resources depletion and global warming. Both sago pith and rice husk ash are available in huge quantity and has almost no to very low commercial value in raw condition [10, 11]. The hybrid component of organic-inorganic research is now gaining a wide interest along with nanotechnology application since it poses significant improvement of mechanical properties [12] such as improve strength, thermal stability , gases barrier characteristic, resistance to solvent, adhesive force, and controlled gradient properties [13]. Generally there are three methods to synthetize Nano-scale material with identical size i.e.: sol-gel, layered organic–inorganic assembly and bio-mineralization method [14, 15].

Food packaging is aimed to avoid potential contaminations of food, maintain the food quality, and extend food shelf life [16, 17] by preventing moisture access, oxidation or microbial contamination [18]. In fact, synthetic plastics made from petroleum are still extensively used as food packaging materials due to the endurance, stability, clearance, and low weight as its attractive factors [19-21]. However, plastic packaging poses high potential hazards to the human's health [22], wildlife and environment regarding degradability which took thousand years to be destroyed [23-26]. During recent years, many biomass and agricultural derived materials have been developed to be composite of degradable polymers, polylactic acid, and bio-thermoplastic due to its lower risk, low cost, abundant sources, inherent biodegradability and eco friendly material [27, 28].

The development of sol–gel chemistry was started during nuclear industry era in the 19thcentury involved preparation of alkoxide compound from SiCl4 [29]. Solid oxide material can be obtained in Nano-scale from sol-gel method by experiencing several chemical alterations from liquid as a sol phase into gel formation [30, 31]. This method gain popularity among scientists since it can be performed under relative low temperature and generates solid pure oxide material with even uniform size [32-34]. The report on hybrid packaging material for food packaging is still very limited. Hence, this study is aimed to develop hybrid Nano filler biodegradable plastic that can be safely applied for food packaging and as replacements for conventional plastics.

Materials and methods

Materials

Sago waste pith used in this research was obtained locally from Pentojangan village, South Sulawesi, Indonesia. Rice Husk Ash (RHA) was be supplied from local market in Makassar Indonesia. Reagent grade glycerol, Poly Lactic Acid (PLA) was purchased from NatureWorks LLC, (Minnetonka, Minnesota, United States) and n-butanol was purchased from Sigma-Aldrich Co (NSW Australia). HCl, NaOH, H_2SO_4 purchased from Merck Millipore (VIC, Australia).

Preparation of composites

Preparation of High Refined Cellulose (HRC) from Sago Pith waste (SPW). The collection of the pith followed the method by Abral, Putra [11] by cleaning the fibers with water several times to remove undesired materials and subsequently dehumidified for 48 hours to obtain the sago pith as a fiber for further processing of HRC .

The chemical pretreatment of sago pith waste was conducted as per the methods by Supratno, Tawfiequrrahman, & Yunanto, (2013) [35]. The method initated by adding the delignification agent of HNO_3, NaOH and H_2O_2 to remove undesired materials and obtain Highly Refined Cellulose (HRC) product. The nitric acid concentration of 4,5%, sodium hydroxide concentration of 2N, hydrogen peroxide concentration of 3,5% is the optimal condition of the delignification process of Sago wood fiber [35]. The experiments carried out in a 1000 mL (Brand® glass beaker with spout, low form, Sigma-Aldrich Pty Ltd Australia, NSW, Castle Hill), stirring rods (Aldrich® stirring rods, Australia, NSW, Castle Hill) and thermometer (Easy-Read® thermometer, Australia, NSW, Castle Hill). Three-steps atmospheric processes was involved, first addition of nitric acid solution at 80 °C for 2 hours, then the second step using sodium hydroxide at 80 °C for 2 hours and finishing using hydrogen peroxide at 80 °C for 30-300 min as the final step as shown in Figure 1 [36].

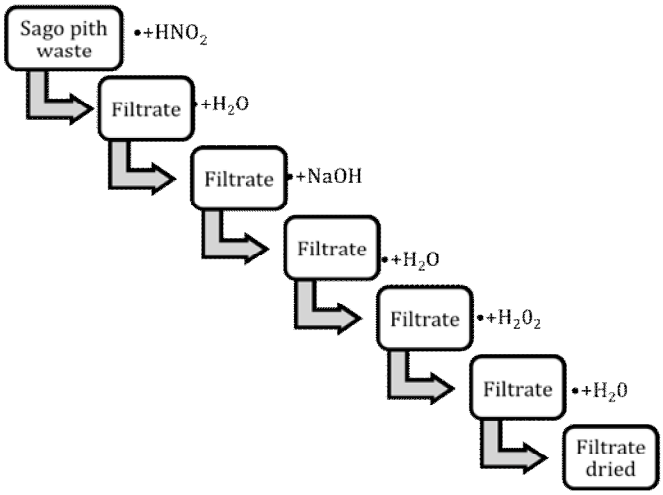

Figure 1. Preparation of high refined cellulose (HRC) from sago pith waste (SPW)

Preparation of nanosilica. Silica nano particles were prepared as per Livage, Henry, & Sanchez and as modified by Sindoro, Yanai, Jee, & Granick, [8]. Pretreatment of the RHA (Steps 1-3) and preparation of silica nanoparticles synthesis (4–5) can be shown on Figure 2.

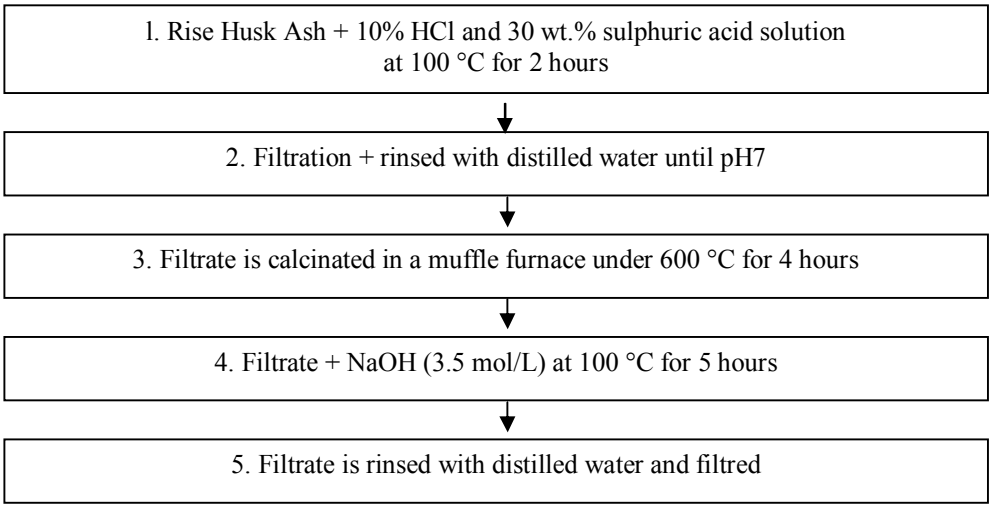

Figure 2. Preparation of nanosilica

Pretreatment of the RHA. In order to remove assimilated hydrocarbons, RHA is treated with 10% chloric acid and percolated with 30wt.% H_2SO_4 at 100 °C for 2 hours. The result is filtered and rinsed with distilled water until reaching neutral pH prior to calcination in a muffle furnace under 600 °C for 4 hours [5].

Synthesis of silica nanoparticles

The synthesis followed the method by Liou and Yang [37] i.e. 100 gr silica/carbon powder was added to a flask containing a 1.5 M sodium hydroxide (NaOH) solution (Merck & Co.). The sample was then boiled at 100 °C for 1 h with constant stirring, thus converting silica into a sodium silicate solution. The solution was centrifuged (Corning® LSE™ compact centrifuges, Australia, NSW, Castle Hill) to remove carbon solids and filtered using a glass filter Grade GF/F circles, 25 mm (Whatman plc, England) to remove small quantities of metal and carbon residues. The filtration process was repeated several times to obtain a clear and colorless solution. Deionized water was used to dilute the solution to 1.0 M. The sodium silicate then neutralized with hydrochloric (HCl). The sodium silicate solution was titrated slowly to the 1.0 M acid solution and, to avoid local changes in pH during gel formation. The mixture was stirred at a constant rate inside the beaker. The solution monitored with a pH meter to control pH at a constant value of 3–11. After acidification, aquagels were transferred into closed plastic vessels and allowed to age at a constant room temperature (24–26 °C) for 1–96 h. Deionized water was added to the gels. The gel was then centrifuged to remove solute salts. The washing step was repeated, and the solids were collected and dried at 80 °C for 48 h. Therefore, the following calculation can be used for extracting silica yield from (RHA):

$$(\%)\ Silica\ extraction\ yield = \frac{Mass\ of\ produced\ silica}{Mass\ of\ carbonized\ husk \cdot 0.5015} \cdot 100$$

Making of hybrid bio-nanofiller degradable plastic

After preparation of high refined cellulose of Sago Pith Waste and nano silica, both materials will be formulated into five samples combined with Polilactic Acid (PLA) and Glycerine. Each sample combination of these natural based compound can be seen on table 1.

Table 1 Combination of nano-silica, sago pith and plasticizer

Sample	Composition	Volume (%)
A	PLA	60
	Nano silica	20
	SPW	20
B	PLA	70
	Nano silica	20
	SPW	10
C	PLA	70
	Nano silica	10
	SPW	20
D	PLA	65
	Nano silica	15
	SPW	15
E	PLA (control)	100

The sample combinations will be mixed by using magnetic stirrer with stainless steel heating plate (RH Basic 2, IKA, Germany) at 100 °C, within 1700-2,000 rpm for 10 minutes in the beaker 100 ml. The process was kept at a constant temperature under continuous agitation by a magnetic stirrer. The best combination will be chosen after undergoing further tests i.g. tensile testing, microwave testing and water absorption properties. Furthermore, the thicknesses were measured in eight places using a digital micrometer (Accu Remote, Model, Manufacturer, City and State, USA). In order to get representative result, fourteen replicates were measured for each film and the average values were reported based on Syima and Shahid [38] research.

Mechanical testing

The mechanical properties (hardness test) of the developed plastic sheet will be determined according to Standard Test Method for Tensile Properties of Plastics ASTM standard method D785–03 (ASTM, 2012). A Perten TVT 300-XPH (Perten, Hagersten, Sweden) texture analyser equipped with a 5 kg load cell will be used to conduct textural analyses [39]. The maximum force and distance at the break point were determined automatically by a software texture analyzer. All samples were cut into rectangular strips 10mm wide and 60mm long, after conditioning at 50 ± 1% relative humidity (RH) for 24h. The samples strips were set with grip separation (40 mm) and stretched at a crosshead speed of 0.6 mm/s.

Microwave testing

The microwave response of samples was studied by using household microwave oven (MS2041F, LG, Yeongdeungpo-gu, Seoul, South Korea). The specimen was prepared and then placed in the microwave oven at testing condition at 700 watt for 1 and 1.5 min. After complete testing, the specimen was taken out from the oven and immediately measured the temperature on the surface. The physical changing of specimen was also recorded. As a comparison, same test was conducted with submerging treatment in the water. Four duplicates of each sample were repeatedly tested and the mean temperature was reported [40].

Water absorption properties

The water absorption of the film will be conducted according to ISO standards 62: 2008. The percentage of water absorption is calculated according to the following equation:

$$WA\% = \frac{W2 - W1}{W1} \cdot 100\%$$

where W1 is the weight of oven-dried composite sample before immersion and W2 is the weight of the composite sample after immersion.

The period of immersion is at the 30±2 min, and then specimens were removed from the boiling water and cooled in distilled water at room temperature. Subsequently, after 16 min, the specimens were removed from the water, and all surface water was detached with a tissue paper. The water content was weighed within an interval of 30 ± 2 min. After each of these intervals, the test specimens were removed from the water, cooled in distilled water, dried and measured. The results reported is the average of assessment [28].

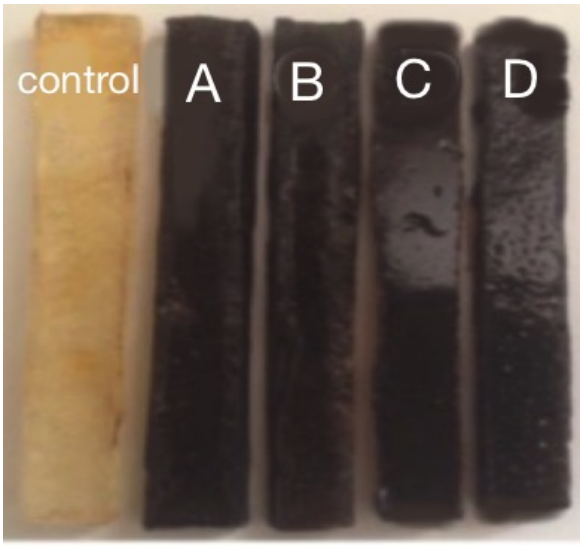

Figure. 3 Image of the sample made of nanosilica, SPW fiber and PLA combination A (60:20:20), B (70:20:10), C (70:10:20), D (65,15,15), Control (0:0:100).

Results and discussion

Mechanical property analysis

According to Liou, Chang [41] method, and calculation, the silica content in carbonized RHA is approximately 50.15 wt%. The effects of the SPW and Silica from RHA on mechanical properties of PLA composite sheets are demonstrated for the hardness strength, respectively, shown as shown in Figure 3. Four specimens of each formula were repeatedly tested and the average value was reported. In the average, sample A poses the highest strength ($\bar{x}$ 140.50 N) compare to rest of the samples. Compared to the other samples, sample B shows the weakest structure ($\bar{x}$ 62.37 N).

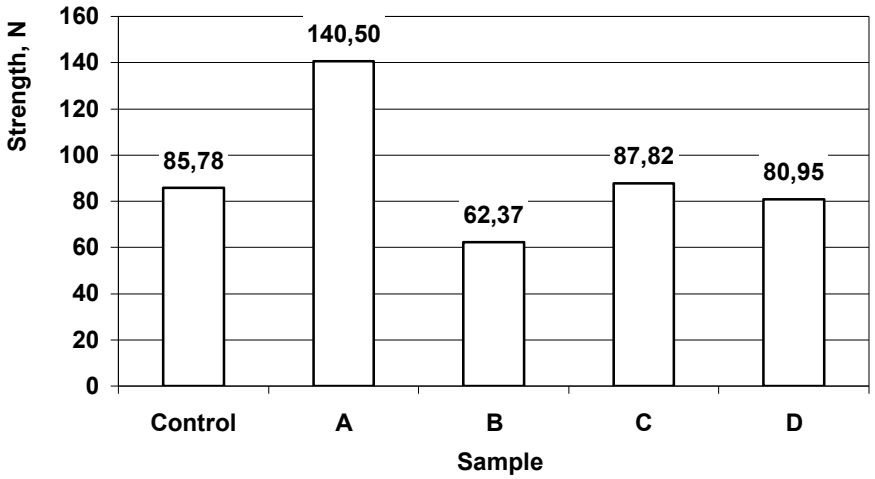

Figure 4. Average hardness results of 5 samples:
Control (SD 9.13), A (SD 1.96), B (SD 19.32), C (SD 20.49), D (SD 12.36)

Each polymers naturally has specific mechanical response when mixed with nanoparticles composite particularly their strength and elasticity of its component. The results showed that nanosilica (nano-SiO) and fiber embedded in PLA matrix at the certain comparison has shown improvement of mechanical properties, particularly in hardness compared to PLA itself. According to Liou and Yang [37], the nanosilica was produced from alkali-extracted rice husk ash and has a uniform size of 5–30 nm particle which dispersed in PLA matrix . The benefit of nanosize material of the silica result in larger surface area/ unit volume which strongly affect the chemical and physical interaction of the polymer, hence the application in the packaging industry would benefit the reliability of the combination materials [42–44]. The sample A (consists of 20% of nanosilica and SPW fiber) demonstrates the effective of PLA combination tailored with the fillers and indicated the strongest sample from the rests. The sample becomes more rigid and sturdy due to crosslinking interphase in the composites in comparison with control and the rest of the sample [45, 46].

Microwavability of modified PLA

The microwave response of PLA samples in microwave oven at various conditions treatment were showed in the Figure 5.

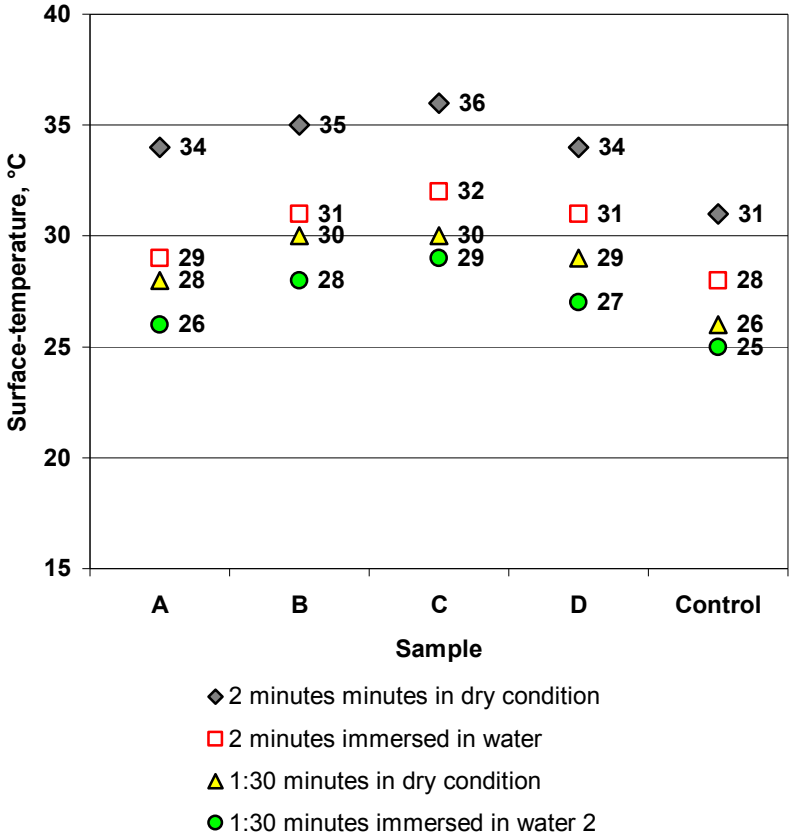

Figure 5. The average surface-temperature of control, sample A, B, C, and D at various settings in the microwave power 700 Watt

The surface temperature was measured to present the PLA response towards microwave exposure. Comparing between two condition i.e dry and immersed in water, it can be seen that all modified PLA samples have higher temperature than pure PLA sample. In 2 minutes dry condition the control showed 31 °C on average, while on average, the rest of the sample, A, B, C, and D showed higher temperature (33, 35, 36, and 34 °C respectively). Similar trends also showed in 2 minutes immersed in water, 1.30 minutes in dry condition and 1.30 minutes in water. The mean of sample C indicated the highest value of all sample in four categories ($\bar{x}$= 36, 32, 30, and 29 °C respectively). This might have been caused by the nanosilica composite exhibited an excellent thermal insulation and slow thermal desorption during thermal exposure be accumulated in the polymer matrix and result to higher temperature among modified and pure PLA [47, 48].

The graph also showed that, the pattern of the wave exposure showed that the higher density of matrix especially nanosilica the lower temperature reached by the sample surfaces . These trends were similar for both sample conditions, in dry and immersed in water. The crosslinked structure of the filler with the matrix (PLA) in this case nanosilica and SPW fiber as a hybrid filler, reduced space for polymer molecules to move during microwave radiation. Furthermore, compared to dry condition, in immersed water condition sample showed lower temperature. This response was caused by water in vapor form absorb more energy than filler itself and has lower ability to release heat that in liquid the form [22, 23, 49].

Water absorption behaviour

Besides mechanical and effect of microwave towards PLA properties, water absorption is another critical consideration for plastic packaging. This factor is useful to measure durability of the sample against various treatments especially when washing and submerged in water. The results of water absorption of composites after boiling in distilled water with different percentage of nanosilica and SPW fiber loading are shown in table 2.

Table 2

Water absorption of PLA formula

Sample	Mean weight before treatment (g)	Standard deviation (SD)	Mean weight after treatment (g)	Standard deviation
Control	3.88	0.04	3.95	0.03
A	3.11	0.14	3.15	0.15
B	2.46	0.19	2.69	0.07
C	3.16	0.24	3.26	0.24
D	3.22	0.06	3.27	0.06

In daily application such as, as a food container high water absorption can be significantly reduced by adding low molecular weight compounds such as triethyl citrate, glycerol, sorbitol, and ethylene glycol [50, 51]. The water penetrability of modified PLA can be a source of material degradation. The water remaining in the matrix can be utilized by microorganism to grow, which could contaminate food items. Due to PLA price relatively costly, combination with natural fiber exhibits advantages such as tensile strength and tensile modulus increased yet with a slight decline in the elongation compared with pure PLA [52, 53].

In this experiment, each sample shows vary percentage weight after measurement; the mean of water absorbed for sample A, B, C, D, E are 1.55%; 0.96%; 1.89%; 2.85%; 3.12% respectively. It can be observed ,as a control, sample A absorbed more water compare to all samples whereas sample B shows the lowest percentage of all. Sample B indicated the hydrophobicity of modified PLA. Sample B contains more silica than fiber (20:10) in the matrix that increases the brittleness of the PLA sample blend. Combination of nanosilica sample decreases the water uptake of modified composites compared to control/pure compound. This occurred due to the convoluted barrier built by nanosilica inhibited water molecule to penetrate into PLA sample composite [54, 55].

The high possibility further development of this hybrid material is potentially used as substitution of one time use food and beverages container such as processed instant food, raw food from supermarkets (meat, vegetables, fruits, etc), ready to eat food and beverages from shops or drive through food stalls (ice cream, juice, tea, coffee, etc). Globally, reported from world packaging organisation, plastic packaging , derived from petroleum, was the second largest waste under paper and cardboard for packaging [56]. Whereas container made of polystyrene foam causes environmental and health issues. Several cities in the USA for instance Seattle , New York's Glen Cove, Massachusetts' Brookline, Boston, Amherst and in Hawaii [57, 58].

After doing three experiments, this hybrid combination has been shown high potential for replacing function of conventional plastic and Styrofoam as a food packaging. As a bio filler, the material reduced the use of plasticizer agent that directly minimise the production cost in the industrial scale. Furthermore, the use of SPW and RHA significantly contribute to decrease this agricultural waste at the same time increase the economical value of the materials. The results showed the proper combination of material generated high density and strength more than control (PLA itself). While microwavability and water absorption test show insignificant changes of behaviour compared to the control sample. Hence, the formula combination SPW and RHA with PLA showed strong possibility to be applied as eco friendly packaging for specially for one time use food container.

Conclusion

The plastic sheet test result indicated the potential usage of nanosilica and SPW fiber from agricultural waste. We directly reduce the agricultural waste and turn it into eco-friendly plastic sheet as the basic form of food container development. The main characteristic of this sample is reach the sturdy level of oil based/conventional plastic, less water absorbtion, and stable in the microwave and heat. In the experiment, slight changes in the temperature of a modified hybrid-filler sample indicated that the sample was remained stable for both condition. Hence, when the sample applied into food packaging, whether in wet or high temperature condition, the packaging has no effect to the food or beverages. Furthermore, this study examined the effect of nanosilica and SPW fiber as hybrid agent on the physical and mechanical properties of PLA. The crosslinking of the hybrid filler with the PLA matrix effectively improves hardness properties in PLA with combination 60:40 (filler) an is also the key of stability during the tests. In this experiment we found insignificant temperature changes of the modified sample with hybrid filler both in wet and dry condition than the neat PLA samples as the majority of the sample is still PLA itself. Additionally, the higher density of matrix especially nanosilica, the lower temperature reached by the sample surfaces due to smaller space for molecule movement. Combination of nanosilica sample (PLA: nano silica: SPW fiber; 70:20:10) optimally decreases the water uptake compared to control/pure PLA. The complex barrier built by nanosilica and SPW fibre inhibited water molecule to infiltrate into modified PLA sample. The future development of this material is potentially substitute one time use food and beverages container derived from petroleum and made of polystyrene foam that cause environmental and health issues.

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Influence of fermentative modification of rice flour starch on bread quality for patients with celiac disease

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Abstract

Introduction. The expedient use of ferments with amylolytic activity for carbohydrate composition modification of rice flour aiming to improve the quality of gluten-free bread is scientifically based.

Materials and methods. Rice flour starch has been hydrolyzed with the help of mushroom α-amylase and glucoamylase. General amount of saccharides has been determined by iodometric method. Dextrin contents – by their ability to be precipitated in conditions of different concentrations of ethanol in the solution. The course of microbiological processes in the dough has been examined by its gasification ability using volumetric method and general acidity using titration method.

Results and discussion. The use of α-amylase in amount of 0,005% and glucoamulase in amount of 0,03% to mass of rice flour causes sugar accumulation in amount of 5,5–6%, which is necessary for the intensification of course of microbiological processes in the dough. To hydrolyze the starch more fully, it is expedient to prepare a semi-finished product hydrolysate with 50% of rice flour from its recipe humidity of 65% with further kneading the dough on its basis. To accumulate monosaccharides and disaccharides to the amount, which is optimal for active yeast functionality and for improvement of gasification in the dough, duration of rice flour starch hydrolysis while preparing the semi-finished product, hydrolysate is 2 hours.

The products of rice flour starch hydrolysis, which were created as a result of fermentative modification by α-amylase and glucoamylase, particularly monosaccharides and disaccharides, intensify the process of dough fermentation, which is affirmed by increase of CO_2 for 57,8% and increase of acidity for 0,6 degr. in comparison to control example, consequently to this the ready-made products are characterized by structurally mechanical quality scores. Increase of dextrin amount in the dough influences deceleration of starch retrogradation while keeping ready-made products.

Conclusions. Hydrolyzation of rice flour starch with the help of amylolytic ferments in preparation of a bread for patients suffering from celiac disease helps to intensify microbiological processes in the dough, to improve quality scores of ready-made products and prolonging of their expiration date.

Introduction

Changes in the nature of nutrition, caused by peculiarities of modern way of life and work are becoming the reason of more intensive spreading of chronical noninfectious disturbance of an organism's normal vital activity. The use of special products for nutrition, among of which a special role is played by the products for the category of people with diseases of intolerance to some food components (diabetes, celiac disease, phenylketonuria etc.) is one of effective and efficient ways of correction and prophylaxis of different diseases.

Celiac disease is a progressive autoimmune ailment, which is spread on 0,9-1,2% of population in European regions, Northern and Southern America, Northern Africa and Indian subcontinent [1, 2], caused as a result of gluten introduction to people's genetically inclined organisms. The group of toxic grain proteins for people suffering from celiac disease is denoted by the term of "gluten", which includes wheat prolamins (gliadin), rye (secalin), and barley (hordein) [3], as they are characterized by high content of proline and glutamine in the structure of protein molecule. Wheat glutenin, which consists of gliadin-like subunits conjugated by disulfide bond, is toxic as well. Gluten consumption by patients with celiac disease leads to villi atrophy and damage to the mucus membrane of small intestine, which is accompanied by malabsorption of many important nutrients [4, 5]. It may lead to diseases related to digestive disorders, such as osteoporosis, type I diabetes, skin maladies [3, 6]. Despite considerable scientific progress in prevention of celiac disease symptoms displays, strict adherence to the gluten-free diet during the whole patient's life is the only treatment method of this disease, that leads to the clinical recovery and reduction of mucus membrane [7, 8].

Besides, in Ukraine the production of dietary foods for patients with celiac disease is not set up. The most burning problem is to provide them with gluten-free baked goods, which have wheat flour in their contents as a main component, that is forbidden to consume. Gliadin and glutenin swell while the dough from wheat flour is being kneaded, making gluten, which joins dampish starch grains with each other, creating a frame with spatial structure, that provides with developed porosity of crumb and uniformity of ready product [6, 9]. However, taking into the consideration the toxicity of these goods for the patients with celiac disease, there's a need of full exchange of the flour by raw stuff with gluten-free cereals.

Rice flour is an alternative for gluten raw stuff (wheat, rye and barley) in the production of gluten-free bread. Rice product of processing do not contain prolamin fraction of "gluten", that can be allergic, with digestive disorders (celiac disease), and that's why they're used in dietary foods for people of all ages. Rice flour has soft taste, white color, high digestibility and hypoallergic properties and is the source of plant proteins, full in amino acid composition, contains natrium, potassium, magnesium, vitamins B_1,B_2 and PP [6,10]. Nevertheless, its use in bakery is limited by impossibility to form the flour with structural mechanical properties and to provide with high quality of the goods [23]. It means, that the problem of searching for new ways of improving the quality of bread from rice flour for the patients with celiac disease is rather burning and actual.

Analysis of literary data and problem statement

Analysis of scientific research conducted with the aim of improving the quality of bread from rice flour shows the possibility to use it in the technology of different nutritional supplements: hydrocolloids (hydroxymethyl propyl cellulose, xanthan and guar gum,

modified starches) and emulsifier (glycerin ester, diacetyl and fatty acids (DATEM), sodium stearoyl actinate, distilled monoglycerides, lecithin), and some of the ferments (transglutaminase, papain, bacillolysin, subtilisin) [6, 9, 11-13]. The use of methods, which allow to modify the properties of the main chemical components of gluten-free flour with the help of ferments is an actual field in production technology of bakery for patients with celiac disease [9]. The use of the methods in production of gluten-free bread has been limited for a long time, as wheat flour and starch were the carriers of these supplements. However, appearance of ferments, which even do not contain microquantity of gluten, has opened new perspectives for improving quality of bakery with the help of these preparations. Scientists offered to use a ferment transglutaminase as a former of the structure to prepare rice rough for bread. It is able to bond proteins of different origin: casein and milk albumins, animal protein of eggs and milk, soy and wheat protein. Adding transglutaminase leads to crosslinking of proteins, which allows to create gluten-like chain, by reaction catalysis of forming of specific isopeptide bond between carboxyamide group of glutamine and amino group of lysine [12].

Nowadays research in the field of improving bread quality with the help of ferments of amylolytic action, that hydrolyze flour starch and as a result the content of fermented sugars in dough gets higher, is actively developing [14]. Rice flour is perspective raw stuff for modification of its carbohydrate composition by using these preparations, as it's characterized by high content of polysaccharide (79,1%), not big amount of saccharides (up to 0,7%) and low activity of α- and β-amylase. That's why, it is expedient to determine the possibility of improving rice bread quality by use of ferment modification od starch with the help of ferments with amylolytic activity.

The aim of research is to justify the possibility of the use of rice flour starch fermentative modification aiming to accumulate mono- and disaccharides with the help of ferments of amylolytic action in the technology of gluten-free bread and determination of its influence on the course of microbiological processes in the dough and the quality of ready made goods.

To solve the goal, the following tasks have been formulated:

- to determine influence of amylolytic action on accumulation of products of rice flour starch hydrolyzation, particularly saccharides and dextrines;
- to research influence of ferments of amylolytic action on microbiological courses in the rice dough, particularly intensity of its fermentation and acid accumulation;
- to determine the effect of supplements on quality markers of readymade gluten-free bread and keeping its freshness.

Materials and methods

Materials

Rice flour with "crossed wheat ear" marking was used as the main raw material of making bread for patients with celiac disease, which affirms absence of contact of gluten-free flour with gluten-containing raw materials in production, its domination, the use of equipment designated for grinding "gluten-free" cereals only (CODEX STAN 118-1981, amended 1983) [10]. Ferments of amylolytic action were used for rice flour starch hydrolyzing, particularly α-amylase of mushroom origin "Alphamalt VC 5000 SN" (5000 SKB/g, optimal pH 4,7-5,8, temperature is 40-50°C, Muhlenchemie, Germany) and glucoamylase "Glucomil", produced by Aspergillus niger (500 AMG/g, optimal pH 3,0-5,5,

temperature is 40-64 °C, Germany). The following raw materials were used in the research: bread yeast [21], food grade salt (CODEX STAN 150-1985), citric acid [CAC/MISC 6-2015], drinking water (CODEX STAN 193-1995).

Making of semi-finished product hydrolysate from rice flour

The temperature of the environment was set as 40ºC and pH 4,7 to provide with optimal conditions of effect simultaneously of both α-amylase and glucoamylase. However, temperature optimum for active yeast functioning while dough fermentation is 28-32 ºC, which is not effective for ferments activity. Basing on this, semi-finished product-hydrolysate from rice flour has been prepared with the temperature of 40 ºC with the next dough kneading on its basis, that provides with deeper hydrolysis of the starch and allows to enrich the environment with saccharides. Citric acid in the amount of 0,065% to the mass of flour was used to keep appropriate pH conditions 4,7. Mass fraction of humidity of semi-finished product-hydrolysate from rice flour has been set as 53%, 56%, 65%, 78%. The mixture of rice flour, citric acid, ferments and water has been prepared, which was hydrolyzed in thermostat with 40ºC up to saccharides accumulation to 5,5-6%. Ferments have been previously dissolved in water with temperature of 25-30ºC at a ratio of 1:10.

Determination of carbohydrate content

General amount of saccharides (in terms of maltose) has been determined by Shrol's method [15], the peculiarity is that the amount of cuprum (II) which hasn't reacted is determined by it. Felling's reagent I (solution of $CuSO_4$ with the concentration of 6,925%) and Felling's reagent II (346g of $KNaC_4H_4O_6 \cdot 4H_2O$ and 100g of NaOH in 1 dm^3 of solution) have been added to hydrolysate. After that the solution has been boiled for 2 minutes and quickly cooled. 10 cm^3 of 30% solution of KI and 10 cm^3 of H_2SO_4 with concentration of 25% was added to determine the cuprum amount, which didn't react. Iodine, which stood out, was titrated by 0.1 moles/dm^3 solution of $Na_2S_2O_3$ to light-yellow color, 2 cm^3 of 1% starch solution was added, and continued to titrate up to blue color disappearing. So, the amount of $Na_2S_2O_3$ used to titrate I_2 is equivalent to the amount of CuO, that didn't react. To determine cuprum amount, which reacted with saccharides, control research was conducted, in which the appropriate amount of water instead of hydrolysate for reactions with Fleming's solutions was taken. The amount of cuprum (II) that reacted and the appropriate amount of saccharides were determined by the difference between the amount of $Na_2S_2O_3$ used for titration of I_2 in the control and work researches. Saccharides content x, % to was counted by the formula:

$$x = \frac{(V_k - V_h) \cdot K \cdot 100 \cdot 100}{H(100 - W)},$$

where $V_h V_h$ – the amount of 0,1 moles/dm^3 of $Na_2S_2O_3$ solution, used for titration in the control and work researches, cm^3; K – conversion factor to maltose (5,4); H – mass of product, which corresponds to the volume of the hydrolysate, mg; W – mass fraction of humidity in the product, %.

The content of dextrines has been determined by their ability to precipitate with different ethanol concentration in solution [15]. Firstly amylolytic ferments have been inactivated by 96% of C_2H_5OH on heated bath to its full evaporation. The next step was to

remove water-soluble carbohydrates from the batch. To do that, the batch was carried to dimensional bulb for 100 cm^3, infused for 1 hour, brought to the mark with water and filtered. Saccharides, which were in the solution were removed by fermentation of bread pressed yeast with the temperature of 25 ºC. Glucose, saccharose, fructose, maltose were fermented, and dextrines and pentoses remained. To determine the content of dextrines, three portions of 30 cm^3 in which they were precipitated by ethanol were taken with the concentrations of: 1 – 40% (amylodextines), 2 – 65% (amylo- and erythrodextrines), 3 – without adding of ethanol (amylo-, erythro-, ahro- and maltodextrines). After thatdextrines have been dissolved by water and hydrolyzed by 20% HCl to glucose for 3 hours on boiling heated bath.

Mass fraction of glucose in dextrin hydrolysate has been determined be method of Wilschtetter and Schudl [15]. 30 cm^3 0,1 moles/dm^3 of NaOH solution and 25 cm^3 0,1 moles/dm^3 of I_2 solution have been added to 10 cm^3 of hydrolysate. The bulb was closed by clock glass and left for 15-20 minutes in the dark place. Then 4,5-5cm^3 1 moles/dm^3 of H_2SO_4 solution was added and titrated 0,1 moles/dm^3 solution of $Na_2S_2O_3$. Mass fraction of dextrines, x, % per dry matter, was calculated by the following formula:

$$x = \frac{(V - V_1) \cdot K \cdot 0,009 \cdot 0,9 \cdot 100 \cdot 100}{M(100 - W)}.$$

Bread production

Bread pressed yeast (3%) has been dissolved in water at the temperature of 26-32 ºC. Aqueous saline solution with the concentration of 1,2% at 30ºC has been prepared and filtered. Rice flour dough has been kneaded on the basis of previously prepared semi-finished product-hydrolysate with humidity of 53% by adding yeast suspension, saline solution and the other part of flour according to recipe. After that, dough batches weighing 350g have been formed and fermented in a cabinet for 45 minutes at a temperature of 32ºC with 85% relative humidity in air. Baking has been carried out at a temperature of 180ºC for 25 minutes. Readymade bread has been cooled for 25 minutes and kept at a temperature of 23-27ºC.

Research of the course of microbiological processes in the dough

Intensity of ethanol fermentation in the dough has been determined by volumetric method with a device AG-1 with the indicator of gas-forming ability, i.e. the volume of CO_2 produced, cm^3/100g at 30ºC, for the period of dough fermentation.

The change of total acidity of the dough has been determined during its fermentation each 15 minutes by titration of 0,1 moles/dm^3 solution of NaOH 5g of dough semi-finished product, rubbed with 50 cm^3 of water, with 1% of ethanol solution of phenolphthalein to pink coloring [15].

Evaluation of bread quality

Bread was analyzed not earlier than in 3 hours after baking by the main indicators.

Specific volume was determined as the ratio of volume they occupy to their mass.

Bread staleness has been determined by the following methods: measuring degree of crumb deformation on atomized penetrometer by firm of "AP-4/1" and determination of

fragility of bread by a whit content, which appeared as a result of shaking on the vibrating mixer.

Porosity has been determined with the help of device [15]. In the piece of the crumb three hollows have been made by a cylinder of the device at a distance not less than 1 cm from crust, and weighed after. Porosity, %, was calculated by the formula:

$$P = \frac{V - \frac{m}{\rho}}{V}$$

where V – being general volume of bread hollows, cm^3; m – mass of the hollows, g; ρ – density of non-porous mass of the crumb, g/cm^3.

Density of non-porous mass for gluten-free bread has been determined by the following way. A hollow was made by device, squeezed thoroughly by wooden piston in a cylinder of a device for removing of pores. Then the hollow in the form of compressed cylinder was weighed and the height of it was measured.

Density of non-porous mass, g/cm^3, was calculated by a formula:

$$\rho = \frac{m}{\pi \cdot r^2 \cdot h}$$

where m – being the mass of the hollow, g; r – radius of the hollow, cm; h – height of the hollow, cm.

Results and discussion

Choice justification of dozing the ferments for modification of rice flour starch

One of the main problems in rice bread production is its structural mechanical quality indicators [10, 22]. It is explained by a low level of its own mono- and disaccharides in the flour from rice grains (0,7%), which are assimilated by yeast on the initial stage of the dough maturation. Besides, rice flour has a small activity of amylolytic ferments (α- and β-amylase), that's why it cannot provide with necessary intensity of ethanol fermentation in gluten-free dough to loosen the dough preparations, as a result the bread made of such flour has a small volume, low porosity and pale crust. Success of technological process course and providing with high quality bakery depend much on the amount of saccharides in the dough, which is the source of nutrition for yeast cells as well as for a process of starch biotransformation under the effect of its own α- and β-amylase of the flour with maltose formation. That's why we offered to add ferments with amylolytic activity to the dough to raise the amount of saccharides in the dough, which is necessary to provide with the process of fermentation.

Fermentative effect on the starch allows to increase the amount of saccharides in the dough, that leads to intensification of its fermentation process, improving of gas formation during the process of maturation and early stages of baking. It leads to volume increase of the goods, improvement of porosity and texture of crumb [14, 16]. The choice of ferments is determined by the expected carbohydrate composition of ready product. On analyzing ferment preparations with amylolytic activity we chose mushroom α-amylase "Alphamalt VC 5000 SN" with the activity of 5000 SKB/g and glucoamylase "Glucomil" – 500 AMG/g. So, α-amylase hydrolyzes irregularly α-1,4 glycoside bonds in the amylose molecule, as a result maltose and products of incomplete hydrolysis of starch – dextrines

are formed. Unlike α-amylase, that can split only unbranched bonds of starch molecule, glucoamylase is able to catalase hydrolytic decomposition of α-1,6-glucoside bonds of branched bonds of starch amylopectin. It also transforms dextrines, which are formed under the effect of amylase, to glucose [16-18].

Dosage of ferments depends on their amylolytic activity. As and enhancer for the bread, it is recommended to use mushroom α-amylase "Alphamalt VC 5000 SN" in the amount of 250-500 un. SKB per 1 kilo of wheat flour, i.e. 5-10g of the ferment for 5000 un. SKB/g per 100 kilos [19]. But there are no recommendations as for its dosage to rice, as the speed of splitting of starch by amylase from different cultures is different, which depends on the size and shape of starch grains, their structure peculiarities. So the size of rice starch grains is 5-6 microns, at the same time the size of wheat starch grains – 25–35 microns. Evidently, similar dosage of α-amylase would effect on rice and wheat starch differently, that would be showed up in formation of new products of hydrolysis. Taking into consideration this fact, the effect of dosage of α-amylase "Alphamalt VC 5000 SN" in the amount of 0,01% to flour mass was studied, which is optimal according to manufacturer's recommendations for accumulation of mono- and disaccharides (Figure 1). Non-yeast dough was prepared of rice flour with the humidity of 53%. Non-yeast dough of wheat flour with mass fraction of humidity 44,5% was used as a control example for comparative analysis. The increase of estimated humidity of the rice dough is conditioned by water absorption capacity of the rice grains flour, which is explained by smaller size of starch granules and high content of amylopectin in it (82%), due to hydrophilic properties the starch granules are very hygroscopic. Duration of fermentation was 3 hours at an environment temperature 40 ºC.

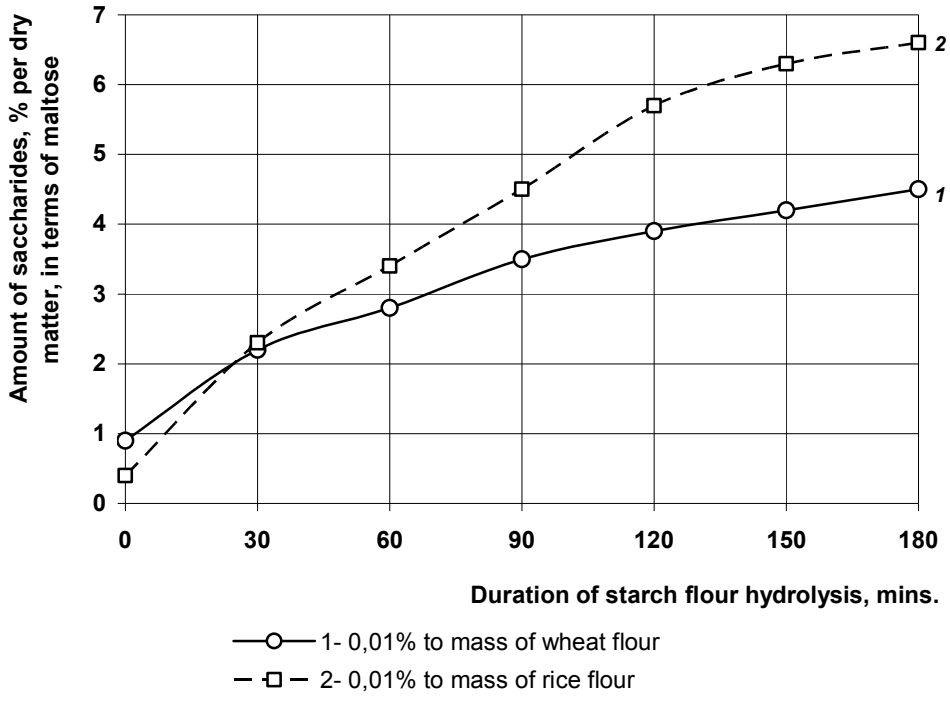

Figure 1. Effect of α-amylase on accumulation of saccharides in rice and wheat flour dough

It is determined, that the amount of accumulated saccharides during 3 hours of hydrolysis of rice flour starch was 32% higher than in the wheat one. It is explained by reduction of dispersion of starch grains starch attacking increases, as their relative surface of contact with ferments increases, as a result the amount of products of hydrolysis is getting higher. That's why the dosage of mushroom α-amylase "Alphamalt VC 5000 SN" should be decreased on order to improve the quality of rice flour bread.

We know, that it's needed 5,5-6% of saccharides from the mass of flour dry matter for the whole cycle of bread preparation [20]. That's why the recommended amount of ferment was determined by accumulation of mono- and disaccharides to the amount mentioned before with the addition of α-amylase in the amount of 0,002, 0,005 and 0,007% to the mass of rice flour (Figure 2).

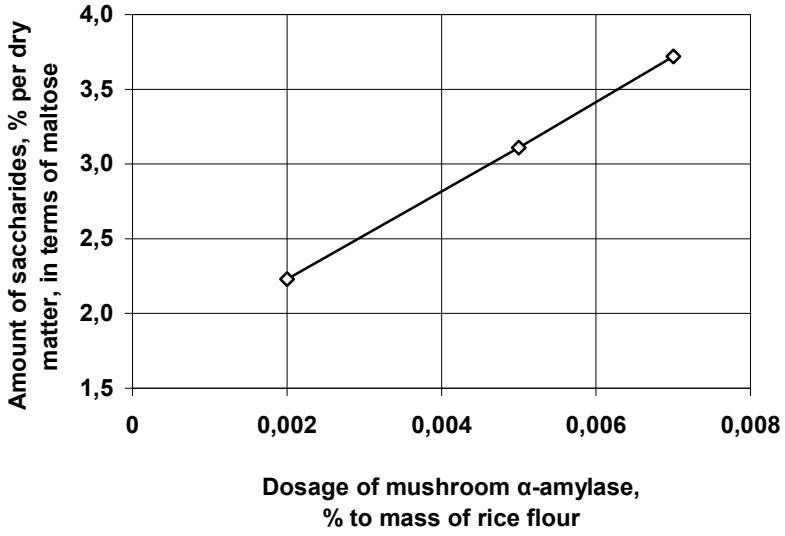

Figure 2. Effect of different dosages of α-amylase on saccharides accumulation in the rice dough

It was determined by the results of the research, that adding α-amylase of mushroom origin in the amount of 0,005 and 0,007% to mass of rice flour leads to saccharides accumulation accordingly 3,1 and 3,7%, which is 29–40% more, than in use of this ferment in the amount of 0,002%. According to the data we got, the recommended dosage of α-amylase "Alphamalt VC 5000 SN" is 0,007% to mass of rice flour, as in such conditions the biggest amount of saccharides is accumulated. However, it is more economically expedient to use α-amylase in the amount of 0,005% to mass of flour, as the amount of saccharides which were formed is slightly different.

The use of α-amylase only to enrich dough semi-finished product with saccharides is not efficient because of significant duration of hydrolysis. So, it takes 3 hours to accumulate mono- and disaccharides in amount of 4,5%. That's why to speed up starch splitting and increasing of mono- and disaccharides, glucoamylase "Glucomil" has been additionally used, recommended dosage of which is 0,7 g per 1 kilo of starch to hydrolyze

wheat starch effectively, that in terms of the content of this polysaccharide in the rice flour is 0,065% to its mass.

On the basis of previous research it is determined that decrease of dosage of α-amylase is efficient. That's why, taking into the consideration rice starch properties and its give to effect of amylolytic ferments, in the further research the effect of glucoamylase on saccharides accumulation at its adding in the amount of 0,03% and 0,05% to mass of flour to non-yeast dough during fermentation for 3 hours at a temperature of 40ºC, was determined (Figure 3).

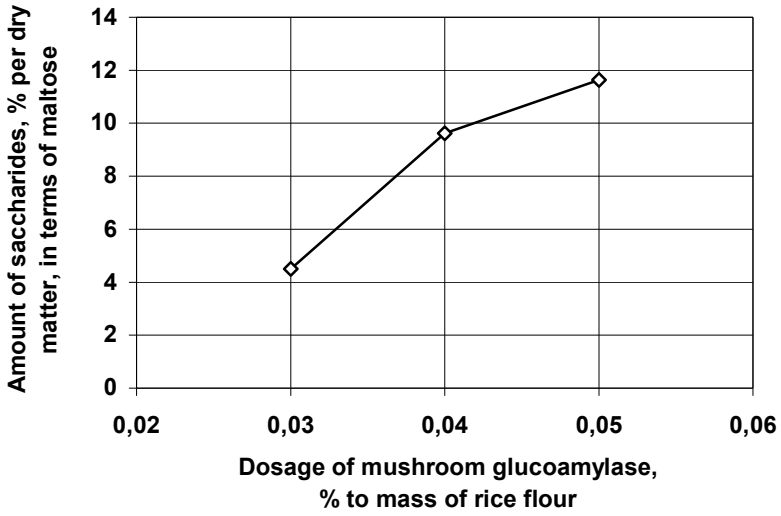

Figure 3. Effect of different dosages of glucoamylase on saccharides accumulation in rice dough

The analysis of the results we got showed, that adding of glucoamylase to rice dough in the study range of dosages helps to increase in it saccharides, which were formed in the process of hydrolyzing of flour starch during 3 hours of fermentation. Herewith the part of accumulated saccharides at adding glucoamylase of 0,04% and 0,05% is accordingly 9,6% and 11,6% to dry matter. Such amount of saccharides in the dough semi-finished product is ineligible, as the activity of yeast cells are suppressed by the increase of saccharides for more than 6%, as a result of increase of osmotic pressure in the liquid phase of the dough. As well, superabundance of mono- and disaccharides is the reason of activization of the Maillard reaction, and as a result the crust of readymade bread gets brown, which is not peculiar for it. Adding of glucoamylase in the amount of 0,03% to the flour mass leads to formation of 4,5% to dry matter of saccharides. That's why it can be assumed, that simultaneous use of α-amylase in the amount of 0,005% and glucoamylase in the amount of 0,03% to the dough mass will provide with synergic effect, owing to this the fermentative modification of the rice flour starch would be more effective, and the amount of products of its hydrolysis, particularly saccharides and dextrines, would help to intensify dough fermentation and prolong freshness of readymade goods.

Effect of ferments of α-amylase and glucoamylase on carbohydrate content hydrolyzed rice semi-finished product

Taking into consideration amylase and glucoamylase action interval, mentioned by a manufacturer, the optimal temperature for both ferments action is 40ºC and pH 4,7. As the dough fermentation occurs at a temperature of 28-32ºC, adding of the ferments on the stage of dough kneading is not effective enough. That's why, to accumulate the appropriate amount of saccharides for the whole cycle of bread baking, preparation of semi-finished product-hydrolysate from rice flour at 40ºC with the following dough kneading on its basis is reasonable. As the rice flour has its active acidity of 5,65 un. of the device, to order to create optimal pH conditions 4.7 for ferments action, citric acid in the amount of 0,065% to mass of flour has been used.

We know that hydrolyzing action of amylolytic ferments is seen only at its water combination. Herewith, there is direct dependence between humidity of an environment and the activities of the last ones. Because of that, the effectiveness of fermentative reaction by starch hydrolyzing products accumulation, particularly mono-and disaccharides, has been studied in the course of further researches, with the time of semi-finished product-hydrolysate preparation with different humidity (Table 1). Mass fraction of humidity has been determined from a calculation of the use of 100, 75, 50 and 25% of rice flour in accordance to the recipe.

Table 1

Replacement of saccharides during the process of preparation of semi-finished product-hydrolysate from rice flour

Hydrolysis duration, min.	Saccharides content (in terms of maltose), % to DM							
	With adding of α-amylase				With adding of α-amylase and glucoamylase			
	Amount of flour, % from general mass							
	100	75	50	25	100	75	50	25
	Humidity, %							
	53,0	56,0	65,0	78,0	53,0	56,0	65,0	78,0
0	0,41	0,32	0,21	0,12	0,41	0,32	0,21	0,12
30	0,90	0,95	0,98	0,96	1,12	1,88	2,64	2,32
60	1,50	1,88	2,26	2,03	2,54	2,83	3,12	2,98
90	1,72	2,34	2,95	2,71	3,05	3,76	4,52	4,20
120	1,95	2,85	3,80	3,34	4,22	5,06	5,90	5,36
150	2,40	3,32	4,25	3,80	4,86	5,68	6,50	6,09
180	3,11	3,80	4,60	4,20	5,11	6,03	6,95	6,45

Data analysis showed, that the content of saccharides increased for 2,6% DM in non-yeast semi-final product of rice flour with humidity mass fraction of 53% with α-amylase in three hours of hydrolysis, at the same time the use of α-amylase and glucoamylase led to their increase to 4,7% DM. So, simultaneous use of the ferments provides with their synergic effect, which is explained by the hydrolytic action of glucoamylase, which cleaves glucose from starch molecules and products of its incomplete decay, particularly dextrines, formed under the effect of α-amylase. Besides, the use of 50% recipe amount of rice flour for preparation of semi-final product-hydrolysate with 65% humidity, helped to accumulate more saccharides, because the speed of ferments catalyzed reaction gets higher when humidity mass fraction increases. Further humidity increasing to 78% is not feasible, as the

amount accumulated products of starch hydrolysis decreases, that is due to ferment-substrate ratio violation.

The intensity of dough fermentation depends of saccharides concentration, which are the source of nutrition of yeast. Improvement of their fermentation activity and gas formation is observed at adding of mono- and disaccharides to 6% [20]. The presence of their bigger amount increases osmotic pressure in the dough liquid phase and leads to plasmolysis of yeast cells (body contraction of living cell with membrane scaling), as a result alcohol fermentation is slowed down, gas formation decreases, dough looseness worsens. Making the conclusion from this, using the data from the Table 1, we can determine, that the optimal concentration of mono- and disaccharides is 5,9% to DM for high activity of yeast and improvement of gas formation ability of rice flour. To accumulate such amount of saccharides in the semi-finished product the hydrolysis duration is 2 hours (120 minutes) at humidity of 65%, under the conditions of use for its preparation of 50% of flour from general recipe amount.

α-amylase action is directed to starch depolymerization and formation of enough amount of mono- and disaccharides, which will be fermented by the yeast at the dough maturation. Still, the use of mushroom α-amylase for making semi-final product-hydrolysate from rice flour helps to accumulate dextrines as well. Their redundant content leads to dough clamminess, and as a result, the bread crumb is easily creased, and its elastic properties worsen. That's why, in the further research the accumulation of dextrines during 2 hours of starch hydrolysis for semi-finished product-hydrolysate form rice flour has been determined (Figure 4).

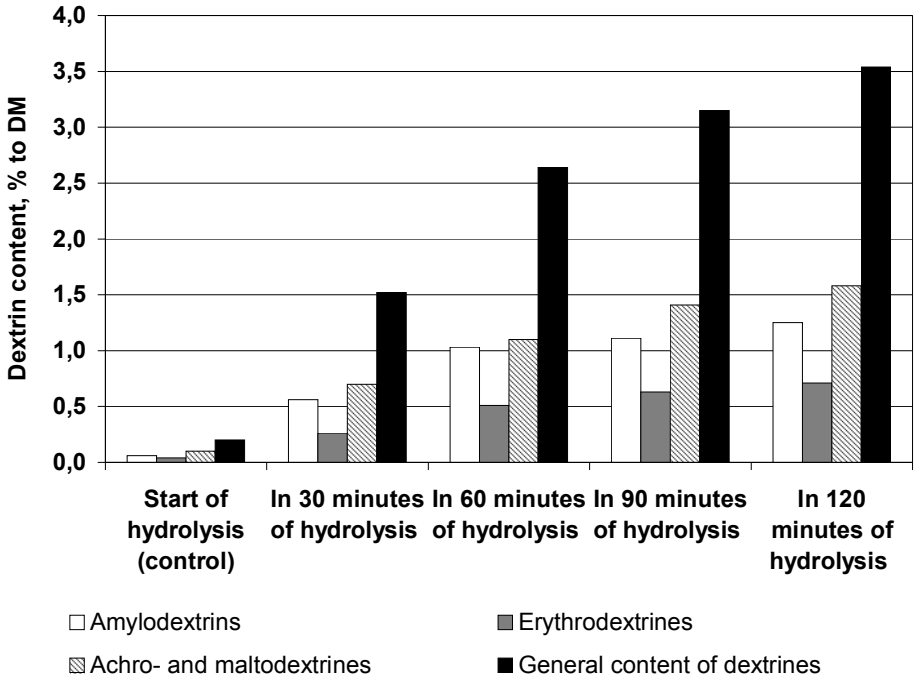

Figure 4. The effect of α-amylase on dextrin mass fraction

The analysis of the results we got showed, that general amount of dextrines in production of semi-finished product-hydrolysate increased for 94% in comparison to control example. At the same time the content of low molecular dextrines, such as achrodextrines and maltodextrines, has increased for 1,48% DM. It's known, that dextrines are hydrophilic compounds, which increase the amount of bonded moisture and provide with conspicuous effect of the slowing down of starch retrogradation process, that leads to staling of bread.

Effect of fermentative modified rice flour semi-finished product on microbiological processes in yeast dough

Taking into consideration the fact, that biotechnological processes of living conditions of microorganisms are the main things in the technology of bakery: bread yeast and acid bacteria, it would be expedient to study the effect of additives on the course of technological process and quality of rice bread.

During the research the dough was prepared by non-fermented method, on the basis of semi-finished product-hydrolysate from 50% of rice flour from its general mass with humidity of 65%. When kneading the dough the other part of flour, yeast in the amount of 3% and salt have been added. Its estimated humidity was 53%. The dough for the control example has been prepared without adding of ferments of amylolytic action.

The main indicators, that characterize the course of technological process in goods production from yeast dough is gas formation ability, the looseness of bread crumb depends on which, and acid accumulation, which provides with the taste and flavor of readymade products. The obtained results of research of the effect of used semi-finished products-hydrolysate from the rice flour on gas formation in the dough (Figure 5) affirm about increasing of carbon dioxide produced, for 57,8% in comparison to control example. It's explained by adding of extra amount of mono- and disaccharides, formed as a result of hydrolytic starch formation, in consequence of its fermentative modification, which are assimilated by yeast.

We can judge the intensity of fermentation process and dough readiness by increasing of titrated acidity of dough semi-finished products. The analysis of obtained data showed (Figure 6), that in case of use of starch fermentative modification with the help of α-amylase and glucoamylase, more intensive increase of acidity is observed in maturation of the dough in the experimental example, in comparison to the control one.

The increase of titrated acidity in the dough, prepared on the basis of semi-finished product-hydrolysate from rice flour, during the whole period of maturation for 1,5 degr, in comparison with control, is caused by adding of citric acid, aiming to provide with optimal pH conditions for α-amylase and glucoamylase action. Besides, in the end of the fermentation process of the dough, using starch fermentative modification, its acidity increases for 0,6 degr, at the same time the control example – only for 0,3 degr. It is probably related to more active vitality of lactic acid bacteria and yeast, that very much depends of the content of nutrient environment, as well as the amount of mono- and disaccharides.

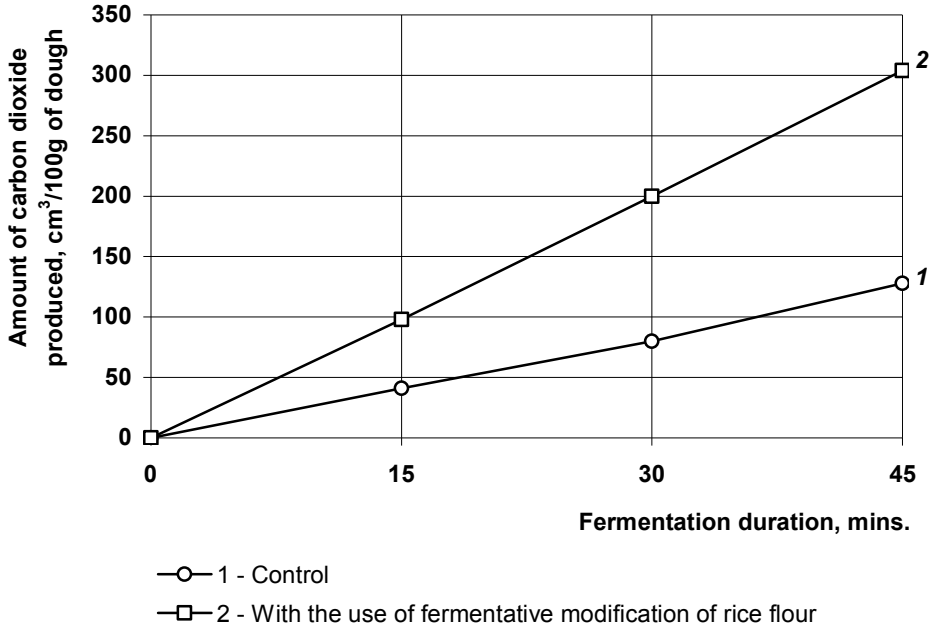

Figure 5. Gas formation ability of rice dough

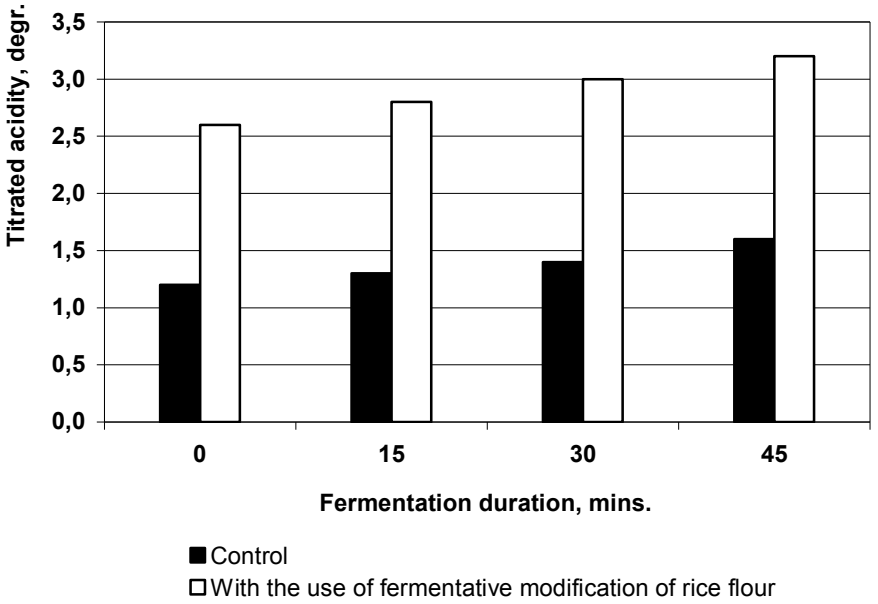

Figure 6. Change of titrated acidity of rice dough

Effect of fermentative modification of rice flour starch on the quality of readymade bread

As a result of increasing of readily available sugar, which is assimilated by yeast cells, the process of alcohol fermentation intensifies, in consequence improvement of porosity structure and volume of readymade bread is expected. In the course of further research, the effect of fermentative modification of starch on the quality of readymade goods was determined (Table 2).

Table 2

Rice bread quality score

Score	Characteristics of bread quality score	
	Rice flour bread (without additives)	Bread with the use of semi-finished product-hydrolysate from rice flour
Specific volume, cm^3/g	1,27	1,44
Acidity, degr.	1,3	2,8
Porosity, %	36,7	41,4
Fragility, %		
in 3 hrs	2,50	1,30
in 24 hrs	6,95	2,60
Bread crumb deformation, un. of penetrometer		
in 3 hrs	48	59
in 24 hrs	34	46

Analysis of readymade products shows positive effect of the use of starch fermentative modification of rice flour on the change of structural mechanical properties of readymade goods. Bread freshness is one or the main scores of its quality and storage suitability. It's determined by the results of research of crumb deformation level, that after cooling (after 3 hours of storage), the use of the offered technology of rice bread provides with increasing of softness for 18%, and after 24 hours – for 24%. Herewith, decrease of bread penetration degree with the use of starch fermentative modification is less intensive, than the control one. It's explained by accumulation of low molecular dextrines when preparing of semi-finished product-hydrolysate from rice flour under the effect of mushroom α-amylase (Figure 4), that provides with longer period of keeping the readymade products fresh.

Better keeping of the freshness of the experimental example of rice bread in comparison to the control one, is confirmed by the results of determining of their fragility. It's determined, that the use of rice flour starch fermentative hydrolysis in bread production leads to decreasing of this score for 1,9 times, in comparison to control for freshly baked products.

Improvement of specific volume and porosity of readymade bread is stipulated by intensification of gas formation process in the dough, with the use of α-amylase and glucoamylase, because of increasing of carbon dioxide amount, produced in the process of its fermentation. But the analysis of obtained results shows, that the specific volume and porosity of gluten-free bread, prepared on the basis of semi-finished products-hydrolysate,

increases only for 13,4% and 12,5% in comparison to control example, which won't allow to improve the quality of readymade products, at the same time gas formation increases for 57,8% (Figure 5). Determined dependence can be explained by the thing, that as a result of absence of gluten carcass, that has elastic properties, it has a low gas retention capacity, that's why carbon dioxide accumulation is ineffective. Carbon dioxide, which is formed in alcohol fermentation, causes the pressure in dough preparation, as a result cracks appear on its surface, through which the main loses of CO_2 occur, as a result the dough is irreversibly depleted.

Obtained data testify to the necessity of enhancer, that could improve dough rheological properties. That's why further researches will be associated with the development of measures aiming to improve gas retaining capacity in the rice flour dough. One of the ways to improve bread quality for patients with celiac disease might be the use of surfactants.

Conclusions

As a result of research, the expediency of hydrolysis of rice flour starch by amylolytic ferments in bread technology for patients with celiac disease has been determined. The dosage of mushroom α-amylase in the amount of 0,005% and glucoamylase – 0,03% to mass of rice flour helps to accumulate saccharides in the amount of 5,5-6%, which are necessary for intensification of the course of microbiological processes in the dough. For more complete starch hydrolysis, the expediency of preparation of semi-finished product-hydrolysate with the moisture content of 65% from 50% of rice flour from its recipe amount with the further kneading of the dough on its basis. The use of rice flour starch fermentative modification in bread technology intensifies gas formation and acid accumulation in the process of dough maturation, as a result, readymade goods are characterized by improved structural mechanical quality scores. Besides, the production of bread using the ferment of α-amylase allows longer shelf life.

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Modeling the efficiency of microfiltration process in reducing the hardness, improvement the non-sugar component rejection and purity of raw sugar beet juice

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Abstract

Introduction. The aim of this study is determining the best configuration of artificial neural network, different networks with neuron number varying from 2 to 20, were designed. Their mean square errors, square normalized errors, absolute errors and correlation coefficients were investigated for different learning rules and transfer functions.

Material and Methods. In this study, the potential of microfiltration process in reduction of hardness, improvement of purity and non-sugar rejection of raw beet juice was modeled with different parameters as temperature (30 and 60 °C) transmembrane pressure (1, 1.75 and 2.5 Bar) and time (regular time intervals from 1 to 60 min) by artificial neural network (ANN). ANN modeling was carried out by Neurosolution software v6 to determine the best type of transport function, learning rule, and determination of applied percentages for training, validation and testing stages.

Results and discussion. The best neural network was the one hidden layer in Levenberg learning rules with tangent transfer function which included 8 neurons and resulted in maximum correlation coefficient for hardness according to temperature, pressure and time variation. The neural network with one hidden layer including 4 neurons with sigmoid transfer function under Levenberg learning rule had the least error and highest r for purity variation. Finally, the neural network with one hidden layer including 2 neurons, under Levenberg learning rule and tangent transfer function had the lowest error and highest correlation for non-sugar rejection percentage. Modeling was carried out with different percentages of data for training that the best prediction correlation for all parameters (turbidity, purity, non-sugar rejection) obtained when 60% of the data were used for training, 35% of them were employed for validation and 5% of the data were used for testing. The correlation of experimental data with the predicted values of the model obtained, too. According to the obtained models, ANN resulted in data with proper correlation with experimental data of hardness, purity and non-sugar rejection with respective correlation coefficients of 0.987, 0.980 and 0.981. This study also addressed the model sensitivity to input data. The best model sensitivity of the model for prediction of turbidity, purity and non-sugar rejection was related to time.

Conclusion. The best rule for network training for prediction of hardness, purity and non-sugar rejection was Levenberg rule. The model was able to predict the hardness, purity and non-sugar rejection percentage under different operational models in a way that the modeled data showed high correlation with experimental data.

Introduction

In spite of passing through purification stages, purified sugar beet juice still contains undesirable non-sugar compounds which can adversely affect the final quality of the sugar. These undesirable compounds include a wide range of organic and inorganic materials such as amino acids, amides, proteins, minerals and etc. Among them nitrogenized compounds and single-valance cations cause molasses (Djuri, 2004). On the other hand, conventional purification methods have high energy consumption and lack of accurate control on addition of lime and carbon dioxide will result in defects in non-sugar rejection due to destruction of surface adsorption of impurities from calcium carbonate crystals. In this regard, membrane processes are now in the center of the focus due to advantages such as reduction in energy consumption, increase of efficiency, no need for chemicals and feasibility (Gyura, 2005; Ghosh, 2003; balakrishnan, 2000). Membrane processes based on microfiltration pressure driving force has attracted the attention of numerous researchers in the field of sugar production.

First, Lancernon et al analyzed application of a ceramic micro-filter (pore size of 0.1-10 micron) for sugar cane syrup purification in 1993. Then, in 1994, Domir et al investigated the optimal condition of sugar cane extract filtration and expressed that the increase in pressure and slope transverse flow speed can improve flux. Vern et al. (1997) reported the filtration of sugar cane syrup by a micro-filter with pore size of 01 micron, in a way that the resultants could be directly used for crystallization. Farmani et al. (2007) managed to increase the purity of sugar cane clarifier by 0.87 with the use of microfiltration process.

On the other hand, process modeling can play an important role in process design as they are capable of predicting the system performance. Neural network can model complex nonlinear systems with numerous input and outputs (Delgerange, 1998). Artificial neural network is inspired from human brain and neural network and like that, it includes numerous neurons. Similar to human brain, this network can also learn. In cases with numerous input and outputs, application of ANN can be helpful in modeling the system or obtain a structure of data. So far, various topologies and applications have been presented for ANNs that cover a wide range of topics (Menhaj, 2000). Therefore, researchers pay a specific attention to modeling the membrane processes in different industries. For example, Mascula et al. introduced an empirical model to predict the created cake layer for membrane blockage in ultrafiltration processes. Shahidi et al investigated the potential of nanofiltration in treatment of sugar beet pressing wastewater and then modeled in by ANN. The results showed that a network with one hidden layer including 16 neurons with hyperbolic tangent linear transfer function under Levenberg learning rule can provide a proper correlation between the modeled and experimental data.

In this regard, the present research addressed modeling of microfiltration process in reduction of hardness, non-sugar rejection and improvement of raw sugar beet juice as some of the indices of raw syrup purification by ANN method.

Materials and methods

Membrane process

Raw sugar beet juice microfiltration process was carried out by a pilot equipped with ceramic membrane with tubular module (made by Bioken Russia and Milar Khorasan

Companies). The experiments were carried out at two temperatures of 30 and 60 °C at three pressure levels (1, 1.75 and 2.5 Barr) and 8 equal time intervals from 1 to 60 min (48 experiments) on variation of hardness, non-sugar rejection and purity of permeated flow [8]. The technical properties of the membrane system are listed in Table 1.

Table 1

Technical properties of microfiltration membrane system for purification of raw sugar beet juice

Membrane material	module	MWCO	Membrane effective area	pH tolerance	Temperature tolerance	Maximum tolerable pressure
Ceramic	Tubular	0.2 μm	0.28 m^2	1-11	10-95 °C	3 Bar

Assays

Samples purity was calculated based on their polarimetry and brix values from equation 1:

$$Purity = (pol/Brix) \times 100 \quad (1)$$

Sample hardness was measured by syrup titration with EDTA solution, at concentration of 0.025 moles/lit, according to ICUMSA method. The process was as follows: first, 50 ml of syrup was mixed with 50 ml distilled water and then 10 ml Buffer solution was added to that. Then it underwent titration at the presence of Eriochrome Black reagent and EDTA till reaching to blue color. In this condition, if n ml of EDTA was consumed for each 100 ml of syrup, the hardness based on CaO could be obtained from equation 2 (ICUMSA,2000):

$$Hardness = 1.002 \times n \quad (2)$$

To calculate percentage of non-sucrose component rejection the pol and Brix of permeat and feed were measured by substitution in equation 3 (Ghosh, 2003; Balakrishnan, 2000):

$$Non-sugar\ rejection = \left[1 - \frac{(Brix - Pol)_{permeat}}{(Brix - Pol)_{feed}}\right] \times 100 \quad (3)$$

Artificial neural network modeling

ANN modeling was conducted by Neurosolution V6. To investigate and evaluate different networks, the data were randomly classified into three sections; in a way that a percentage of data were used for training, some were used for validation and the other part was employed for network testing. During training process, ANN learnt neuron relationships in each cycle of training in order to reach to the predicted values closer to the desirable output values. To find a network with proper architecture, mean square error (MSE), mean absolute error (MAE) and correlation coefficient (R2) were used. Correlation coefficient varies from -1 to 1. The farther from 0, the more serious the alignment or opposition of the two investigated parameters will be (Razavi, 2003).

First, all the test data (48) were randomized; then network structure with one hidden layer and different number of neurons under Levenberg learning rules and momentum and two functions of tangent and Sigmoid, were examined. Moreover, the best data percentage for training, validation and testing of this network were determined and finally the sensitivity of purity variation, hardness and non-sugar rejection to temperature, time and pressure was assessed. For model validation, the correlation between the predicted and experimental data was also calculated (Shahidi, 2012).

Results and discussion

To find the best configuration of artificial neural network, different networks with neuron number varying from 2 to 20, were designed. Their mean square errors, mean square normalized errors, mean absolute errors and correlation coefficients were investigated for different learning rules and functions as shown in Tables 2 to 4. In continue the best percentage for training, validation and test with minimum error and maximum correlation coefficient were examined. As Table 2 suggests, the best neural network was the one with one hidden layer in Levenberg learning rules with tangent transfer function which included 8 neurons and resulted in maximum correlation coefficient for hardness according to temperature, pressure and time variation.

Table 2

Different architectures of ANN with different neurons in the hidden layer and transfer functions in the hidden and output layers used for permeate hardness in sugar beet juice microfiltration

Hardness	Levenberg							
No of neurons	Sigmoid				Tanh			
	MSE	NMSE	MAE	R	MSE	NMSE	MAE	R
2	3.632	0.444	1.671	0.808	3.188	0.390	1.587	0.843
3	3.803	0.465	1.660	0.790	1.003	0.122	0.827	0.956
4	1.254	0.153	0.976	0.930	0.331	0.040	0.429	0.989
5	0.600	0.073	0.687	0.978	0.340	0.041	0.488	0.986
6	0.853	0.104	0.615	0.958	0.561	0.052	0.910	0.974
7	0.554	0.067	0.686	0.982	0.229	0.028	0.455	0.993
8	0.576	0.070	0.662	0.979	**0.158**	**0.019**	**0.334**	**0.993**
9	0.527	0.064	0.601	0.978	0.399	0.048	0.564	0.985
10	0.619	0.075	0.616	0.970	0.529	0.064	0.621	0.990
11	0.473	0.023	0.543	0.990	0.357	0.043	0.493	0.984
12	0.571	0.069	0.584	0.968	0.215	0.026	0.399	0.988
13	0.565	0.069	0.599	0.972	0.233	0.028	0.435	0.988
14	0.487	0.059	0.652	0.989	0.258	0.031	0.438	0.988
15	0.601	0.073	0.708	0.982	0.311	0.038	0.518	0.992
16	0.559	0.068	0.594	0.971	0.280	0.034	0.468	0.985
17	0.379	0.046	0.506	0.981	0.370	0.045	0.535	0.980
18	0.446	0.054	0.511	0.974	0.169	0.020	0.333	0.991
19	1.175	0.143	0.806	0.942	0.227	0.027	0.408	0.993
20	0.323	0.039	0.486	0.988	0.194	0.023	0.383	0.992

As Table 3 shows, the neural network with one hidden layer including 4 neurons with sigmoid transfer function under Levenberg learning rule had the least error and highest r for purity variation.

Table 3

Different architectures of ANN with different neurons in the hidden layer and transfer functions in the hidden and output layers used for permeate purity in sugar beet juice microfiltration

Purity	Levenberg							
No of	Sigmoid				Tanh			
neurons	MSE	NMSE	MAE	R	MSE	NMSE	MAE	R
2	0.018	0.134	0.115	0.955	0.169	0.126	0.091	0.956
3	0.036	0.269	0.137	0.893	0.016	0.123	0.100	0.978
4	**0.004**	**0.031**	**0.057**	**0.990**	0.009	0.746	0.083	0.0978
5	0.011	0.081	0.088	0.990	0.011	0.084	0.081	0.979
6	0.008	0.060	0.075	0.987	0.006	0.050	0.077	0.989
7	0.010	0.076	0.084	0.972	0.007	0.056	0.073	0.984
8	0.005	0.043	0.062	0.981	0.018	0.137	0.091	0.961
9	0.007	0.057	0.077	0.987	0.008	0.064	0.072	0.981
10	0.015	0.112	0.106	0.982	0.003	0.026	0.043	0.989
11	0.003	0.026	0.045	0.988	0.004	0.036	0.064	0.985
12	0.010	0.080	0.086	0.983	0.003	0.029	0.042	0.986
13	0.007	0.058	0.073	0.984	0.004	0.035	0.051	0.983
14	0.020	0.156	0.098	0.970	0.006	0.047	0.065	0.984
15	0.006	0.046	0.067	0.983	0.005	0.041	0.056	0.979
16	0.009	0.069	0.084	0.988	0.005	0.038	0.056	0.981
17	0.14	0.107	0.100	0.980	0.003	0.025	0.047	0.988
18	0.005	0.038	0.060	0.981	0.011	0.086	0.081	0.980
19	0.008	0.067	0.076	0.973	0.006	0.044	0.048	0.978
20	0.007	0.059	0.076	0.985	0.004	0.032	0.046	0.983

Finally, the neural network with one hidden layer (including 2 neurons), under Levenberg learning rule and tangent transfer function had the lowest error and highest correlation for non-sugar rejection percentage.

As it can be seen in Table 5, a comparison was made between momentum and Levenberg learning rules in terms of presenting the best transfer function with minimum error and maximum correlation for hardness, purity and non-sugar rejection.

Table 4

Different architectures of ANN with different neurons in the hidden layer and transfer functions in the hidden and output layers used for Non-sugar rejection in sugar beet juice microfiltration

Non sugar rejection	Levenberg							
No of neurons	sigmoid				Tanh			
	MSE	NMSE	MAE	r	MSE	NMSE	MAE	R
2	1.205	0.059	0.860	0.981	**0.419**	**0.20**	**0.514**	**0.993**
3	1.270	0.063	0.974	0.984	1.132	0.056	0.929	0.978
4	0.476	0.024	0.600	0.990	1.382	0.068	0.939	0.965
5	1.677	0.083	1.020	0.959	0.826	0.041	0.718	0.979
6	0.34	0.036	0.670	0.982	1.059	0.052	0.910	0.974
7	1.183	0.058	1.001	0.972	0.367	0.018	0.484	0.992
8	1.096	0.054	0.893	0.974	0.704	0.035	0.566	0.983
9	0.784	0.039	0.668	0.980	0.620	0.030	0.620	0.984
10	0.661	0.032	0.679	0.984	0.720	0.035	0.591	0.987
11	0.468	0.023	0.543	0.990	0.499	0.024	0.562	0.988
12	0.824	0.041	0.780	0.979	0.356	0.017	0.376	0.991
13	0.963	0.047	0.806	0.975	0.342	0.017	0.430	0.977
14	0.732	0.036	0.584	0.983	0.501	0.024	0.532	0.989
15	0.645	0.032	0.643	0.984	0.580	0.028	0.606	0.989
16	0.679	0.033	0.689	0.983	0.404	0.020	0.439	0.992
17	0.792	0.039	0.739	0.980	0.458	0.022	0.528	0.989
18	0.982	0.048	0.826	0.980	0.633	0.031	0.610	0.985
19	0.639	0.031	0.608	0.984	0.438	0.021	0.450	0.991
20	0.774	0.038	0.742	0.980	0.422	0.021	0.489	0.992

Table 5

Comparison of two learning rules used for selected ANN architectures to permeate Hardness, purity and non-sugar rejection in sugar beet juice microfiltration

Momentum						Levenberg						Parameter
r	MAE	NMSE	MSE	Transfer function	Number of neuron	r	MAE	NMSE	MSE	Transfer function	Number of neuron	
0.935	0.808	0.132	1.083	Tangent	20	0.993	0.334	0.019	0.158	Tangent	8	Hardness
0.985	0.093	0.085	0.011	Tangent	18	0.990	0.057	0.031	0.004	sigmoid	4	purity
0.969	0.998	0.066	1.324	Tangent	19	0.993	0.514	0.020	0.419	Tangent	2	Non sugar Rejection

Proper percentages for training, validation and testing

Modeling was carried out with different percentages of data for training, validation and testing. For this purpose, first the best percentage of data for training was selected according to correlation coefficient. Based on that, the best data percentage for validation and testing were selected as shown in Tables 6-8.

Table 6

Comparison of different percentages of data used for training of selected ANN architectures to model the permeate hardness

Training Data (%)	Validation Data (%)	Testing Data (%)	MSE	NMSE	MAE	R
5	47.5	47.5	20.496	1.279	3.493	0.560
10	45.0	45.0	22.165	1.451	3.698	0.619
15	42.5	42.5	17.391	0.980	3.384	0.503
20	40.0	40.0	8.058	0.577	2.416	0.802
25	37.5	37.5	2.163	0.212	0.999	0.919
30	35.0	35.0	0.733	0.040	0.715	0.981
35	32.5	32.5	1.044	0.092	0.836	0.978
40	30.0	30.0	2.785	0.305	1.298	0.837
45	27.5	27.5	1.120	0.106	0.810	0.974
50	25.0	25.0	0.577	0.035	0.595	0.991
55	22.5	22.5	0.158	0.016	0.365	0.992
60	20.0	20.0	0.158	0.019	0.334	0.993

Table 7

Comparison of different percentages of data used for training of selected ANN architectures to model the permeate purity

Training Data (%)	Validation Data (%)	Testing Data (%)	MSE	NMSE	MAE	R
5	47.5	47.5	0.680	2.325	0.648	0.354
10	45.0	45.0	0.227	0.601	0.344	0.734
15	42.5	42.5	0.101	0.406	0.225	0.857
20	40.0	40.0	0.225	2.830	0.401	0.789
25	37.5	37.5	0.047	0.301	0.188	0.908
30	35.0	35.0	0.018	0.089	0.109	0.961
35	32.5	32.5	0.031	0.087	0.150	0.971
40	30.0	30.0	0.102	0.380	0.228	0.916
45	27.5	27.5	0.017	0.061	0.087	0.984
50	25.0	25.0	0.029	0.065	0.119	0.982
55	22.5	22.5	0.008	0.026	0.080	0.989
60	**20**.0	**20**.0	**0.004**	**0.031**	**0.057**	**0.990**

Table 8

Comparison of different percentages of data used for training of selected ANN architectures to model the non-sugar rejection

Training Data (%)	Validation Data (%)	Testing Data (%)	MSE	NMSE	MAE	R
5	47.5	47.5	25.616	0.907	4.156	0.874
10	45.0	45.0	10.524	0.523	2.846	18.181
15	42.5	42.5	1.562	0.076	1.090	0.961
20	40.0	40.0	7.202	0.366	1.770	0.822
25	37.5	37.5	11.941	0.917	2.091	77.777
30	35.0	35.0	2.326	0.090	1.190	0.963
35	32.5	32.5	3.136	0.148	1.441	0.925
40	30.0	30.0	0.711	0.034	0.690	0.983
45	27.5	27.5	0.903	0.039	0.788	0.982
50	25.0	25.0	1.429	0.051	1.056	0.981
55	22.5	22.5	0.848	0.043	0.710	0.989
60	**20.0**	**20.0**	**0.468**	**0.023**	**0.543**	**0.990**

As mentioned before, after determination of the best data percentages for network training, proper percentages were examined for validation and testing as presented in Tables 9–11.

Table9

Comparison of different percentages of data used for cross validation and testing of selected ANN architectures to model the permeate hardness

Training Data (%)	Validation Data (%)	Testing Data (%)	MSE	NMSE	MAE	R
60	5	35	0.324	0.021	0.419	0.989
60	10	30	3.738	0.205	1.306	0.936
60	15	25	0.810	0.081	0.760	0.960
60	20	20	0.424	0.028	0.451	0.989
60	25	15	0.515	0.026	0.485	0.994
60	30	10	0.219	0.030	0.359	0.985
60	**35**	**5**	**0.565**	**0.213**	**0.699**	**1**

Table10

Comparison of different percentages of data used for cross validation and testing of selected ANN architectures to model the permeate purity

Training Data (%)	Validation Data (%)	Testing Data (%)	MSE	NMSE	MAE	R
60	5	35	0.043	0.184	0.163	0.936
60	10	30	0.007	0.042	0.073	0.979
60	15	25	0.006	0.045	0.071	0.984
60	20	20	0.011	0.050	0.097	0.979
60	25	15	0.032	0.067	0.112	0.981
60	30	10	0.005	0.023	0.070	0.933
60	**35**	**5**	**0.015**	**0.303**	**0.118**	**1**

Table11

Comparison of different percentages of data used for cross validation and testing of selected ANN architectures to model the non-sugar rejection

Training Data (%)	Validation Data (%)	Testing Data (%)	MSE	NMSE	MAE	R
60	5	35	1.063	0.066	0.884	0.986
60	10	30	1.346	0.069	0.874	0.967
60	15	25	0.763	0.034	0.565	0.984
60	20	20	0.734	0.028	0.728	0.991
60	25	15	0.512	0.089	0.566	0.962
60	30	10	0.550	0.026	0.621	0.996
60	**35**	**5**	**0.225**	**0.204**	**0.363**	**1**

As seen in Tables 6–11, the best prediction correlation for all parameters (turbidity, purity, non-sugar rejection) obtained when 60% of the data were used for training, 35% of them were employed for validation and 5% of the data were used for testing.

Correlation between the tested vales and experimental data

Figure 1 shows the correlation of experimental data with the predicted values of the model. According to the obtained models, ANN resulted in data with proper correlation with experimental data of hardness, purity and non-sugar rejection with respective correlation coefficients of 0.987, 0.980 and 0.981.

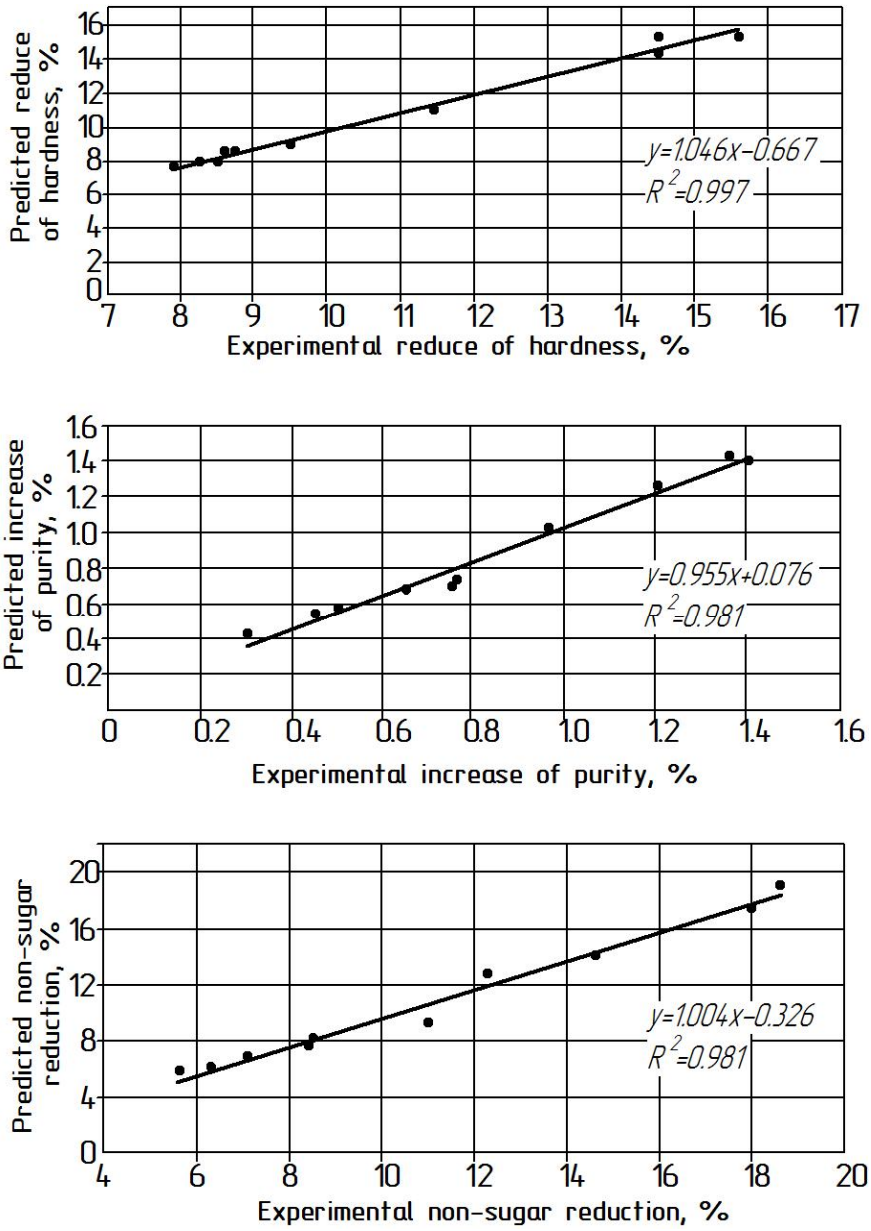

Figure 1. Correlation of the experimental data with the predicted values

Sensitivity of the model to input data

This study also addressed the model sensitivity to input data. As Figure 2 demonstrated, the best model sensitivity of the model for prediction of turbidity, purity and non-sugar rejection was related to time.

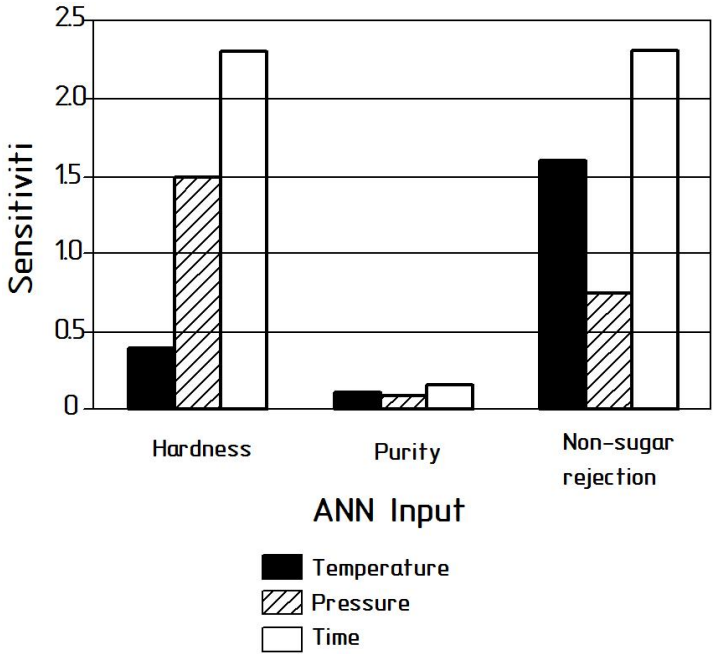

Figure 2. Models' sensitivity to prediction of flux, color and turbidity

Conclusion

Results of modeling microfiltration process in raw beet juice purification showed that the best rule for network training for prediction of hardness, purity and non-sugar rejection was Levenberg rule. The best data percentages for training, validation and testing were 60%, 35% and 5%, respectively. the model was able to predict the hardness, purity and non-sugar rejection percentage under different operational models in a way that the modeled data showed high correlation with experimental data (Table 12).

Table 12

Summarized result of modeling of hardness, purity and non-sugar rejection changes in purification of raw beet juice by microfiltration

Correlation coefficient	Percentage of learning/ validation/ test	Learning rule	Transfer function	Number of neuron	Hidden layer	Dependent variable
1	60/35/5	Levenberge	Tangent	8	1	Hardness
1	60/35/5	Levenberge	Sigmoid	4	1	Purity
1	60/35/5	Levenberge	Tangent	2	1	Non sugar rejection

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Functional products and preparations in the systemic concept of health

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Abstract

Introduction. The analytical and experimental researches on the scientific substantiation of functional products and preparations in the new systemic concept of health have been carried out.

Materials and methods. Sunflower and linseed oil, oil compositions and products, antioxidants, unsaturated fatty acids, the role of cholesterol, the systemic concept of health. were researched. The kinetics of oxidation of oils at temperature processing characterized the average rate of change in their indexes (peroxide and acid numbers). Chromatographic method was used to evaluate volatile compounds.

Results and discussion. According to research results of the role of polyunsaturated fatty acids of omega-3 and omega-6 in vegetable oils and functional products and the problem of cholesterol in the life and health of people of different age groups it was suggestion the physiological-functional system of CTIOL, which is an integrated choice of factors in individual prevention, treatment and rehabilitation.

It was found that KTIOL-BF (1%) reduces the average oxidation rate of sunflower oil at 150 °C (3 hours) in 12.2 times, at 200 °C (6 hours) in 13.6 times, the average acidity of the oil decreases by 9 and 2.2 times respectively. It was established that under similar conditions the average rate of oxidation of linseed oil decreases by 1.4 and 1.5 times, respectively. Acidity of oil practically does not decrease. It has been found that KTIOL-LS2 oil with 1% KTIOL-BF at 20–25 °C is stored for 6 months. By component composition mayonnaise without cholesterol and lactose belongs to the diet group.

On the basis of the analysis of the gas chromatographic profiles of the oilseed composition KTIOL-LS2, it was is expressed a hypothesis concerning the possible reduction of the amount of volatile compounds in it, both due to the composition of the oil, and through the interaction of individual volatile ingredients.

Conclusions. Special products which are based on sunflower and linen compositions KTIOL-LS2 improve the physiological state of people of different age groups for the occurrence of disease-related and concomitant pathologies.

Introduction

In today's ecological, economic and social conditions, as before, the problem of health and healthy lifestyle is topical. After all, most people understand that products and preparations (biologically active additives) should not only be tasty, but functional and safe.

The design and manufacture of safe and competitive functional products and preparations (FPP) on the world market and, in East Europe, are in demand. In particular, in Japan, the European Union and the United States, especially in the context of public health, a healthy, creative and active lifestyle.

The etiology and pathogenetic links of the development of major age and concomitant diseases, such as ophthalmologic (macular degeneration, glaucoma, cataract, etc.), are still not fully studied, and hence the absence of highly effective therapeutic and prophylactic products and preparations, methods and techniques [1].

As of 2005, in East European citizen the older people were diagnosed with a deterioration in health (a deficit and imbalance in the diet of many biologically active nutrients). The conclusion was reached on the urgency of developing scientific approaches to the creation of functional products. Products with a pronounced biological effect on the human body by type of substitution therapy [2].

According to a study conducted by the World Health Organization (WHO), around 600 million people in the world each year suffer from illnesses caused by poor quality food.

According to E.I. Chazova, depending on the age of a person, his way of life, nutrition and the state of the environment, its organisms at one time or another, resists the infection. That is, the process is gradually and in the first years asymptomatic. Some signs arise when the infection transits the bar of counteraction to the human immune system and begins the active destruction of body tissues. From classical prevention, he advises to lead a healthy lifestyle [3].

In the complex environmental, economic and social conditions of today, scientific substantiation of the technologies of functional products and preparations (FPP) of the special and ophthalmologic direction and the improvement of the concept of health ecology in relation to prevention, treatment and rehabilitation of a person is necessary.

By definition, WHO "Health is a state of complete physical, mental and social well-being." According to the Ministry of Health of Ukraine, the health of the population depends on the lifestyle, including nutrition (by 50–70%), the level of development of the health care system (by 10–15%), heredity (by 10–15%), and from the environmental situation (10–20%). Official statistics also indicate that there are serious problems in the health of the population (about 80% have a pathology, 48 – 60% overweight, etc.).

Modern changes in the science of nutrition and food technology are associated with the emergence of a new variety of food products, in particular physiologically functional, or shortened FPP. FPP is a food product that, in addition to its nutritional properties, has the ability to influence individual functions of the body, thereby reducing the risk of chronic diseases for their regular use [4]. Production of FPP in the leading countries is due to the general aging of the population. In addition, anthropogenic pressure on the environment is increasing, which also negatively affects the health of all segments of the population, regardless of age and social status.

In recent years, food for specific nutritional uses has become more and more confident with Food for Specific Health Use. The difference of these products from their traditional counterparts is that they not only have certain nutritional properties, but also have a purposeful effect on the functional activity of individual organs, systems and the organism as a whole, stimulating their capacity for work with a specific preventive and therapeutic

and recreational purpose. In 1991, the concept of functional nutrition was developed in Japan, which was reflected in the special government order "On foods for special nutrition" (FOSHU).

Nicberg I.I. notes that even in scientific literature and in official documents, there is no unity in the definition of concepts relating to FPP and their scope [5]. And although in some cases they are positioned as food products (different from biological additives and proprietary drugs), others, on the contrary, indicate that they are most useful bioadditives or other therapeutic and prophylactic preparations. Although one of the significant distinctive characteristics of foods related to functional nutrition, according to pioneers of the definition of FPPs and their followers, is that they are not considered as medicinal substances. But there are many supporters of a different point of view. They believe that many products of functional nutrition are now in the area between preparations and food. Therefore, they can be attributed to foodstuffs themselves, as well as to their dietary varieties or even to medical preparations

The Australian National Center for Excellence in Functional Products (NCEFF) has defined these products: "Functional products are products that support the health and well-being of humans, providing health benefits against basic nutrition." The Australian market has a large number of availableFPP. These are dairy products, probiotics, omega-3 fatty acid products, cereal foods with supplementary food fibers, margarine with plant sterols, low blood cholesterol, products with low glycemic index, etc. According to Nickberg II more than 20% of the population have elevated cholesterol levels, which prompts them to give preference to FPP in order to reduce the risk of cardiovascular disease. According to Australian experts, reducing cholesterol by 10% may reduce the risk of heart disease by 25% or more [5].

In the system of complex modern technologies KTIOL® for solution of the problem are used: integrated technologies, engineering, equipment, lines. It allows to carry out projects ranging from ideas, innovations, know-how and to the organization of production of high-quality and competitive products with functional properties [6, 7]. In the difficult conditions of the present, the problem of the design and use of FPP, the relationship of the endoecology of the individual with the environment, the way of life and human health in Ukraine is relevant.

The most important problem in a market economy, in particular, in the WOT and the EU, is the introduction of innovative technologies and the organization of production. This will ensure the production of export and import of substitute products in accordance with modern requirements of safety, quality, competitiveness, functional and nutritional value [6–8].

Common oils (sunflower, soya, rapeseed, palm, etc.) do not have the optimum fatty acid and ingredient composition and do not suit many consumers in their characteristics [6, 9].

In order to obtain complete natural oils of functional and well-being purposes with a balanced biochemical composition, it is necessary that they have not been modified yet. Such oils and oleaginous products are not only products with a good price-quality ratio (the main criterion for market success), but also products that meet the specific needs of consumers for the prevention and treatment of chronic diseases.

Natural and composite oils are the suppliers of functional ingredients that have the potential to cause (due to their systematic consumption) a beneficial effect on the physiological functions and metabolism of the human body. The group of physiologically functional ingredients in oils and fats include polyunsaturated fatty acids (PUFAs), medium chain fatty acids, fat-soluble vitamins and biologically active substances (BAS). The main

group of functional ingredients is a linear structure PUFA with a paired number of carbon atoms (from C18 to C24) cis configuration. Linoleum, linolenic and arachidonic acids are essential acids, the lack or lack of which in food negatively affects the human body. Vegetables, including linseed, hemp, corn, sunflower, rapeseed, and soya, serve as the main food source of linoleic and linolenic acid.

In the human body, omega-3 PUFAs are included in the lipid double layer of cell membranes, regulating their properties in the composition of phospholipids of membranes. They also contribute to the metabolism of cholesterol in the liver and its elimination from the body. Due to the lack of omega-3 PUFAs, their place is occupied by omega-6 PUFAs delivered from food.

The reduction in cholesterol content is also facilitated by the presence of lipids in the fatty diet, which include acyl carboxylic acids with an average chain length of 6 to 10 carbon atoms. The effectiveness of the physiological action of PUFA depends on the number and ratio of various acids coming from the food.

According to modern ideas in the diet of a healthy person, the ratio of omega-6 and omega-3 PUFA should be 10: 1. For different pathological states, the ratio of these acids in the diet changes in the direction of increasing the proportion of linolenic acid and may reach 5: 1 and even 2: 1. The second group of functional ingredients in oils and oleaginous products is fat-soluble vitamins (A, D, E, K) and provitamin A (β-carotene), whose consumption deficit is 40–60% and 20-30% respectively. An adequate level of consumption of fat-soluble vitamins can be guaranteed by the technological adoption of vitamins, which does not require significant changes in the hardware pattern of production. Oils and oilseeds, unlike traditional counterparts, should contain PUFA and fat-soluble vitamins that relate to an adequate level of their intake and meet the physiological needs of the body in these ingredients.

It should be noted that one of the directions of designing the functional properties of oils, oil products and preparations is the use of composite oils for food production: emulsion, milk, diet, special, baby food products, etc. – with the necessary content and ratio of acids omega-6 and omega- 3 [10–13].

PUFAs of the family of omega-3 as part of cell membranes determine their functions and participate in the transformation of signals from the environment. This leads to a change in cellular metabolism. Membrane enzymes, interacting with acids omega-3, exhibit biochemical activity. This is of particular importance in tissues with high electro-physiological activity, for example, in brain tissues or retina of the eye [14].

The oils obtained from mixtures of flaxseed, sesame and thistle seeds have a balanced fatty acid composition according to the ratio of omega-6/omega-3 fatty acids; contain in a favorable ratio gamma – and alpha-tocopherols; have high antiradical activity and are resistant to oxidative changes during storage. On the basis of the comparative analysis, it was concluded that the oils obtained by pressing the mixture of seeds (flax, sesame and thistle) have advantages over the compositions made by mixing the corresponding oils. First, this technology allows one to get the oil in one step, while for the oil mixture, the desired oils are first obtained, and then the composition is prepared, which can lead to an increase in the peroxide number. Secondly, the natural composition of the minor components contributes to increasing the resistance to oxidative changes during storage at room temperature [15]. There is also an opportunity for the recovery of oils (fats) after technological, temperature and/or adsorption processing [15–17].

Cholesterol (CS) plays an important role in the life processes of the body, as it participates in various biochemical processes. In healthy people, the level of cholesterol is usually maintained at a certain constant level. But under the influence of harmful factors, in

particular, long-term disorders of eating behavior, chronic diseases, age-related hormonal changes, etc., the body undergoes a violation of lipid metabolism with an increase in the level of cholesterol in the blood. Elevated levels of CS and other lipid metabolism disorders are a risk factor and one of the causes of cardiovascular and other diseases. It should be noted that in the diet of Ukrainians mainly sunflower oil is used. Other oils are rape, soya beans, mustard, hemp, coriander, olive, and the like.

Diseases caused by acid deficiency of omega-3s include obesity, arrhythmia, hypertension, atherosclerosis, diabetes, and the like. That is why during the last two decades, the acids of omega-3 are the subject of close attention of researchers [6, 18].

Indicator of information content of general cholesterol is a blood test. Results of the complex study presented in the review [17]. They indicate a lack of information on the level of general X-ray in the blood as an indicator of the atherosclerotic process, its progression, and the need for a more in-depth analysis of atherogenesis factors to assess the risk of developing coronary heart disease and the effectiveness of the therapy being performed.

An elevated blood cholesterol level is considered a key risk factor for developing cardiovascular disease and stroke, two of the world's leading killers in the United States. Saturated fat, mainly in meat, poultry, raw and other products of animal origin, is the main driving force of raising the level of cholesterol in the blood.

Studies in recent years have confirmed the decrease in blood cholesterol by up to 35% (from the original) for the use of a plant diet. In many cases, such a decrease corresponds to the result with the use of medication, but without negative side effects. People who need drugs to lower the level of cholesterol to prevent cardiovascular disease can only achieve this with the use of a plant diet. In general, a herbal diet lowers blood cholesterol levels due to the fact that this diet contains unsaturated fats and zero cholesterol. Moreover, the plant diet is rich in fiber, which in turn also reduces the level of cholesterol. Soy also reduces the level of X-rays from those who include it in their diet.

It should be noted that deserving attention of scientists, physicists, chemists, nutritionists and technologists discussing the importance of and influence of CS on the body of people of different age groups. Thus, the article [20] emphasizes the need to consider the inadequate functioning of the thyroid gland and eliminate the use of "dense" carbohydrates (sweet, rich starch, refined food).

Today, emphasis in gerontology is aimed at prolonging the very active lifestyle and long-term capacity of a person. In principle, you can immerse any conscious person in the state of active longevity and the health of the environment. Taking into account the data of the analytical review of scientific sources [2, 4, 5, 13, 18, 21] and the results of own research of FPP it is expedient to determine the system and innovative concept of prevention, treatment and rehabilitation of patients with ophthalmologic and concomitant diseases.

Materials and methods

It were researched: scientific and practical substantiation of the concept of ecology of health in the system of KTIOL for ophthalmological and gerontological practice, antioxidant resistance of oils to preparations and the creation of FPP KTIOL (without cholesterol and lactose).

The research was carried out using sunflower oil and linseed oil. Experimental samples of oil compositions were prepared by mixing the original oils at a given ratio at room

temperature. The obtained KTIOL oil compositions were stored in the refrigerator at a temperature of 4 to 6 °C. Highly temperature treatment of samples in time is made using KTIOL preparations. The kinetics of oxidation of each sample of oil characterized the average rate of change in their indexes (peroxide and acid numbers) during the experiment.

Chromatographic method was used for qualitative evaluation of volatile compounds of the original oils and functional oil composition of KTIOL [6].

Results and discussion

Systemic concept of ecology of health

Knowing the key health factors, it is possible to identify the problem at an early stage of its occurrence. For example, it is important for everyone to know and control such indicators as body mass index, blood pressure, level and types of cholesterol in the blood, state of the visual system, etc. Unfortunately, a significant part of people do not know what indicators can be considered normal and how to normalize and maintain them rationally. In the conception of the ecology of health, the keys are the systems of KTIOL.

They include:

- scientific and practical substantiation of safe functional, special and gerontological products and preparations on micro and nano-level (system KTIOL-I);
- a complex of scientific and practical measures aimed at the improvement of the personality and endoecology of health (system KTIOL-II) for maintenance of safe human life.

The ecological and technological system of KTIOL-I (Complex Technologies of Engineering, Equipment, Lines) was first aimed at the synthesis of special products with a nanostructure for high pressures. Key provisions of the system KTIOL-I:

1. Maintenance of the structure of the product (preparation) on the micro and nano-level;
2. Ecological and economic efficiency;
3. System approach to the techno methodology concerning the self-realization of the personality in the technologies of production and therapy of safe food, pharmaceutical, cosmetic products and preparations.

The health-therapeutic (physiological-functional) system of KTIOL-II (Integrated Therapy of Individual Health Improvement of People) is based on the analysis of the quality and safety of water, food products and drugs (dietary, biologically active additives), environmental and endoecological aspects of personal health. The KTIOL-II system as a basic component (key words) includes: hygiene of thoughts (positive thinking); prevention (individual, periodic, instrumental); safe water, healing; breathing health, curative; nutrition health and medical (products and preparations); load physical, individual, selective (walking, swimming, yoga, etc.); massage (general, local, biologically active points); meditation (healing mood); sleep health-therapeutic and so on.

It should be noted that now in the concept of wellness nutrition it is observed a priority tendency to increase in the diet of oils with high content of PUFAs omega-3 and the development of oils compositions with the optimal ratio of acids omega-3/omega-6 for consumers of different age groups [6, 7, 19].

Accelerated methods for determining the stability and shelf life of edible vegetable oils assume oxidation at elevated temperatures. It is known that due to different oxidation routes, the proportion between the rates of accumulation of primary and secondary

oxidation products in vegetable oils is different and stored up to 80 °C. Oxidation of oils at higher temperatures is accompanied by a violation of proportionality. Therefore, it is necessary to confirm the compliance of the indicators at the temperature used and under standard stage conditions.

Oxidation of sunflower and flaxseed oil with KTIOL preparations

Since the oxidation of vegetable oils is a complicated multistage process in which simultaneously many reactions occur, differing in speed, direction and sequence [6, 15, 22], the establishment of temperature dependence was carried out empirically on the basis of long experiments.

Experimentally, the effect of three KTIOL preparations at a dose of 0.5% on the resistance to oxidation of sunflower oil was determined by heating at a temperature of 200 °C and a duration of 3 hours (Table 1). For antioxidant action, KTIOL-BF was taken for further investigation.

Indicators of the preparation KTIOL-BF: mass fraction of moisture and volatile substances – 2.5%, water-retaining ability – 40.2%, oil-retaining ability – 22.5%, granulometric composition: fraction up to 0.25 mm – 45%, 0.25–1 mm – 34%. 1–2 mm – 21%. It should be noted that the index of oil retention capacity of the preparations KTIOL-BF is smaller than the imported preparations Tonsil – 312 (34%).

Table 1

Influence of KTIOL preparations on the resistance of sunflower oil to oxidation during heating

Indicator	Preparations			
	KTIOL-1NL	KTIOL-CF	KTIOL-BF	Control (oil)
Peroxide number, mmol ½ O/kg:				
before heating up	**4,2**	**3,4**	**3,9**	**1,5**
after heating	**7,3**	**4,4**	**4,1**	**8,9**
Acid number, mg KOH/g				
before heating up	**1,8**	**0,7**	**0,5**	**2,7**
after heating/	**2,7**	**3,0**	**2,2**	**3,2**

The kinetics of oxidation of oils was characterized by an average rate of change in the parameters for the duration of the experiment.

Increased temperature treatment of sunflower and linseed oil and the dosage of KTIOL was studied to determine the average oxidation velocity (VO) and acidity (VA) of the oil.The initial peroxide number of sunflower oil is 4.25 mmol ½ O/kg, the initial amount of acid oil is 0.47 mg KOH/g. The data is presented in Tables 2 and 3, respectively.

It was found (Table 2 and 3) that the use of the KTIOL-BF preparation at a dose of 1% reduces the average oxidation rate of sunflower oil at 150 °C (3 hours) by 12.2 times at 200 °C (6 hours at 13.6 times. The average rate of acidity of sunflower oil decreases at 150 °C (3 hours) 9 times, at 200 °C (6 hours) 2.2 times.

Average velocity of oxidation (VO) and acidity (VA) of linseed oil is determined by the preparation of KTIOL – BF at high temperature in time. The initial peroxide value of

the oil is 4.4 mmoles ½O/kg, the initial acid number is 1.49 mg KOH/g. The data is presented in slabs 4 and 5, respectively.

Table 2

Effect of the dose of the preparation of KTIOL-BF, temperature and duration of processing sunflower oil on the average rate of its oxidation (VO)

N	Preparation dose, %	Temperature, °C			
		150		200	
		Processing time, h			
		3	6	3	6
		Average rate of oxidation, VO			
1	0	0,98	1,31	1,92	1,64
2	0.25	0,34	0,25	0,40	0,75
3	0,5	0,40	0,33	0,47	0,22
4	1,0	0,08	0,12	0,15	0,12
5	1,5	0,13	0,17	0,20	0,33
6	2,0	0,34	0,25	0,41	0,75

Table 3

Effect of the dose of the preparation of KTIOL-BF, temperature and duration of sunflower oil processing on the average rate of its acidity (VA)

N	Preparation dose, %	Temperature, °C			
		150		200	
		Processing time, h			
		3	6	3	6
		Average rate of increase in acidity, VA			
1	0	0,09	0,16	0,07	0,11
2	0,25	0,06	0,09	0,05	0,10
3	0,5	0,04	0,07	0,03	0,09
4	1,0	0,01	0,03	0,01	0,05
5	1,5	0,01	0,05	0,00	0,06
6	2,0	0,06	0,09	0,05	0,11

Table 4

Effect of the dose of the preparation of KTIOL-BF, temperature and duration of treatment of linseed oil on the average rate of its oxidation (VO)

N	Preparation dose, %	Temperature, °C			
		150		200	
		Processing time, h			
		3	6	3	6
		Average rate of oxidation, VO			
1	0	1,95	2,43	2,57	1,80
2	0,5	1,45	2,11	2,45	1,50
3	1,0	1,35	1,93	2,18	1,18
4	2,0	1,38	1,95	2,34	1,30

Table 5

Effect of the dose of the preparation of KTIOL-BF, temperature and length of processing of linseed oil on the average rate of its acidity (VK)

N	Preparation dose, %	Temperature, °C			
		150		200	
		Processing time, h			
		3	6	3	6
		Average rate of increase in acidity, VA			
1	0	1,17	0,86	1,83	1,28
2	0,5	1,09	0,79	1,73	1.04
3	1,0	1,04	0,72	1,50	0,96
4	2,0	1,05	0,78	1,65	1,01

It was found (Table 4 and 5) that the use of KTIOL-BF in a dose of 1% reduces the average rate of oxidation of flaxseed oil at 150 °C (3 hours) 1.4 times, at 200 °C (6 hours) 1.5 times. The average rate of acidity of flaxseed oil decreases at 150 °C (3 hours) by 1.1 times, at 200 °C (6 hours) by 1.3 times.

The data obtained are used by us when the FPD is conserved on the basis of vegetable oils, fats and their compositions. Further study requires the direction of selective treatment of lipid-containing plant material, FPP prophylactic, therapeutic and rehabilitation purposes.

Justification the sensory properties of oil composition

On the basis of the data obtained for the production of the oil composition, sunflower oil and linseed oil was taken [6, 20, 21]. Sunflower-refined oil was used as the basis for the oil-based composition of KTIOL. Oils with omega-3 fatty acids – linen for the first cold spin. According to sensory properties parameters, the content of vitamin E and fatty acids of omega-3 (ω-3) is better recognized as the composition of KTIOL-LS2. Characteristic of KITOL-LS2 composite oil: color – bright yellow; smell – inherent to this composition without the construction, almost not noticeable; taste – inherent composition without a posteriori, not expressed; the content of omega-3 fatty acids (ω-3),% -11.1; the content of omega-6 fatty acids (ω-6),% – 22.9; ratio of omega-3 fatty acids to omega-6 (ω-3 : ω-6) – 1:2; The content of vitamin E is 72.4 mg%.

Gas chromatographic researches results

Gas chromatographic method was used to evaluate the volatile compounds of the original oils and the functional composition oil KTIOL-LS2 [6]. Chromatograms are shown in Figure 1–3. From the data analysis of Figure 1–3 found the following:

1. Volatile compounds of sunflower oil are distributed in the time interval of 10–35 minutes. at maximum signal altitude 90;
2. Volatile compounds of linseed oil are distributed in the time interval of 20–35 minutes. at maximum signal altitude 50;
3. Volatile compounds of composite oil KTIOL-LS2 are distributed in the time interval of 10–35 minutes at maximum signal strength 40. The hypothesis concerning the possible reduction of the volatile compounds of KTIOL-LS2 composite oil, both due to the composition of the oil, and through the interaction of individual volatile ingredients, is expressed.

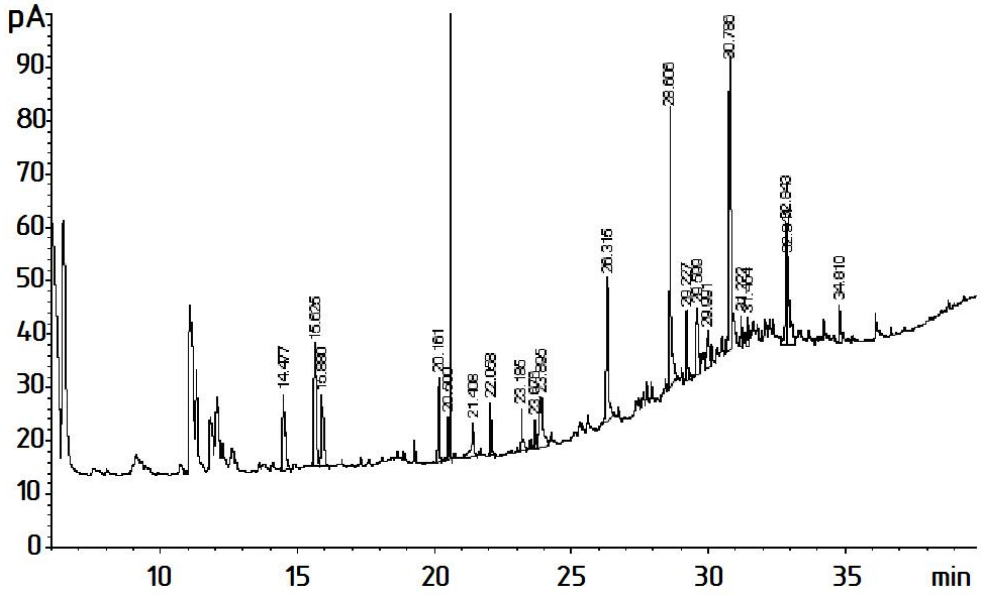

Figure 1. Chromatographic profile of volatile compounds of sunflower oil

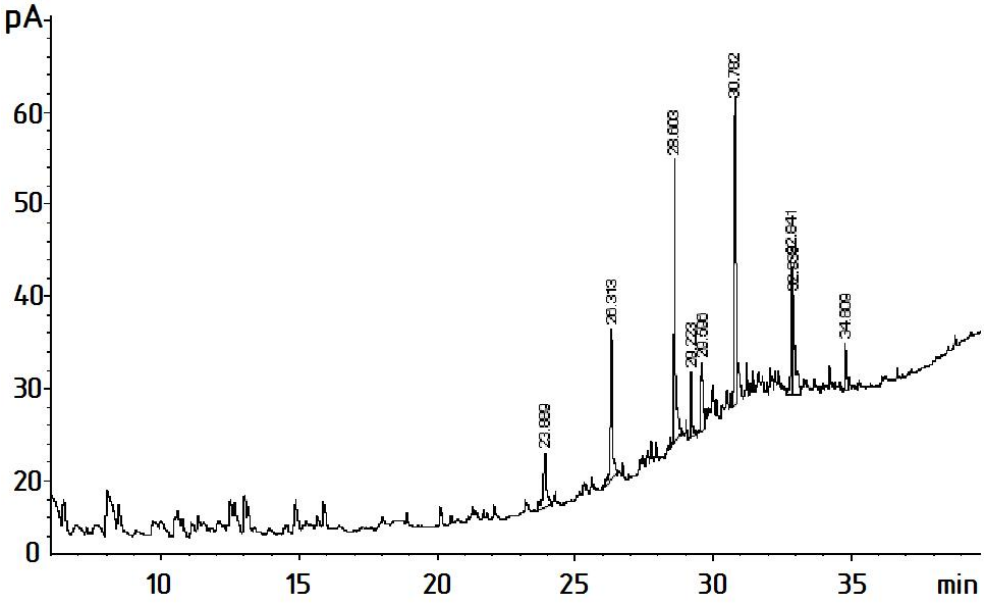

Figure 2. Chromatographic profile of volatile compounds of the original linseed oil

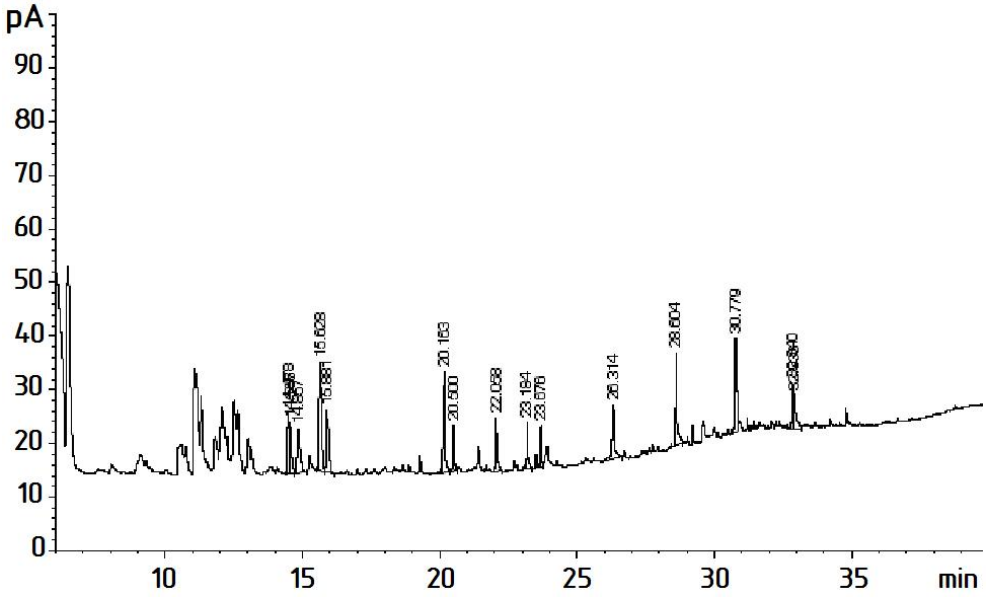

Figure 3. Chromatographic profile of volatile compounds of composite oil KTIOL-LS2

The developed composition oil KTIOL-LS2 it is expedient to use as a functional product or as a preparation of sanitary-and-therapeutic action and as a part of oily-fat emulsion systems. The presence of volatile compounds in the oil-and-oil system (oils, compositions, etc.) is associated with oxidation processes and the content of primary and secondary oxidation products of unsaturated acylglycerols and fatty acids.

Reducing the content of oxidation products in the oil-and-fat system indicates the neutralization and/or inhibition of oxidation processes.

It is noted that KTIOL-LS2 composite oil with 1% of the preparation KTIOL-BF according to the complex index of oxidation resistance (acid number $\leq$ 1.5, peroxide number $\leq$10) is stored at 20–25 °C for 6 months.

Practical using of research resutls

Based on the compositional oil of KTIOL-LS2, low-calorie mayonnaise with flavoring additives KTIOL-BIO was developed. In the formulation used the original component composition. The size of the particles of the system is brought to micro- and nanosize by repeated processing in a mixer.

The new technical solution is protected by a patent UA 086341U. By component composition, mayonnaise refers to a dietary assortment group whose emulsion products are manufactured using standard technology. The use of the new composition of mayonnaise KTIOL-BIO makes it possible to produce a stable, high-quality, safe low-calorie product with flavorless additives without cholesterol and lactose, with improved organoleptic and physico-chemical parameters.

Conclusions

Creation of functional and special products and preparations that improve the physiological state of people of different age groups for the occurrence of disease and related pathologies, is an important area of the problem of ensuring active and creative life of the population.

The innovative concept includes the use of the KTIOL-II system for complex prevention and curing of ophthalmologic and concomitant diseases.

New data on the average oxidation rate and increase in the acidity of sunflower and linseed oils during their high temperature treatment up to 200 °C in time are obtained. It was established that the use of the preparation KTIOL-BF in a rational dose of 1% provides an increase in the antioxidant stability of the oils under study. The composition of the oil-based composition of KTIOl-SL2 for functional products of KTIOL of preventive and health-treatment action was substantiated.

On the basis of theoretical and experimental researches, a new functional product of KTIOL-BIO has been developed for use in cholesterol, lactoid and healing and therapeutic diets.

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Thermal, structural and pasting properties of brazilian ginger (Zingiber officinale Roscoe) starch

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Abstract

Introduction. Unconventional starch sources are interesting industrial alternatives, each presenting different properties. Thermal, morphological, structural and pasting characteristics from ginger starch were investigated in this study.

Materials and methods. Ginger starch was extracted by aqueous process and its characteristics were analysed by thermogravimetry/derivative thermogravimetry, differential scanning calorimetry, rapid viscoamylographic analysis, scanning electron microscopy and X-ray powder diffractometry.

Results and discussion. Similar thermal stability and three mass losses were found for the starch samples. Higher transition temperatures and enthalpy of gelatinisation were found for commercial sample, which was related to the longer amylopectin chains due to B-type crystallinity. Starch obtained from "*doce*" ginger showed the highest peak and final viscosities associated with the lowest pasting temperature, which is a interesant result for food applications, in addition to the low energy required for gelatinisation. An ellipsoidal shape and no fissures on the surface of the granules were visuallised by microscopy, and the diameter and the commercial sample had the smallest granules. A-type diffraction was obtained for doce and "*forte*" ginger starches, while commercial starch presented B-type pattern. The highest relative crystallinity was exhibited by the "*forte*" ginger starch.

Conclusions. Commercial samples presented differences compared to known varieties. Interesting properties were found, highlighting the "*doce*" ginger variety.

Introduction

After cellulose, the main carbohydrate storage material in higher plants is starch. It is synthesized as granules in the amyloplasts and stored in seeds, leaves, roots, etc., from which it can be extracted. This carbohydrate consists of a large number of glucose units linked by glycosidic bonds. These molecules can be linear or branched, called amylose and amylopectin, respectively. The starch granules may have a size between 1-110 μm with rounded, oval, lenticular or polygonal shape according to their biological origin [1-4].

The starch has application in various industrial processes, acting as gelling agents, thickeners, stabilizers, as well as base material for the formation of edible coatings and biodegradable packaging films in the food industry, or as a binder, excipient, diluent, disintegrant and stabilizer, in the pharmaceutical industry [5-7].

In recent years, developments in the food industry have increased and the unique properties of starches as natural polymer have attracted the attention of researchers mainly to obtain new starches with specific characteristics [8-9].

Ginger (*Zingiber officinalle*) is a rhizome belonging to the *Zingiberaceae* family. It is originates in South Asia and is a spice with odor and flavour characteristics due to the presence of essential oils. It is widely used in foods and beverages or applied in medicine for gastrointestinal disorders, pain and inflammation [10-11].

The untreated starches present variable characteristics that depend mainly on the origin and the method that were extracted. Therefore, physico-chemical characterisation and instrumental analyses are necessary to understand the behaviour and properties exhibited by these polysaccharides in their native form, allowing for subsequent modifications according to the technological interests. As instrumental analysis, the thermal methods: thermogravimetry (TG) and differential scanning calorimetry (DSC), as well as the fast viscosity analysis (RVA) and scanning electron microscopy (SEM) have been promising. The Δm (mass variation) can be measured when a substance is heated or cooled according to ΔT or Δt (temperature or time variation) by thermogravimetry (TG). The differential scanning calorimetry (DSC) measures the heat flow between a sample and a reference material when both are subjected to a controlled temperature change. Through these and some others techniques such as morphological, structural and viscosity analysis changes in starch behaviour can be identified [12-13].

In this investigation we present the extraction of ginger starch, an unconventional source (*Zingiber officinalle*). The extraction was performed in aqueous medium [14] and the main properties were studied by thermogravimetry/derivative thermogravimetry – TG/DTG, differential scanning calorimetry – DSC, rapid viscoamylographic analysis – RVA, scanning electron microscopy – SEM and X-ray powder diffractometry – XRD.

Materials and methods

Materials

Three samples of Brazilian ginger were collected in Ponta Grossa-PR-Brazil, two of which were known as (a) "*doce*", (b) "*forte*", and the third was acquired in local commerce, identified as commercial (c). Each sample was extracted in aqueous medium according to previously described methodology [14]. After the extraction process, each sample was kept in desiccator with calcium chloride until constant mass.

Methods

Thermogravimetry/Derivative Thermogravimetry (TG/DTG)

The mass loss of each sample and the temperatures of each thermal event were obtained using the TGA-50 thermal analysis system (Shimadzu, Japan) with the aid of TA-60WS software, for which it was also possible to obtain DTG values, which are a mathematical resource for a more precise identification of the temperatures involved in the mass loss of the samples.

The sample mass was about 7-9 mg in open alumina crucible. The analysis conditions were: heating from 30 °C to 650 °C at a heating rate of 10 ºC min^{-1}, under air flow of 100 mL min^{-1}. Derivative thermogravimetric (DTG) curves (first derivative of TG curves) were calculated.

Before analysis, the instrument was preliminarily calibrated with standard weight and tested with standard calcium oxalate monohydrate [9, 13].

Differential Scanning Calorimetry (DSC)

The DSC curves were obtained using a DSC-Q200 (TA-Instr., USA) thermal analysis system, with the following parameters: heating rate of 10°C min^{-1} under air flow of 50 mL min^{-1}, and samples weighing about 2.5 mg. A suspension was prepared at a 4:1 ratio (water: starch, w/w) and held for 60 minutes to equilibrate the moisture content. The aluminium crucibles were sealed and after one hour the curves were performed. The instrument was previously calibrated with indium (99.99% purity, T_p = 156.6°C, ΔH = 28.56 J g^{-1}) [5, 13].

Pasting Properties (RVA)

For the analysis of pasting properties of each ginger starch sample, the Rapid Visco Analyser instrument (Newport Sci., Australia) was used. A sample containing 8% starch was suspended in distilled water to a final volume of 28 g in an aluminum canister. Samples were submitted to a controlled heating process followed by cooling under constant stirring (160 rpm). Initially, the samples were heated from 50 °C to 90 °C at a rate of 6°C min^{-1}. Then, the sample was maintained at 95 °C for 5 min, cooled to 50 °C and maintained at this temperature for 2 min. The whole process lasted 23 minutes [13, 14].

Scanning Electron Microscopy (SEM)

The morphology and measurements of the starch granules were performed in a Vega 3 (Tescan, Chech Rep.) scanning electron microscope (SEM), under acceleration voltage of 25 kV and 1.500 x magnification. Before analysis the samples were metallised with gold. The area of granules was calculated using Image J 1.47 for Windows software [5].

X-ray Diffractometry (XRD)

The X-ray Diffraction (XRD) analysis was adapted from the methodology proposed in the literature [12, 15], using an Ultima 4 (Rigaku, Japan) X-ray diffractometer. CuKα radiation (λ = 1.5418 Å) and settings of 40 kV and 30 mA were used. The scattered radiation was detected in the angular range of 5-50º (2Θ), with a scanning speed of 2 min^{-1} and a step of 0.02º. The degree of relative crystallinity was calculated [4, 12] from the ratio

between peak area and the total diffraction area: Xc = Ap / (Ap + Ab) . 100; where: Xc = relative crystallinity; Ap = peak area; Ab = basis area.

Statistical Analysis

The analysis were performed in triplicate. All the averages of the samples were analysed by variance analysis (ANOVA) and Tukey's test with a 95% confidence interval ($p<0.05$), using STATISTICA 7.0 software (StatSoft, Inc., Tulsa, OK, USA).

Results and discussion

Extraction of Ginger Starch

The fresh ginger rhizomes (*Zingiber officinale* Roscoe) were carefully washed and ground in a food processor. The starch extraction was conducted according to the methodology of Bet et al. [3]. Initially an aqueous milling was performed with each ginger sample in industrial blender, followed by sieving (150 and 270 mesh) and decanting in refrigerator (4-7 °C). The samples were centrifuged at 10000 rpm (Rotina 420R, Hettich Zentrifugen/UK) and the starch was dried in an oven at 40 °C for 24 h. The samples were kept in a desiccator with anhydrous calcium chloride.

Thermogravimetry/Derivative Thermogravimetry (TG/DTG)

The TG/DTG curves showed similar behaviour with mass losses distributed in three steps. The first mass loss was due to dehydration followed of a stability period. Starch extracted from yellow ginger tuber showed loss of water up to 100 ºC and a stability plateau up to 277 ºC [15]. According to the literature [16, 17], after the thermal stability and around 300 ºC under oxidising atmosphere, occurs the depolymerisation of the starch. So, the second and third mass losses occurred in consecutive steps, which were attributed to the decomposition and oxidation of organic matter once the TG curves were performed in air atmosphere. Similar results can be observed with other starches [5, 13].

The ash content of each sample was (a) 4.18, (b) 3.59 and (c) 4.54 %, respectively. The obtained results are depicted in Table 1.

Table 1

TG/DTG curves of starches (a) "*doce*"; (b) "*forte*" and (c) commercial

	1st step		2nd step		3rd step	
Sample	**ΔT/°C**	**Δm/%**	**ΔT/°C**	**Δm/%**	**ΔT/°C**	**Δm/%**
a	42,8 – 169,9	12,30	276,7 – 434,4	64,85	434,4 – 593,7	18,67
b	31,0 – 181,3	17,25	286,0 – 430,4	63,10	430,4 – 605,8	16,06
c	33,7 – 185,4	14,24	269,4 – 429,8	64,64	429,8 – 593,8	16,58

ΔT, temperature range of mass loss; Δm, % of mass loss

DTG (1st derivative of the TG curve) was used to aid in the calculation of the mass loss, as well as in determining the temperature range that each event occurred.

Differential Scanning Calorimetry (DSC)

The results of the DSC curves are shown in Figure 1, where the endothermic phenomenon that occurs during heating of the starch in excess of water, called gelatinisation, can be studied.

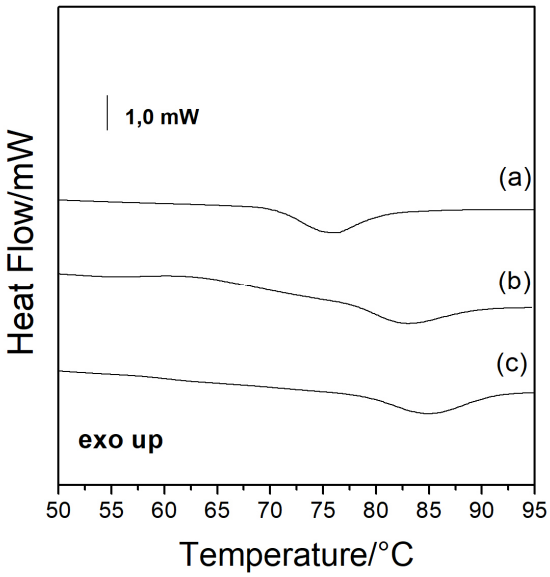

Figure 1. DSC curves of starches (a) "*doce*"; (b) "*forte*" and (c) commercial

Starches are practically insoluble in cold water. However, during the heat treatment of starch in the presence of sufficient amount of water, gelatinisation occurs. Amylose is leached into the external solution, when water penetrates the granules, leading to swelling. Thus, destabilisation of the crystalline structure occurs resulting in granular fragmentation and loss of birefringence. Among the factors that may affect this kinetic (the ratio between crystalline and amorphous regions, tend to absorb water more easily), are important in DSC conditions: hermetic crucibles, heating rate, starch:water ratio, as described in Materials and methods.

Each starch analysed showed specific values of onset (T_o), peak (T_p) and conclusion (T_c) temperatures as well as the calculated gelatinisation enthalpy (ΔH_{gel}), which values are in Table 2. Higher values of temperature and ΔH_{gel} were obtained for the commercial sample.

Within the same species, differences in starch properties can be found as a result of the variety of size and shape of the granules, composition, amylose ratio: amylopectin, among other factors [18].

Table 2

DSC Gelatinisation, XRD and SEM results

	DSC results				XRD	SEM
Sample	**T_o/°C**	**T_p/°C**	**T_c/°C**	**ΔH_{gel}/J g^{-1}**	**Relative Cristallinity/%**	**Average diameter/µm**
a	70,8 ± 0,08[a]	75,8 ± 0,20[a]	80,0 ± 0,22[a]	9,6 ± 0,50[ab]	27,3 ± 0,72[a]	39,7 ± 6,60[c]
b	77,5 ± 0,19[b]	83,2 ± 0,05[c]	88,0 ± 0,11[c]	8,8 ± 0,70[a]	36,2 ± 1,52[b]	24,2 ± 4,01[b]
c	78,9 ± 0,16[c]	85,1 ± 0,13[b]	90,1 ± 0,01[b]	10,82 ± 0,43[b]	24,9 ± 0,87[a]	17,7 ± 2,49[a]

(*) To "onset" or initial temperature, Tp peak temperature, Tc "endset" or conclusion temperature, ΔHgel gelatinisation enthalpy. Values presented as mean values ± standard deviation after analysing in triplicate

Values followed by the same letter in the same column do not differ statistically by Tukey's test ($p<0.05$)

Starch isolated from mango ginger starch (*Curcuma amada* Roxb.), a rhizome with similar morphology to ginger starch, showed lower transition temperatures, which were attributed to the presence of abundant short amylopectin chains [19]. Regarding gelatinisation enthalpy, turmeric and ginger starches presented higher values than the ginger varieties studied in the present study [20]. Studies attributed higher enthalpy values to the presence of longer chains of amylopectin, requiring higher temperatures for their destructuring [21], according to the crystallinity pattern obtained by X-ray diffraction analysis.

Pasting Properties (RVA)

The viscosity profiles for the isolated starch of the three ginger varieties are shown in Fig. 2. This analysis results in the pasting properties of a starch, which is of great importance for defining aspects such as cooking and quality of the gel produced [22].

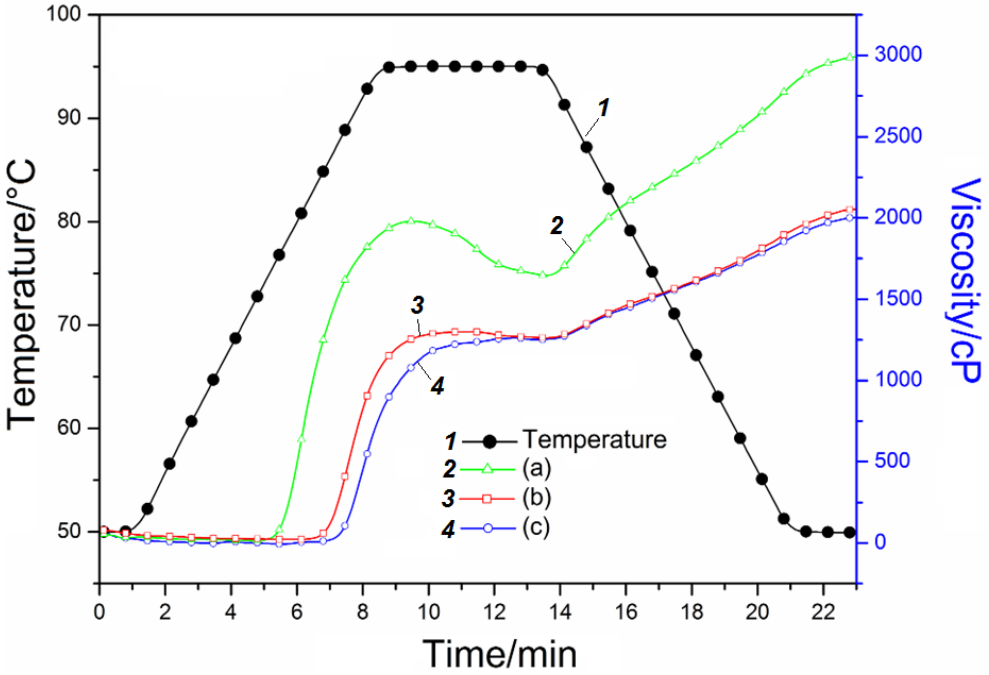

Figure 2. Pasting properties: RVA curves of starches (a) "*doce*"; (b) "*forte*" and (c) commercial

During gelatinisation, intragranular forces weaken due to the presence of sufficient water and shear, favouring the absorption of water by the granules, swelling them and resulting in an increase in viscosity. Following this, a critical point of perturbation of the system is reached, with collapse of the structure and reorganisation of the amylose and amylopectin chains. Thus, the viscosity decrease and water expulsion occurs, a process known as breakdown followed by starch retrogradation [23].

Differences can be visualised between the samples, with higher retrogradation and viscosity for sample (a), which belongs to the ginger "*doce*" variety. Table 3 presents the results extracted from the RVA curves.

Table 3

RVA Results of starches: (a) "*doce*"; (b) "*forte*" and (c) commercial

Sample	Tp/ °C	VP/ mPa·s	Trough/ mPa·s	Breakdown/ mPa·s	VF/ mPa·s	Setback/ mPa·s	tP/ min
a	80.8	1979.8	1646.2	333.7	2991.0	1345.3	9.5
b	89.7	1295.5	1261.9	33.6	2053.5	791.6	10.7
c	91.9	1230.2	1254.7	24.0	2003.8	749.1	11.1

Tp – pasting temperature; VP – peak viscosity; tP – peak time; VF – final viscosity.

Higher pasting temperature was found for commercial variety, which also had lower peak viscosity. Thus, this sample gave lower values of breakdown, tendency to retrogradation and final viscosity. Unlike the "*doce*" variety, in which there was the formation of a paste more viscous, the lower temperature. These data corroborate with the results obtained by DSC.

High temperatures have also been reported for ginger spent starch (88 ºC), which was isolated after the extraction of oleoresin [23]. Braga et al. [20] reported higher peak viscosity (2650 mPa.s), setback (1673 mPa.s) and final viscosity (4060 mPa.s) for starch extracted from *Zingiber officinale* R.

Scanning Electron Microscopy (SEM)

The morphologies of the granules were examined by Scanning Electron Microscopy (SEM) and the images are shown in Figure 3. With this technique it was possible to observe that the starch granules have an oval ellipsoidal shape with little round shape. In addition, no cracks were observed on the surface of the granules, as was reported for mango ginger starch [19] and untreated yellow ginger starch [15].

The average diameter was calculated (width and length, in μm) and values are depicted in Table 2. Starches isolated from *Curcuma longa,* is also part of the ginger family, and *Zingiber officinale* [20, 7] exhibited diameters close to those found in this study. Marama root starch presented a diameter ranged from 5–38 μm [24].

X-ray Diffractometry (XRD)

The semicrystalline structure of the granules is formed by the organisation of the growth ring, comprising alternating layers of amorphous and crystalline regions. The double helices of the amylopectin side branches are responsible for the semi-crystallinity of the starch. Thus, three diffraction patterns (A, B and C) can be observed [25]. This was observed in this investigation (Figure 4) and the relative crystallinity of each starch sample was also calculated, results depicted in Table 2.

The samples (a) and (b) showed a strong peak at 17º at 2θ and small peaks at 15 and 23º, which classifies them with A-type diffraction pattern, as found for native yellow ginger starch [15].

Unlike these samples, the starch obtained from commercial variety showed a small peak at 5.6°, strong peak at 17 ° and a doublet at 22° and 24° (2θ), as reported for mango ginger starch [19]. According to the literature [26], most tuber and root starches exhibit B-type patterns, which main peaks are centered at 2θ around 5.5º, 15º, 17º, 19.7º, 22.2º and 24º.

A-type crystallinity encompasses short amylopectin chains and closed branching points, resulting in double helices chains packaged, while B-type has a greater amount of water, present in the central cavity, with longer amylopectin chains, and more open structure [25]. Thus, it is possible to relate these results to those obtained by DSC, where the samples classified with A-type diffraction pattern presented lower values of gelatinisation enthalpy.

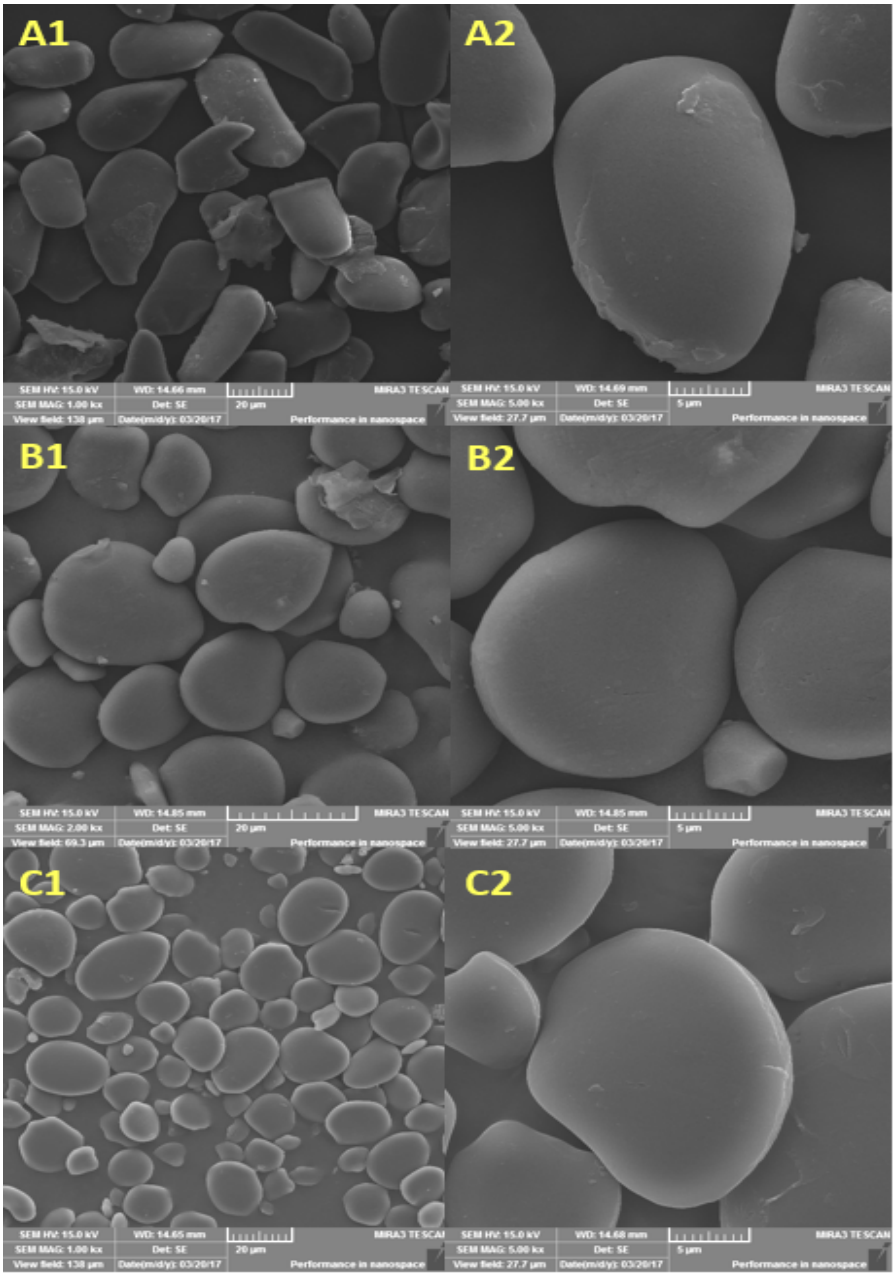

Figure 3. SEM microimages of starches (a) "*doce*"; (b) "*forte*" and (c) commercial (magnification 1500 X).

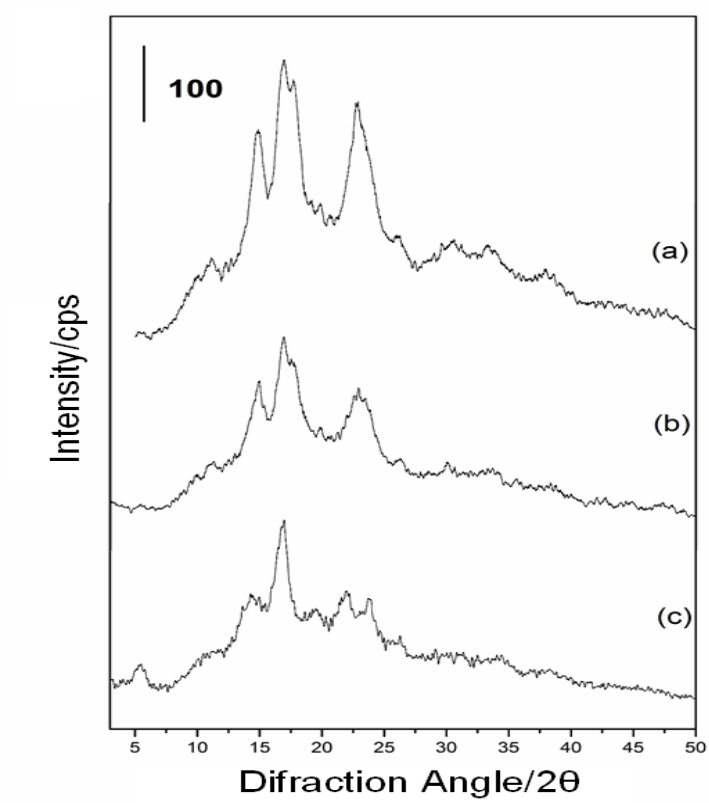

Figure 4. XRD of starches (a) "*doce*"; (b) "*forte*" and (c) commercial

The degree of relative crystallinity was higher for the "*forte*" variety sample, followed by "*doce*" and commercial varieties, respectively. Sukhija, Singh and Riar (2016) [7] found the degree relative crystallinity of 32.61% ±054 to native ginger starch although the extraction process was diferent.

Conclusion

Ginger starch was isolated by aqueous process from different varieties of this rizhom. The commercial sample was compared to the known varieties ("*doce*" and "*forte*"), but the results obtained showed that this sample does not belong to these varieties. Similar thermal stability was obtained for the three samples. From DSC, it was visualised that the commercial variety sample required higher temperatures and enthalpy for the gelatinisation of the granules. It can be related to the B-type diffraction pattern, probably due to the longer chains of amylopectin. "*Doce*" and "*forte*" varieties showed A-type cristallinity. Lower pasting temperature and higher peak and final viscosities were obtained for starch extracted from "*doce*" ginger. All samples showed an oval ellipsoidal shape and no surface cracks.

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Mechanism of transformation of protons in the process of creating aqueous-alcoholic mixtures

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Abstract

Introduction. The aim of the publication is to study the mechanisms of transformation of ethanol protons (ethyl rectified spirit – ERS) and water (drinking water) in the process of creating aqueous-alcoholic mixtures (AAM) by ^1H *NMR* spectroscopy.

Materials and methods. ^1H *NMR* analysis was conducted with the usage of the following: *FT-NMR* Bruker Avance II spectrometer with operating frequency at ^1H – 400 MHz; specially shaped capillary with acetone–d_6 (atomic fraction of deuterium – 99,88 %; chemical shift of the residual proton ^1H – δ=2,75 ppm); high accuracy ampoules № 507-HP for high resolution *NMR*'s spectroscopy (400 MHz); volumetric pipette; dispenser; ERS; drinking water; AAM from ERS and drinking water.

Work methodology: 0,3 ml of a AAM prepared with a volumetric pipette with a predetermined strength (40,0 ± 0,2) % vol.; external standard separated from the testing substance which is required for LOCK's system operation (acetone-d_6) of *NMR*'s deuterium stabilization spectrometer) is added in a special form of a capillary into an ampoule. The obvious advantage of using the external standard is the fact that standard substance's molecules and test's solution do not interact with each other; ^1H *NMR* spectra records and data processing were performed according to the instruction of FT-NMR Bruker Avance II spectrometer (400 MHz).

Results and discussion. In this paper, we have established fundamentally new features in the process of creating AAM that are directly dependent on the time of contact with water and ERS. As a results we have evidence of a complex dynamic of achievement processes of solution equilibrium for AAM prepared in drinking water with pH=7,01 and ERS. At the same time pH of obtained AAM is pH=8,32. Hydroxyl proton of ethanol (*EtOH*) exchange rate is in intermediate area. It happens during the first 48 hours when the concentration of alcohol is constant (strength AAM – 39,94 % vol.) and the system is thermostatic (t=23,5 ºC). Signals are separately located. Protons' exchange is accelerated due to the rearrangement of system's structure, during the interval of τ=48 h to 120 h. Since τ=120 h, there is only one common signal of mobile protons of asymmetrical shape. The size of chemical shift of the summed signal $\delta_{EtOH+H2O}$=4,74 ppm (τ=120 h) is starting to grow and shifts to the «weak fields» with the value of $\delta_{EtOH+H2O}$=4,81 ppm (τ=312 h).

Conclusion. In this paper, we have established fundamentally new features in the process of creating AAM that are directly dependent on the time of contact with drinking water and ERS.

Introduction

NMR spectroscopy is widely used in physics research, industry, agriculture and other industries. *NMR* plays a particularly important role in food chemistry where it used in the study of both simple organic molecules and complex macromolecular structures and their complexes (Singh, Blümich, 2016; Hore, 2017) [1, 2]. A large number of articles discuss the use of *NMR* for research of food products; meat, fish, dairy products, vegetables, fruits, juices, pastry, cheese and alcohol products (Youssouf et al, 2017; Campo et al, 2016; Zhu, 2017; Yuan et al, 2017; Diop et al 2012; Tian et al, 2017, Sucupira et al, 2017, Li et al, 2017; Shumilina et al, 2016; Okaru et al, 2017) [3-12]. This method provides comprehensive information with relatively simple obtaining spectra, thus greatly facilitating and accelerating chemical research (Nose et al, 2005; Richards, Hollerton, 2011; Roberts, 2002; Hu et al, 2010) [13-16].

NMR spectroscopy is most commonly applied to the nuclei of lightest isotope of hydrogen ^{1}H (protium, ^{1}H isotope) proton. The spectra measured using such nuclei are called proton magnetic resonance (*PMR*) spectra. *PMR* accounts for about 90 % of all research on *NMR* spectra. Most of them operate in the Fourier transform mode (Richards, Hollerton, 2011; Roberts, 2002) [14-15]. The principle of *NMR* spectroscopy is based on the magnetic properties of certain atomic nuclei that resonate in the radio frequency range of the electromagnetic spectrum when placed in a strong magnetic field at a certain magnetic field. This allows for the identification of nuclei in different chemical environments (Richards, Hollerton, 2011; Roberts, 2002) [14-15]. This property is explained by the existence of nuclei with non-zero spin (intrinsic mechanical torque), that is determined by the sum of the spins of its constituent protons and neutrons (Richards, Hollerton, 2011) [14].The spin of the isotopes' nuclei with an even number of protons and an even number of neutrons is always equal to zero (zero moment). *NMR* is not observed in these nuclei (Roberts, 2002) [15].

The first ^{1}H *NMR* spectra of ethanol (C_2H_5OH) were developed in 1951 (Arnold et al. 1951) [17]. The first ^{1}H *NMR* spectra of water (H_2O) were obtained in 1946 (Bloch et al. 1946) [18]. At the first glance, it may seem that these are fairly simple organic molecules, at the same time *NMR* spectroscopy exhibits grate variety (Nose et al, 2005; Richards, Hollerton, 2011; Roberts, 2002; Hu et al, 2010) [13-16] in such characteristics as chemical shift, spin-spin interactions and the effect of chemical exchange (Roberts, 2002; Matsugami et al, 2016; Jora et al, 2017) [15, 19, 20].

An ethanol molecule consists of 6 protons located in a 3 proton-containing groups: methyl (CH_3), methylene (CH_2) and hydroxyl (OH) with a relative intensity characteristic CH_3:CH_2:OH – 3:2:1. Nuclear spin-spin interaction is observed between the three proton-containing groups of ethanol, all of which have different resonant frequencies (Roberts, 2002) [15]. "N" number of equivalent protons of one group split the signal of the nearest group into (n+1) lines with the intensity of a Pascal triangle (Richards, Hollerton, 2011) [14]. The ability to observe spin-spin interactions depends on the rate of the intermolecular proton exchange (Jora et al, 2017) [20]. Wherein the hydroxyl proton (OH) of ethanol can interchange with free hydrogen ions (Matsugami et al, 2016) [19]. The hydrogen ions are generated due to self-dissociation of water or traces of acids, alkalis or dissociated ethanol (Jora et al, 2017) [20]. The concentration of free ions is characterized by pH level.

Vodka – is an alcoholic drink with strength from 37,5% to 56%, obtained by mixing ERS with water and treated with activated carbon, with addition of non-volatile ingredients or without them.

In the opinion Hu et al. (2010) [16] vodka is a fairly simple physicochemical system: a

mixture of alcohol and water. However, each brand has its own distinctive taste and features on the molecular level. Research conducted by Hu et al. (2010) [16] confirm that these differences are significant both during the stage of creating AAM, and in the final product – the commercial vodka. The major differences are associated with hydrogen bonds, in particular their strength, as confirmed by various research methods such as ^1H *NMR* spectroscopy, *FTIR* spectroscopy, *Raman* spectroscopy. ^1H *NMR* and *FTIR* spectroscopy demonstrates the presence of water in the hydrate structure $EtOH{\cdot}(5{,}3{\pm}0{,}1)H_2O$. Water can also be observed in AAM as well as in vodka. The authors (Hu et al, 2010) [16] attribute this value with the perception of organoleptic characteristics of vodka.

In their paper, the authors (Hu et al, 2010) [16] introduced the concept of «structurability» – defined as the ability to maintain structure – a parameter that determines the ability of vodka (alcohol) to streamline its structure.

The effect of impurities (such as salts, acids, phenols) strengthening the hydrogen bonds in AAM as well as in the finished product such as sake, has been studied by Nose et al (2005) [13]. Hu et al [16] have identified that the impurity of compounds has an effect on the molecular dynamics in ethanol's hydration process.

Previously, we have conducted primary research of ^1H *NMR* AAM, which were described in the work of Kuzmin et al, 2013-2017 [21-24]. The obtained results give grounds to assert a fundamental difference in the behavior of the AAM prepared from the alcohol and water passing through various processes. This may indicate the presence of such features as separate signals of hydroxyl protons of H_2O and $EtOH$. Also abnormal waveforms of CH_3 and CH_2 characterize a product with a lower tasting properties. The presence of the combined signal of $EtOH{+}H_2O$ and rational form of CH_3 and CH_2 signals (triplet – for CH_3, quartet – for CH_2) – characterizes the AAM with the best tasting properties.

Thus, in the work of Kuzmin O., Sujkov S. et al, 2013 [21] established experimental evidence of instalment nature / (non- instalment) of thermodynamic balance, taking into account the organoleptic characteristics of AAM in dependence on water treatment method and time of system's functioning. However, the questions related to internal mechanism's specification and the rate of establishment of thermodynamic balance depending on type of water used in the process of creating the AAM are remain unsolved.

Therefore, the additional research is required for a detailed study of internal mechanism of thermodynamic balance and insurance in obtaining high quality vodka products – for each type of water separately.

Therefore, the aim of this work is to study the mechanisms of transformation of ethanol protons (ERS) and water (drinking water) in the process of creating AAM by ^1H *NMR* spectroscopy.

Materials and methods

The following characteristics of drinking water were determined: solid residual – 867 mg/dm^3; electrical conductivity – 1150 μS/cm; pH – 7,01; redox (ORP) – «+» 271 mV; total hardness – 7,93 mM/dm^3; permanganate oxidation – 4,27 mg O_2/dm^3; mass concentration (MC) of sodium – 90,75 mg/dm^3; MC of potassium – 4,87 mg/dm^3; MC of ammonium – <2,0 mg/dm^3; MC of calcium – 106,03 mg/dm^3; MC of magnesium – 23,91 mg/dm^3; total alkalinity – 5,38 mM/dm^3.

Characteristics of ERS: volume part of ethanol – 96,37 %, volume part of water – 3,63%; content of aldehydes in anhydrous alcohol (a.a.), based on acetaldehyde – 1,3

mg/dm^3, content of fusel oils in a.a.: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,5 mg/dm^3; content of esters in a.a., based on of ethyl acetate 1,3 mg/dm^3; methanol content in the a.a. – 0,0022 vol. %.

AAM sample of ERS and drinking water has the following physicochemical and organoleptic characteristics: alcoholic strength – 39,94 % vol.; electrical conductivity – 183 μS/cm; ORP – «+» 37 mV; pH – 8,32; aldehyde content in a.a., based on acetaldehyde – 1,5 mg/dm^3; content of fusel oils in a.a.: propyl, isopropyl, butyl, isobutyl and isoamyl – 1,1 mg/dm^3; the content of esters in a.a., based on acetic acid ethyl ester – 1,2 mg/dm^3; methanol content in a.a. – 0,0022 vol. %; alkalinity – 2,5 cm^3 of 0,1 M hydrochloric acid for titration of 100 cm^3 of AAM; oxidation test – 13,5 min; tasting score – 9,43 points (appearance – colorless liquid with residue; smell – sharp alcohol; flavor – heavy).

^1H NMR analysis of AAM was conducted with the usage of the following: *FT-NMR* Bruker Avance II spectrometer with operating frequency at ^1H – 400 MHz (measurement error of the chemical shifts for ^1H ± 0,0005 ppm; 5-mm broadband inverse probe with Z-gradient; thermostatic system (+25°C ... +100°C)); specially shaped capillary with acetone-d_6 $(CD_3)_2CO$ (atomic fraction of deuterium – 99,88 %; chemical shift of the residual proton ^1H – δ=2,75 ppm); high accuracy ampoules № 507-HP for high resolution *NMR*'s spectroscopy (400 MHz); volumetric pipette; dispenser; ERS; drinking water; AAM from ERS and drinking water.

Experimental studies of *^1H NMR* were carried out in the following order:

– preparation of AAM;

– recording of the AAM *^1H NMR* spectrum;

– conclusion and interpretation of work results.

Work methodology (Kuzmin et al, 2013–2017) [21-24]:

– 0,3 ml of a AAM prepared with a volumetric pipette with a predetermined strength (40,0 ± 0,2) % vol.;

– external standard separated from the testing substance which is required for LOCK's system operation (acetone-d_6) of *NMR*'s deuterium stabilization spectrometer) is added in a special form of a capillary into an ampoule. The obvious advantage of using the external standard is the fact that standard substance's molecules and test's solution do not interact with each other;

– *^1H NMR* spectra records and data processing were performed according to the instruction of *FT-NMR* Bruker Avance II spectrometer (400 MHz).

Results and discussions

Will examine spectrum of water (Figure 1), ERS (Figure 2), AAM (Figures 3-4), made of drinking water and ERS at a different instants of system's operation (life after mixing) (h).

We will examine spectra of drinking water, which is characterized by a unitary signal of hydroxyl group of H_2O (Figure 1). The component of protons of H_2O – singlet (*s*), located in a «weak field» with a chemical shift δ_{H2O}=4,60 ppm. Waveform of H_2O protons – is distorted Gaussian curve, with a broadened base and a slight asymmetry of apex, which is offset from the centerline.

We will analyze the spectra of ERS (Figure 2). Hydroxyl group of protons of ERS are represented by two separate peaks. A component of ethanol is represented as a single broad singlet, located in a «low field» with the chemical shift δ_{EtOH}=5,65 ppm. A component of water proton is represented as singlet with a chemical shift of δ_{H2O}=4,85 ppm. The form of H_2O protons' signal is a distorted Gaussian curve, with a broadened base and a certain asymmetry. The difference between the *OH*-proton of ethanol (*EtOH*) and the proton of water (H_2O) in the chemical shifts – $\Delta\delta_1$= 0,80 ppm (Δf_1=320 Hz).

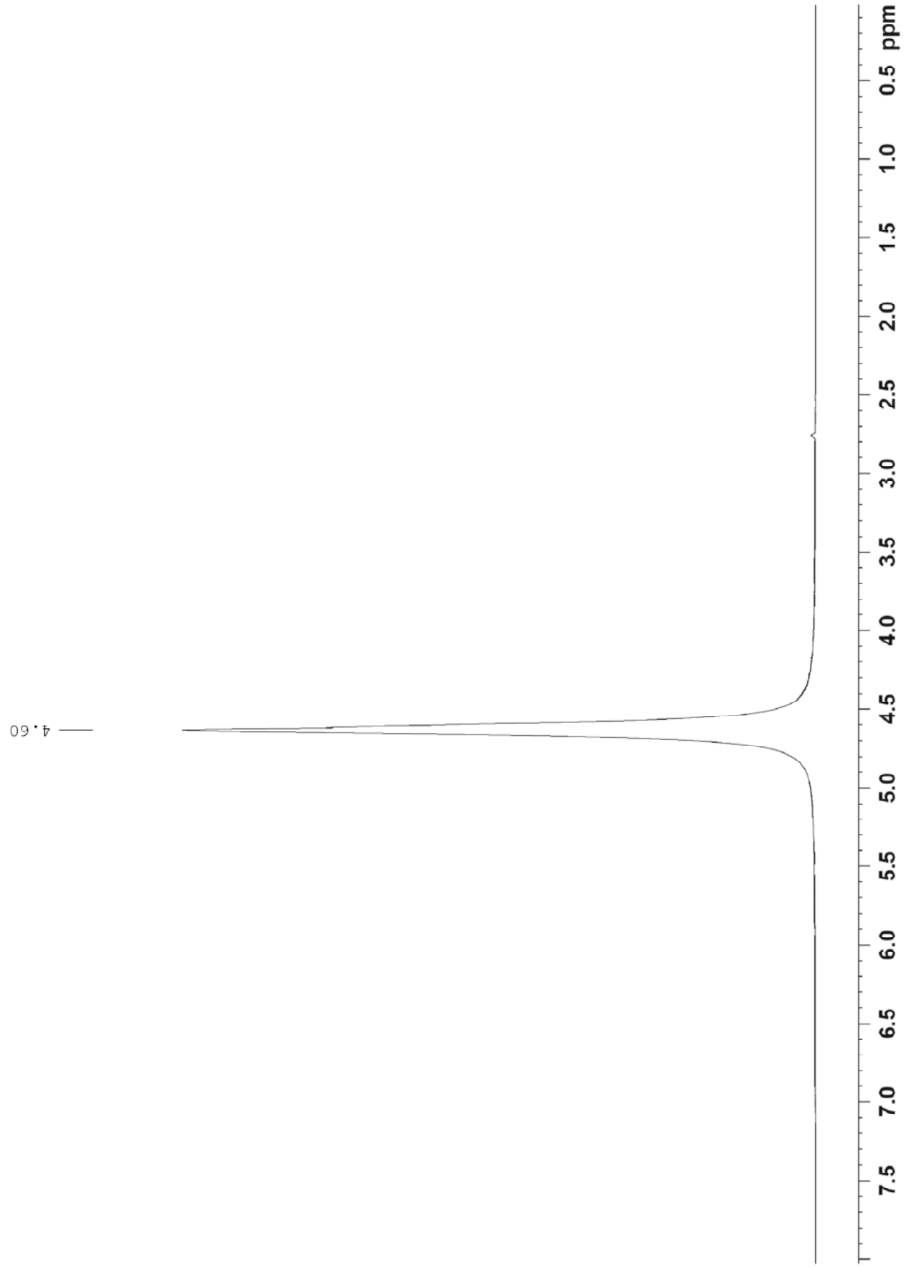

Figure 1. ^{1}H *NMR* spectra of hydroxyl proton of drinking water

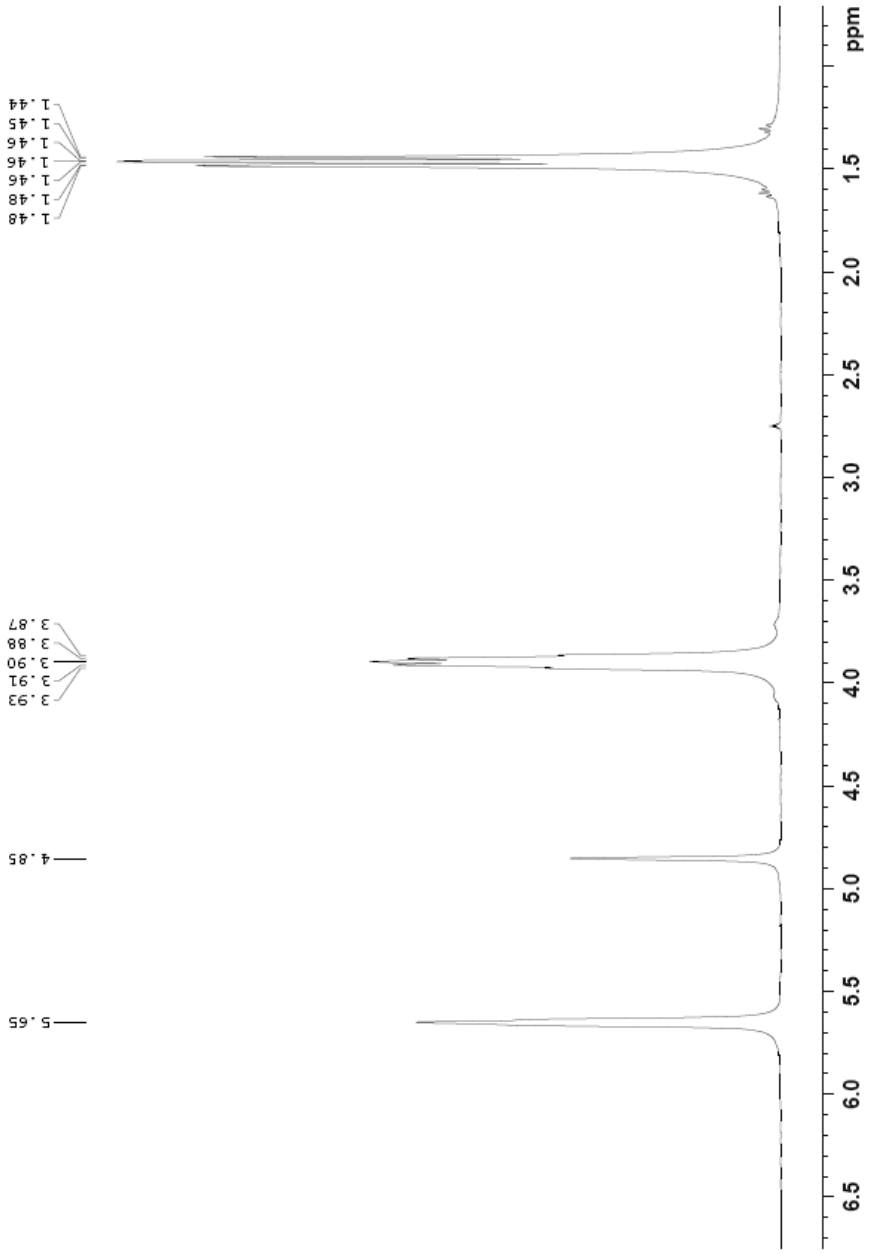

Figure 2. ***^{1}H NMR*** **spectra of proton groups ERS:** *CH_3; CH_2; H_2O; EtOH*

The analysis of the ^1H *NMR*-spectra of protons methyl group of ethanol (CH_3) allows us to state the following. The protons' methyl group is represented as a septet (*sp*) with a relative intensity (1:6:15:20:15:6:1). This is abnormity as according to Pascal's triangle and on the assumption of protons' methyl group spin-spin interactions, methylene group's (CH_3) signal has to be split by an adjacent protons' group (CH_2) as a triplet (*t*) with intensity ratio (1:2:1). Besides the methylene group (CH_2), no other group of protons can have an effect on the active spectrum of the methyl group (CH_3).

The analysis of methylene group's (CH_2) ^1H *NMR*'s protons shows the following. The methylene group's protons (CH_2) are represented as quintet (*qi*) with the intensity (1:4:6:4:1). This is an abnormity. Protons of methyl (CH_3) groups must split the signal of methylene group (CH_2) into four components and form a quartet (*q*) with an intensity ratio of 1:3:3:1, as based on the spin-spin interaction. In turn, protons of hydroxyl (*OH*) groups should split each quartet's component of methylene (CH_2) group into two components to form a double quartet. The signal of methylene (CH_2) groups should remain as quartet. This happens due to the absence of spin-spin interaction between the hydroxyl (*OH*) and methylene (CH_2) groups by the chemical exchange.

The Figures 3-4 shows the proton group's ^1H *NMR* spectra's of freshly prepared AAM sample (0 h) and a sample taken after few days, with an interval of 48…72 h with indication of chemical shift.

Hydroxyl group of protons are represented by two separate peaks (Figure 3) at the time of the initial formation of the AAM and at the time of the functioning of the system (τ=0 h). Multiplet component of hydroxyl (*OH*) proton of ethanol (C_2H_5OH) is presented in a form of bulge. The bulge is based in a weak field with a chemical shift of δ_{EtOH}=5,32 ppm. Signal of water (H_2O) protons is presented as an elongated singlet of symmetrical shape with a broad base which is located at δ_{H2O}=4,71 ppm. The difference in chemical shifts of *OH* proton (C_2H_5OH) and H_2O proton at this stage (τ=0 h) is $\Delta\delta_1$=0,61 ppm (Δf_1=244 Hz).

At the initial instant of AAM formation – τ=48 h the presents of two separate signals hydroxyl protons of ethanol and water. Multiplet component of hydroxyl proton of ethanol (*EtOH*) is presented in a form of bulge with a chemical shift of δ_{EtOH}=5,37 ppm. Signal of water (H_2O) protons is presented as an elongated singlet of symmetrical shape with a broad base which is located at δ_{H2O}=4,76 ppm. The difference in chemical shifts of *OH* proton (*EtOH*) and water (H_2O) proton – $\Delta\delta_1$=0,61 ppm (Δf_1=244 Hz).

The spectra from third to sixth (τ=120-312 h) is characterized by one summarized peak of hydroxyl protons of ethanol and water. The component of *EtOH* proton and H_2O proton is represented by a singlet with the chemical shift of $\delta_{EtOH+H2O}$=4,74-4,81 ppm. The summarized $EtOH+H_2O$ protons signal has a nonesymmetric shape with a widened base and a top of regular form.

The analysis of ^1H *NMR* spectra of AAM methyl group's protons (CH_3) states the following τ=0. The protons' methyl group is represented as a quartet (*q*) with a relative intensity (1:3:3:1) in the initial part of system's operation. This is abnormity as according to Pascal's triangle and on the assumption of protons' methyl group spin-spin interactions, methylene group's (CH_3) signal has to be split by an adjacent protons' group (CH_2) as a triplet (*t*) with intensity ratio (1:2:1). Besides the methylene group (CH_2), no other group of protons can have an effect on the active spectrum of the methyl group (CH_3). Thus, the methyl group of protons (CH_3) is located in a strong field with an average value of the chemical shift as δ_{CH3}=1,08 ppm.

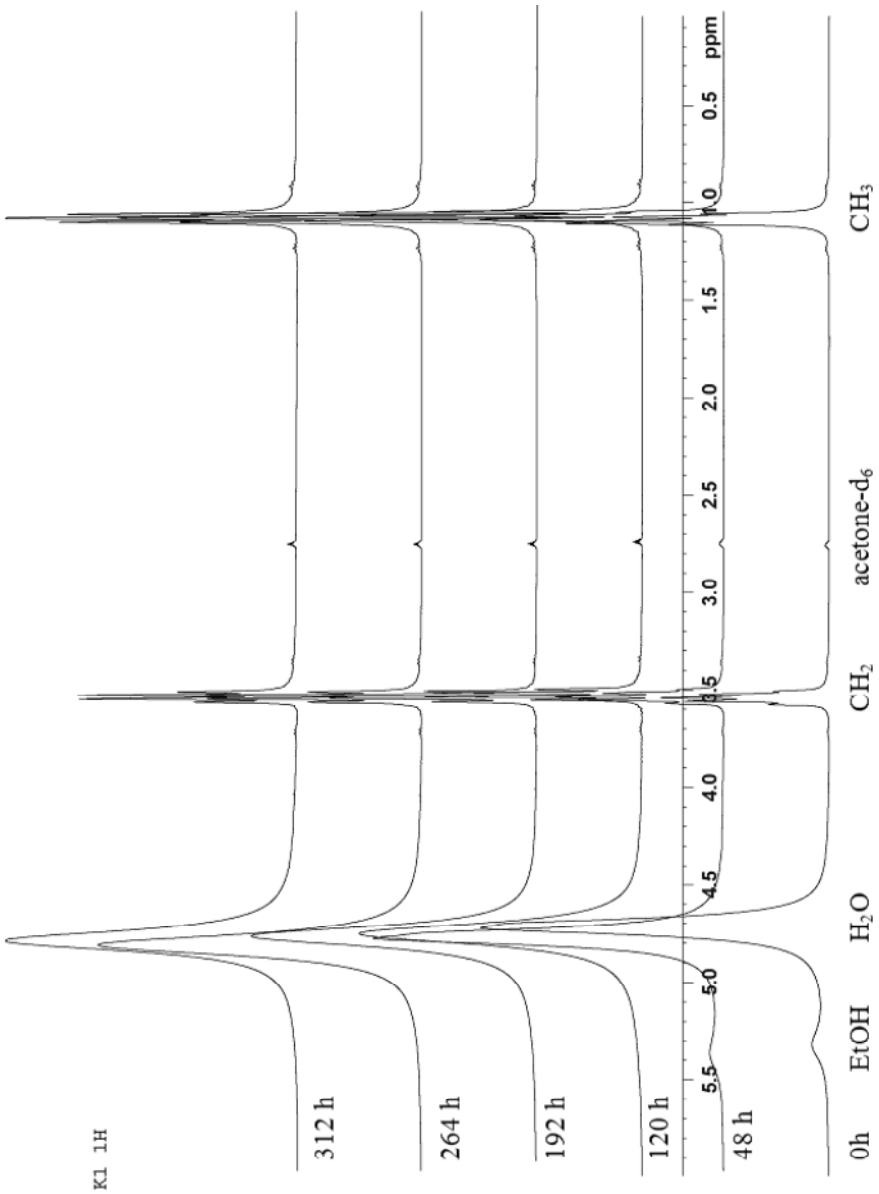

Figure 3. *^{1}H NMR* spectra of proton groups of AAM, prepared in drinking water and ERS: *CH_3; CH_2; H_2O; EtOH*, dependent from system's functioning time (0-312 h)

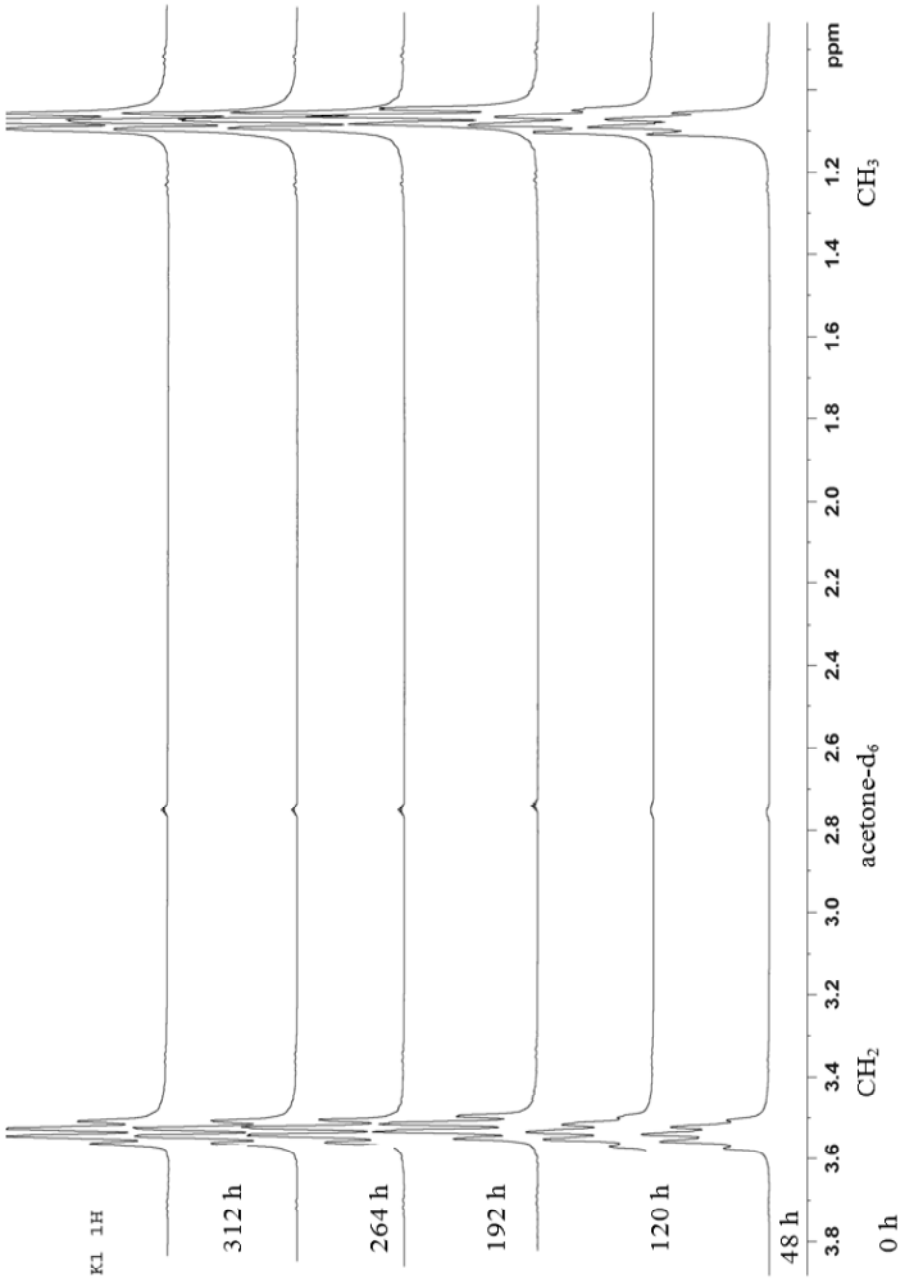

Figure 4. ^{1}H *NMR* spectra of proton groups of AAM, prepared in drinking water and ERS: CH_3; CH_2, acetone-d_6 dependent from system's functioning time (0-312 h)

τ=48 h. Methyl group of protons (CH_3) has shifted by a distance of 0,01 ppm towards the strong field from its original position (τ=0 h) with an average value of the chemical shift δ_{CH3}=1,07 ppm. It has the following individual characteristics of signals' chemical shift's peaks δ_{CH3}=(1,10; 1,08; 1,06; 1,04) ppm; distance between the peaks is 8 Hz relative to each other. Signal's form is quartet (*q*), which is also an abnormity for the interaction of the above spectrum with methylene group (CH_2).

τ=120 h. Methyl spectrum has shifted by a distance of 0,02 ppm from its original position (τ=0 h) with a average value of the chemical shift δ_{CH3}=1,06 ppm. Signal's form is triplet (*t*), which indicates it's stability. This is based on spin-spin interaction with methylene (CH_2) group's protons. Chemical shift of triplet's individual peaks is δ_{CH3}=(1,08; 1,06; 1,04) ppm.

τ=192-312 h. Methyl spectrum has shifted by a distance of 0,01 ppm from its original position (τ=0 h) with a average value of the chemical shift δ_{CH3}=1,07 ppm. Signal's form is triplet (*t*), which indicates it's stability. This is based on spin-spin interaction with methylene (CH_2) group's protons. Chemical shift of triplet's individual peaks is δ_{CH3}=(1,09; 1,07; 1,05) ppm.

The analysis of methylene group's (CH_2) *^{1}H NMR*'s protons shows the following. The methylene group's protons (CH_2) are represented as quintet (*qi*) with the intensity (1:4:6:4:1) at the beginning of AAM's formation process (τ=0 h). This is an abnormity. Protons of methyl (CH_3) groups must split the signal of methylene group *(*CH_2) into four components and form a quartet (*q*) with an intensity ratio of 1:3:3:1, as based on the spin-spin interaction. In turn, protons of hydroxyl (*OH*) groups should split each quartet's component of methylene (CH_2) group into two components to form a double quartet. The signal of methylene (CH_2) groups should remain as quartet. This happens due to the absence of spin-spin interaction between the hydroxyl (*OH*) and methylene (CH_2) groups by the chemical exchange.

The methylene group of protons (CH_2) is in a weak field, with the average value of the chemical shift of δ_{CH2}=3,54 ppm, each peak of quartet is located at a distance of 8 Hz from each other.

The methylene group of protons (CH_2) has shifted from its original position towards the strong field by 0,01 ppm after the 48 hours. The average value of its chemical shift is δ_{CH2}=3,53 ppm. Signal's form is quintet (*qi*). This is an abnormity for the above proton's spectrum.

The first two spectra, in our view, belong to a group with unsteady balance, since the signals' form is abnormal.

Methylene spectrum with an average value of the chemical shift as δ_{CH2}=3,52 ppm has shifted into the strong field with respect to the initial position (τ=0 h) by 0,02 ppm after 120 hours expiration. Signal's form is quartet (*q*), typical for the above proton group, based on the spin-spin interaction with the protons of the methyl (CH_3) group and chemical exchange between hydroxyl (*OH*) and methylene (CH_2) groups. This is the form's stabilization.

Complete structuring of methylene group's (CH_2) signal takes place approximately after 8 days (τ=192 h): signal's form is quartet (*q*); location – chemical shift with an average value of δ_{CH2}= 3,53 ppm, which remains unchanged. The distance between the peaks also remains unchanged – 8 Hz.

Conclusions

As a results we have evidence of a complex dynamic of achievement processes of solution equilibrium for AAM prepared in drinking water with pH=7,01 and ERS. At the same time pH of obtained AAM is pH = 8,32 i.e. alkalescent medium. This value is characterized by a reduced content of free H^+ ions relative to the OH^-, i.e. general alkaline reaction of the system. Hydroxyl proton (*OH*) of ethanol exchange rate is in intermediate area. It happens during the first 48 hours when the concentration of alcohol is constant (strength AAM – 39,94 % vol.) and the system is thermostatic (t=23,5 ºC). Signals are separately located. Protons' exchange is accelerated due to the rearrangement of system's structure, during the interval of τ=48 h to 120 h. Since τ=120 h, there is only one common signal of mobile protons of asymmetrical shape. The size of chemical shift of the summed signal $\delta_{EtOH+H2O}$=4,74 ppm (τ=120 h) is starting to grow and shifts to the «weak fields» with the value of $\delta_{EtOH+H2O}$=4,81 ppm (τ=312 h).

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Optimisation of operating parameters for supercritical carbon dioxide extraction of lycopene from industrial tomato waste

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Abstract

Introduction. Tomato waste can be used as secondary raw materials for obtaining liposoluble extracts. Lycopene, being a lipophilic compound with antioxidant properties found in tomatoes, it may be extracted using supercritical carbon dioxide from the waste obtained in the industrial processing of tomatoes.

Materials and methods. The tomato waste obtained from the manufacture of tomato juice was collected from "Orhei-Vit" JSC, Orhei, Republic of Moldova. Using the full factorial orthogonal experimental design method, was created the planning matrix in real variables, obtaining 15 extraction regimes by varying the parameters: temperature (36–73 °C), pressure (18–42 MPa) and time (24–96 min). The content of lycopene was determined by the spectrophotometric method at 502 nm wavelength.

Results and discussion. Initially, tomato waste was dried from an initial humidity of 80.0% to a final moisture content of 6.5%. In order to increase the contact surface with carbon dioxide, the tomato waste was milled. Under laboratory conditions, samples of CO_2 extracts from tomato waste were obtained at different extraction parameters. The lycopene concentration was taken as the output factor, and it was established the final form of the second order regression equation characterizing the CO_2 extraction process of lycopene in the fat-soluble fraction from the tomato waste. The regression equation allowed the optimization of the response using the gradient ascension method, thus establishing the optimal extraction parameters of the bioactive compound – lycopene. The response surface plot described by the second degree polynomial which characterizes the CO_2 extraction process of lycopene from tomato waste at constant time, pressure or temperature were graphically represented.

Conclusions. The CO_2 extracts from tomato waste are rich in lycopene, the concentration ranging from 10.8 to 47.1 mg/100 g. The optimal parameters for lycopene extraction from tomato waste are the temperature 60–75 °C, the pressure 33–42 MPa and the extraction time 62–68 min.

Introduction

With the increase in world trade of tomato products, the tomato processing industry is also expanding. As a consequence (result), the amount of by-products: tomato seeds and skin grows. At present, only a small amount of tomato by-products are sold at low prices and used as feed or fertilizer, but the remaining seeds are thrown away, thus wasting resources and polluting the environment. Tomato seeds are an excellent source of macronutrients: 28% fat and 29% protein, and micronutrients: linoleic acid and other unsaturated fatty acids, high levels of essential amino acids such as lysine; without toxic ingredients or nutritional inhibitors. Therefore, the way of extracting nutrients from tomato by-products in order to obtain new products and greater economic value is a challenge. [1]

Secondary products from tomato processing can be used as a raw material for the production of tomato oil, so that the turning effect by transforming waste into a resource is achieved and environmental pollution can be reduced. In addition to the conventional pressing method, it is possible to implement the modern supercritical CO_2 extraction technology for the production of tomato seed oil so that the yield of tomato oil can be greatly improved and the quality of the tomato oil could be high. The plant is reliable, the resulting product is safe, and the extraction rate of tomato seed oil is over 95%. Compared to the conventional hot pressing method, the advantage of CO_2 extraction is that it avoids the deterioration of bioactive substances and fat-soluble nutritional components that can be stored in essential quantities in tomato seed oil. [1]

Tomato seed oil has a high nutritional value, contains large amounts of unsaturated fatty acids and is a powerful antioxidant that can effectively reduce stress, improve sleep quality, restore skin's natural glow, improve immunity, has anti-aging effects and protects against UV radiation, prevents osteoporosis and can prevent calcium loss. [1]

Tomatoes and tomato waste, respectively, are highlighted by an increased content of lycopene, a powerful antioxidant.

Lycopene is a tetraterpen from the carotenoid family, namely that of carotenes. This is a red, fat-soluble pigment (vegetable colorant) found mainly in tomatoes and various products derived from thermally processed tomatoes. It is named after the Latin name of tomatoes (*Solanum lycopersicum*), which has the highest natural concentration.

It has a structure consisting of a long chain of conjugated double bonds, with two open rings at the ends.

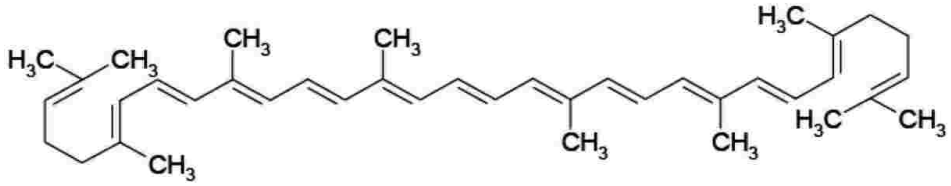


Figure 1. The molecular structure of lycopene

The lycopene molecule is the longest of all carotenoids, which like the β-carotene, the human body does not synthesize.

Although it has a structure similar to that of the well-known antioxidant β-carotene, its antioxidant activity is at least 5 times higher. Lycopene protects cells against DNA

damage and lipid peroxidation, and intervenes in reducing the risk of certain cancers (prostate, digestive, bladder, lung, skin). [2]

The antioxidant activity of lycopene is due to the capture of singlet oxygen from biological systems.

Lycopene is widely used in the alimentary industry as an antioxidant and natural colorant. As antioxidant it is active in non-polar environments, in oils, fats, foods with a lipid content. It has the ability to protect lipids from oxidative degradation by inactivating the reactive forms of oxygen. Namely, the double bonds of the molecules ensure the addition of reactive oxygen. [3]

Thermal treatment or tomato processing does not affect the antioxidant properties of lycopene, on the contrary it increases its availability and is more efficiently assimilated by the human body. [4, 5]

In laboratory conditions lycopene shows antitoxic properties against various toxic substances such as aflatoxin, cyclosporine or cadmium. [5]

According to the European Food Safety Authority (EFSA Journal 2011; 9 (4): 2031 Scientific opinion on the substantiation of health claims related to lycopene according to Article 13, paragraph 1 of Regulation (EC) No 1924/2006) the Dietary Reference Intake (DRI) of lycopene to have antioxidant effect or a normal cardiac function(in case of cardiovascular disease) is 5-15 mg / day [6]. According to the recommendations of the Guidebook MP 2.3.1. 19150-04 of 2004, (Recommended levels of biologically active substances), the DRI of lycopene is 5-10 mg (the maximum daily dose is 15 mg) [7].

This paper presents the content of lycopene in CO_2 extracts from tomato waste, obtained at different extraction regimes. Based on the obtained data, it is determined the influence of the extraction parameters: temperature, pressure and time on lycopene concentration in the fat-soluble CO_2 extracts from tomato waste.

Materials and methods

Materials

Tomato waste was collected from the industrial scale production of tomato juice at "Orhei-Vit" JSC, Orhei, Republic of Moldova.

With the purpose of being used as raw material, tomato waste with an initial moisture content of 80.09 % was dried by the conductive method in Biosec Domus B5 dryer to a final moisture content of 6.50 %. One of the basic criteria for carrying out the supercritical CO_2 extraction is that the raw material subjected to the extraction of the lipid fraction has a humidity of maximum 10…12%. [8]

In order to increase the contact area with the carbon dioxide, to achieve a more efficient extraction, both quantitatively and qualitatively, the tomato waste was milled.

The lipid content in dried tomato waste is 10.5%. [8]

Carbon dioxide is intended for use in the food industry.

The reagents used in analyzes: hexane, ethanol and acetone, meet the quality requirements.

Methods

Supercritical CO_2 extraction. The supercritical extraction with carbon dioxide from tomato waste was carried out under laboratory conditions at the HA 120-50-01C pilot plant within the Practical Scientific Institute of Horticulture and Food Technology.

The technical parameters of the installation are: P_{max}=50 MPa (500 atm), T_{max} = 75°C, volume of the extractor vessel – 1,0 l and maximum extract volume – 0,6l [8].

From the storage tank, the carbon dioxide is pumped through the heat exchanger into the extractor vessel with raw material – tomato waste. Using the pressure and temperature control system the required extraction pressure and temperature are created in the extractor vessel. Once the supercritical CO_2 and the feed reach equilibrium in the extraction vessel, through the manipulation of pressure and temperature to achieve the operating conditions, the extraction process proceeds. The mobile phase, consisting of the superctitical CO_2 fluid and the solubilized components, is transferred to the separators I and II where the fluid is reduced by decreasing the pressure of the system. The extract precipitates in the I or II separator while thesuperctitical CO_2 fluid is either released to the atmosphere or recycled back to the extractor [8, 9].

Determination of Lycopene content. The lycopene from tomato byproducts is extracted using hexane: ethanol: acetone mixture (2:1:1) (v/v) following the Sharma and Le Maquer method, exposed by Alda [10].

One gram of the homogenized samples, and 25 ml of hexane: ethanol: acetone mixture, which was placed into the rotatory mixer for 30 min, adding 10 ml of distilled water and the stirring was continued for another 2 minutes.

The solution was then left to separate into two distinct layers, polar and non-polar. The absorbance was measured at 502 nm, using hexane as a reference sample. The lycopene concentration was calculated using its specific extinction coefficient (E 1%, 1 cm) of 3150 in hexane at λ=502 nm. The concentration of lycopene is expressed in mg/100 g product.

$$C = \frac{E}{3.15} \cdot \frac{20}{m} \quad (1)$$

C – lycopene content, mg/100g
m – mass of product sample, g
E – extinction coefficient.

Statistical analysis. The mathematical processing of the obtained data on the supercritical CO_2 extraction of lycopene from tomato waste was performed using Microsoft Excel 2007 software.

Results and discussion

Central factorial experiment composed in the orthogonal plane

In order to determine practical values of the process parameters, it is necessary to establish interdependencies capable of describing both the nature and the extent of the influences of the input factors, so it is foreseen to determine a mathematical model.

For *the planned experiments*, to the influence factors were assigned two levels of variation: *a upper level* x_{sup} and *a lower level* x_{inf}. These two levels are chosen at equal distance from the *central level* x_0 of the influence factor, also called *base level* or *zero level*.

The zero level indicates the value of the influence factors around which experimental modeling was desired. The interval limited by the lower and upper values of the influence factors defines *the experimental field*. All influence factors can take values within this range of variation. [11, 12, 13]

During the supercritical-CO_2 extraction from tomato waste was examined the oscillation of three process parameters, namely temperature, pressure and time. Respectively, it was obtained the matrix in which the variable parameters of the process were encoded by X_1, X_2 and X_3 and were noted the minimum, center and maximum values that will be used in supercritical carbon dioxide extraction of liposoluble substances, including lycopene.

Table 1

The classical matrix of assigning the values of influence factors

Factor	Coding	Min. (-)	Center	Max. (+)
Temperature, *°C*	X_1	40	55	70
Pressure, *MPa*	X_2	20	30	40
Time, *min.*	X_3	30	60	90

Each input factor was assigned a coded variable.

The variation range, from minimum (-) to maximum (+), was chosen in accordance with the characteristics of the CO_2-extraction plant, so that all experiments were achievable.

To obtain a second-order mathematical model, factorial design of the experiments is used, the most important programs being the composite central programs. When composing the mathematical model in the form of a polynomial of second degree, the number of factors can not be limited to two. Therefore, it should be used 3^k programs in which factors are changed to 3 levels. However, these programs become uneconomic or even unrealistic with a number of factors $k \geq 4$, due to the very large number of determinations. In this sense it has been shown that a program with fewer determinations compared to program 3^k can be obtained by supplementing a 2^k program with certain points of factorial space. [13, 14]

Results:

$$N = N_c + N_\alpha + N_0 \quad (2)$$

where: N – total number of determinations;

N_c – the number of "sphere" determinations;

N_α – the number of "star" points;

N_0 – the number of points in the center.

The programming method of the composite central experiment involves completing the 2^k base factorial matrix with a number of experiences ($N_\alpha = 2k$), while the other factors are at the base level, and with N_0 experiments at the center of the experiment.

Under these circumstances, the total number of experiences is:

$$N = 2^k + 2\,k + N_0 \quad (3)$$

It has been agreed to take as model the orthogonal central matrix.

Initially, the program's center coordinates (zero level x_i^0) and intervals of variation Δx_i were calculated using relations 4 and 5:

$$x_i^0 = \frac{x_i^s + x_i^i}{2} \quad (4)$$

$$\Delta x_i = \frac{x_i^s - x_i^i}{2} \quad (5)$$

Factors coding was performed according to formula 6:

$$X_i = \frac{x_i - x_i^0}{\Delta x_i} \quad (6)$$

$$\Delta x_i = \frac{X - x_i^0}{\alpha} \quad (7)$$

$$X_1 = \frac{40-55}{15} = -1;$$

$$X_2 = \frac{20-30}{10} = -1;$$

$$X_3 = \frac{30-60}{30} = -1.$$

To complement the matrix with the experiences from no. 9 to 15, it is necessary to calculate the star points (+ α and -α), multiplied by the coefficients +1,215 and -1,215 according to formula 7.

Temperature: $+\alpha$: ; $X_{+\alpha}X_{+\alpha}$ =73 °C;$-\alpha$: ; $X_{-\alpha}X_{-\alpha}$ =36 °C;

Pressure:$+\alpha$: ; $X_{+\alpha}X_{+\alpha}$ =42 MPa;$-\alpha$: ; $X_{-\alpha}X_{-\alpha}$ =18 MPa;

Time:$+\alpha$: ; $X_{+\alpha}X_{+\alpha}$ =96 min.; $-\alpha$: ; $X_{-\alpha}X_{-\alpha}$ =24 min.

Table 2

Variation ranges and factor levels

Factor name	**Temperature, °C**	**Pressure, MPa**	**Time, min**
Factor coding	X_1	X_2	X_3
Upper level x_i^s	70	40	90
Lower level x_i^i	40	20	30
Zero level x_i^0	55	30	60
Intervals of variation Δx_i	15	10	30
Level $+\alpha$ $X_{+\alpha}$	73	42	96
Level $-\alpha$ $X_{-\alpha}$	36	18	24

According to the values of the calculated parameters for the orthogonal model, it is observed that the determined star points are included in the technical characteristics of the installation and allow extraction to be performed under supercritical conditions.

Experiences no 9-14 are performed according to star point values for each factor of influence and their combination with the zero level values of the other factors.

The natural values of input factors in points +1 and -1 are determined from the relation $x_i^0 \pm \Delta x_i$.

The values thus obtained are used to perform the experiments. For each experience a measured value of the resultant variable Y is obtained. These data are used to calculate the regression coefficients of the mathematical model.

The performance of the experiments led to the obtaining of information about the dependent variable Y, in different situations, resulting from the combination of the different coded levels of the independent variables.

Table 3

Matrix of planning in real variables

No	Temperature °C	Presure, MPa	Time, min	Y_A	Y_B	$\overline{Y}$
1	40	20	30	10.80	12.88	11.84
2	70	20	30	25.24	25.40	25.32
3	40	40	30	25.84	22.72	24.28
4	70	40	30	47.12	35.28	41.20
5	40	20	90	13.16	15.20	14.18
6	70	20	90	28.80	29.96	29.38
7	40	40	90	25.40	26.44	25.92
8	70	40	90	40.48	44.49	42.49
9	37	30	60	19.68	16.74	18.21
10	73	30	60	36.00	32.88	34.44
11	55	18	60	16.64	16.72	16.68
12	55	42	60	29.56	29.72	29.64
13	55	30	24	22.84	22.96	22.90
14	55	30	96	26.44	28.64	27.54
15	55	30	60	26.08	26.20	26.14

In order to have relevant results on the CO_2 extraction process of lycopene from tomato waste, two parallel experiments of the 15 regimes of extractions were performed, at temperature, pressure and time parameters to maximum, minimum and center values and combinations thereof.

When selecting the extraction parameters, were taken into account the characteristics of the pilot plant type HA 120-50-01C, (P_{max} = 50 MPa, T_{max} = 75 ° C, V_{cel} = 1,0 l) [8], the parameters required to ensure the supercritical state of carbon dioxide (P_{cr} = 7.377 MPa, T_{cr} = 30.978 ° C, ρ_{cr} = 467.6 kg / m^3) [15], but also that these parameters do not affect the quality of the extraction products.

The lycopene concentration in the CO_2 extract of tomato waste, obtained with supercritical carbon dioxide, was taken as the output variable. The mean of the response $\overline{Y}$ was the mean of the concentrations of the two parallel experiments Y_A and Y_B. The data obtained are entered in Table 3.

Thus, the following experiment plannning matrix (Table 4) is obtained:

Table 4

Experiment planning matrix in encoded variables of composed central programming in orthogonal plane

No	X_0	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1^2-0{,}73$	$X_2^2-0{,}73$	$X_3^2-0{,}73$	$\overline{Y}$
1	+	–	–	–	+	+	+	0.27	0.27	0.27	11.84
2	+	+	–	–	–	–	+	0.27	0.27	0.27	25.32
3	+	–	+	–	–	+	–	0.27	0.27	0.27	24.28
4	+	+	+	–	+	–	–	0.27	0.27	0.27	41.20
5	+	–	–	+	+	–	–	0.27	0.27	0.27	14.18
6	+	+	–	+	–	+	–	0.27	0.27	0.27	29.38
7	+	–	+	+	–	–	+	0.27	0.27	0.27	25.92
8	+	+	+	+	+	+	+	0.27	0.27	0.27	42.49
9	+	–1.21	0	0	0	0	0	0.746	–0.73	–0.73	18.21
10	+	+1.21	0	0	0	0	0	0.746	–0.73	–0.73	34.44
11	+	0	–1.21	0	0	0	0	–0.73	0.746	–0.73	16.68
12	+	0	+1.21	0	0	0	0	–0.73	0.746	–0.73	29.64
13	+	0	0	–1.21	0	0	0	–0.73	–0.73	0.746	22.90
14	+	0	0	+1.21	0	0	0	–0.73	–0.73	0.746	27.54
15	+	0	0	0	0	0	0	–0.73	–0.73	–0.73	26.14

Factors X_{12}, X_{13}, X_{23} and X_{123} represent the interaction factors, variables that show their mixed influence.

$\overline{Y}$ is the system response, i.e. the average lycopene concentration, mg / 100 g of CO_2-extract from tomato waste.

Regression coefficients

According to formulas 8-12 the regression coefficients of the equation were calculated.

$$b_0 = b_0' - \phi \sum b_{ii} \tag{8}$$

$$b_0' = \frac{1}{N} \sum X_{0u} Y_u \text{ (9) } b_i = \frac{\sum X_{iu} Y_u}{\sum X_{iu}^2} \tag{10}$$

$$b_{ij} = \frac{\sum X_{iu} X_{ju} Y_u}{\sum (X_{iu} X_{ju})^2} \tag{11}$$

$$b_{ii} = \frac{\sum (X_{iu}^2 - \phi) Y_u}{\sum (X_{iu}^2 - \phi)^2} \tag{12}$$

Table 5

The regression coefficients of the equation

b'_0	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{11}	b_{22}	b_{33}
26.01	24.50	7.48	6.29	1.37	0.60	0.17	-0.43	1.66	-0.49	0.91

Since factor encoding has been performed, the regression equation will take the form:

$$Y = b_0' + \sum b_i X_i + \sum b_{ij} X_i X_j + \sum b_{ii} (X_i^2 - \phi) \tag{13}$$

Thus, the following regression equation of the CO_2 extraction of lycopene from the tomato waste is obtained:

$$\begin{gathered} Y = 24,50 + 7,48X_1 + 6,29X_2 + 1,37X_3 + 0,60X_{12} + 0,17X_{13} - \\ -0,43X_{23} + 1,66X_1^2 - 0,49X_2^2 + 0,91X_3^2 Y = \\ = 24,50 + 7,48X_1 + 6,29X_2 + 1,37X_3 + 0,60X_{12} + \\ +0,17X_{13} - 0,43X_{23} + 1,66X_1^2 - 0,49X_2^2 + 0,91X_3^2 \end{gathered}$$

Then, according to formulas 14-18, the dispersion of the regression coefficients was calculated.

$$S_{b_0}^2 = S_{b'_0}^2 + \sum \phi^2 \cdot S_{b_{ii}}^2 \tag{14}$$

$$S_{b'_0}^2 = \frac{S_y^2}{N} \tag{15}$$

$$S_{b_i}^2 = \frac{S_y^2}{\sum X_{iu}^2} \tag{16}$$

$$S_{b_{ij}}^2 = \frac{S_y^2}{\sum (X_{iu} X_{ju})^2} \tag{17}$$

$$S^2_{b_{ii}} = \frac{S^2_y}{\sum (X^2_{iu} - \phi)^2} \quad (18)$$

Table 6

Dispersion of regression coefficients of the equation

$S^2_{b'_0}$	$S_{b'_0}$	$S^2_{b_i}$	S_{b_i}	$S^2_{b_{ij}}$	$S_{b_{ij}}$	$S^2_{b_{ii}}$	$S_{b_{ii}}$	$S^2_{b_0}$	$S^2_y = S^2_0$
0.44	0.66	0.61	0.78	0.83	0.91	1.54	1.24	2.90	2.58

The mean dispersion on the matrix (dispersion of the experiment) was determined according to formula 19:

$$S^2_0 = \frac{1}{m} \sum_{i=1}^{m} \sigma_i^2 \quad (19)$$

Significance evaluation of calculated coefficients was done according to Student's t-test. Calculated values of $t_{calc.}$ were determined by the formulas 20–22.

$$t_i = \frac{|b_i|}{S_{b_i}} (20); \qquad t_{ij} = \frac{|b_{ij}|}{S_{b_{ij}}} (21); \qquad t_{ii} = \frac{|b_{ii}|}{S_{b_{ii}}} (22).$$

Table 7

t_{calc} coefficient values

t_1	t_2	t_3	**t_{12}**	**t_{13}**	**t_{23}**	t_{11}	**t_{22}**	**t_{33}**
9.57	8.06	1.75	0.66	0.19	0.48	1.33	0.39	0.73

Student's t-table t_{St} coefficient is determined from the Student distribution table, where is indicated the number of degrees of freedom f, the probability P, or the confidence q.

It is known that: b_i is significant if

$b_i b_i$ is insignificant if $|t_i| < t_{St}$

By comparing the calculated values of the Student's t-test and the Student's t-table t_{St}, it was determined that the insignificant coefficients b are $b_{12,}$ $b_{13,}$ $b_{23,}$ b_{22} and b_{33}, and respectively $X_{12,}$ $X_{13,}$ $X_{23,}$ X_{22}, X_{33} are insignificant factors.

Considering only significant regression coefficiants, the model corresponding to the system is represented by the followingregression equation in the final form:

$$Y = 24,80 + 7,48X_1 + 6,29X_2 + 1,37X_3 + 1,66X_1^2 Y =$$
$$= 24,80 + 7,48X_1 + 6,29X_2 + 1,37X_3 + 1,66X_1^2$$

This is the regression equation without the five insignificant regression coefficients. After removing the insignificant terms it is assumed that the $\hat{Y}$ answer is recalculated (table 8).

Table 8

Reference data for testing the suitability of the regression equation

No	T, °C	P, MPa	t, min	Y_A	Y_B	$\overline{Y}$	σ^2	$\hat{Y}$	$\left(\overline{Y}_i-\hat{Y}_i\right)$	$\left(\overline{Y}_i-\hat{Y}_i\right)^2$
1	40	20	30	10.80	12.88	11.84	2.16	9.23	2.61	6.83
2	70	20	30	25.24	25.40	25.32	0.01	24.18	1.14	1.29
3	40	40	30	25.84	22.72	24.28	4.87	21.81	2.47	6.08
4	70	40	30	47.12	35.28	41.20	70.09	36.77	4.43	19.64
5	40	20	90	13.16	15.20	14.18	2.08	11.96	2.22	4.94
6	70	20	90	28.80	29.96	29.38	0.67	26.91	2.47	6.08
7	40	40	90	25.40	26.44	25.92	0.54	24.54	1.38	1.89
8	70	40	90	40.48	44.49	42.49	8.04	39.50	2.99	8.91
9	37	30	60	19.68	16.74	18.21	4.32	15.80	2.41	5.79
10	73	30	60	36.00	32.88	34.44	4.87	33.90	0.54	0.29
11	55	18	60	16.64	16.72	16.68	0.00	16.52	0.16	0.03
12	55	42	60	29.56	29.72	29.64	0.01	31.75	-2.11	4.45
13	55	30	24	22.84	22.96	22.90	0.01	23.20	-0.30	0.09
14	55	30	96	26.44	28.64	27.54	2.42	26.50	1.04	1.07
15	55	30	60	26.08	26.20	26.14	0.01	24.85	1.29	1.66

According to the regression equation, was determined the $\hat{Y}$ value for each row from the planar matrix. Was calculated the difference between the mean value $\overline{Y}$ obtained experimentally and the $\hat{Y}$ value calculated from the regression equation. These differences $\left(\overline{Y}_i-\hat{Y}_i\right)$ were raised to the square $\left(\overline{Y}_i-\hat{Y}_i\right)^2$ and it was calculated their sum.

For the analyzed case the sum of the square differences is $\sum\left(\overline{Y}_i-\hat{Y}_i\right)^2=69,05$

The assessment of the suitability dispersion of the model is determined by formula:

$$S_{ad}^2=\frac{m}{N-l}\sum\left(\overline{Y}_i-\hat{Y}_i\right)^2 \quad (23)$$

Where*m* – the number of parallel experiments

(N-l) – the number of degrees of freedom of the remaining dispersion

N – number of experiments

l – the number of significant regression coefficients, including b_0

According to the formula 23, residual dispersion is equal to $S_{ad}^2 = \frac{2}{15-5} 69,05 = 13,81$

Verification of the reliability of the experimental data was performed based on the Fisher criterion.

$$F = \frac{S_{ad}^2}{S_y^2} \quad (24)$$

Thus,

$$F_{calc} = \frac{13,81}{6,67} = 2,07$$

To verify the veracity of the hypothesis on the suitability of the model, the number of degrees of freedom f_1 (for residual dispersion S_{ad}^2) and f_2 (for remaining dispersion S_y^2) was determined and the table value of Fisher test $F_{tab(q;f_1;f_2)}$ was found depending on degrees of freedom and chosen confidence level P or uncertainty q.

$$q=0,05$$
$$f_1=N-l=15-7=8$$
$$f_2=N(m-1)= 15(2-1)=15$$
$$F_{tab(0,05;8;15)} = 2,64$$

Since $2.07 < 2.64$, ie $F_{calc} < F_{tab(0,05;8;15)}$ it shows that the equation of regression is true, the orthogonal model is also true.

Gradient optimization [16]

The regression equation allows the optimization of the output parameters (the response) using the gradient method.

Gradient elevation value was calculated for each input factor.

$$P(X_i) = \Delta X_i \cdot b_i = \{X_i(+) - X_i(-)\} \cdot b_i \quad (25)$$

The theoretical step to optimize the response for the CO_2 extraction process of lycopene from tomato waste:

$$P(X_1) = \{X_1(+) - X_1(-)\} \cdot b_1 = (70 - 40) \cdot b_1 = 30 \cdot 7,48 = 224,40$$
$$P(X_2) = \{X_2(+) - X_2(-)\} \cdot b_2 = (40 - 20) \cdot b_2 = 20 \cdot 6,29 = 125,80$$
$$P(X_3) = \{X_3(+) - X_3(-)\} \cdot b_3 = (90 - 30) \cdot b_3 = 60 \cdot 1,37 = 82,20$$

Since it is unrealistic to vary the input factors with such values of the theoretical steps, to predict the gradient step of ascension, an intuitive coefficient of $K_{in.} = 44.88$ was used so that the values of the steps were achievable.

Thus, the recalculated step will be:

$$P^*(X_i) = \frac{P(X_i)}{K_{in.}} \quad (26)$$

$P^*(X_1) = 5{,}00$ $P^*(X_2) = 2{,}80$ $P^*(X_3) = 1{,}80$

It has been established that there are required the following experiments with the recalculated step, presented in Table 9.

Table 9

Planned experiences with the recalculated step

Variable parameters	Center	1	2	3	4
X_1 – temperature,°C	55	60	65	70	75
X_2 – pressure, MPa	30	33	36	39	42
X_3 – time, min	60	62	64	66	68

Knowing the factors that influence the CO_2 extraction process of lycopene from tomato waste, according to the table it can be chosen an optimum.

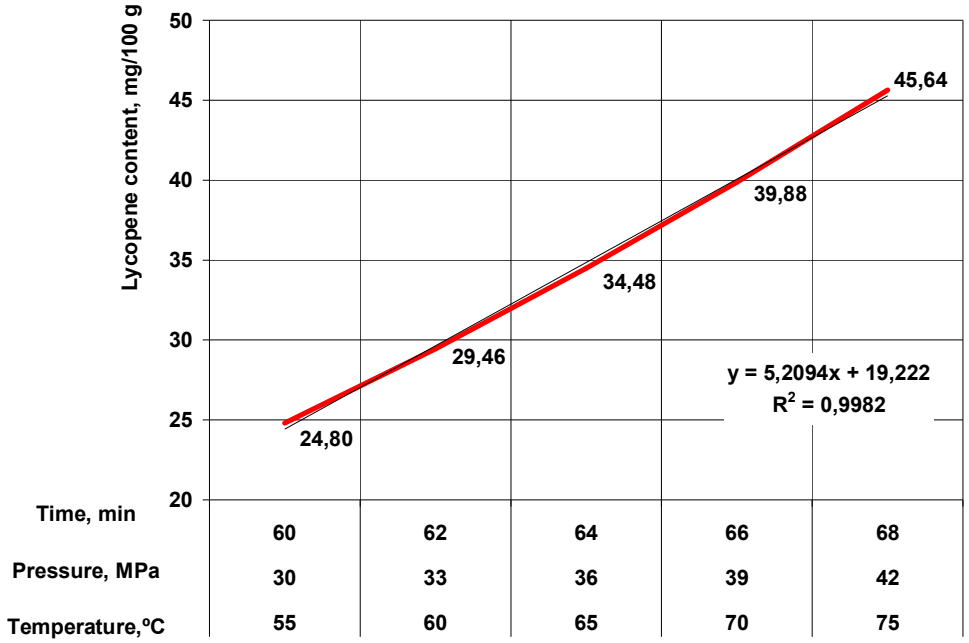


Figure 2. The calculated lycopene content according to the obtained equation at envisaged parameters with the recalculated step

Analyzing the data from Figure 2, it is noted that increasing the temperature by 5.0 °C, the pressure by 3.0 MPa and the extraction time by 2.0 minutes, the lycopene content increases with 4.66 to 5.76 mg/100 g of extract.

Graphs of the response surfaces

In order to obtain the graphs of response surfaces in the final form of regression equation : $\hat{Y} = 24,80 + 7,48X_1 + 6,29X_2 + 1,37X_3 + 1,66X_1^2$ the parameters X_1, X_2, X_3 are replaced with the expressions:

$$X_1=(T-T_0)/\Delta T; \text{ or : } X_1=(T-55)/15$$
$$X_2=(P-P_0)/\Delta P; \text{ or : } X_2=(P-30)/10$$
$$X_3=(t-t_0)/\Delta t; \text{ or : } X_3=(t-60)/30$$

Therefore, the final form of the second degree equation describing the lycopene CO_2 extraction from tomato waste is:

$$\hat{Y} = 24,80 + 7,48(T-55)/15 + 6,29(P-30)/10 + 1,37(t-60)/30 + 1,66((T-55)/15)^2$$

The plot of response surface of lycopene concentration in the CO_2 extracts from tomato waste, at 1 constant input factor (for minimum and maximum values) and 2 variable inputs were modeled.

At constant temperature T = 35 °C (Figure 3a), the minimum and maximum lycopene content calculated by the obtained formula is:

$\hat{Y}_{min}$ =8.63 mg/100 g, at P=18 MPa, t=25 min.
$\hat{Y}_{max}$ =28.81 mg/100 g, at P=45 MPa, t=95 min.

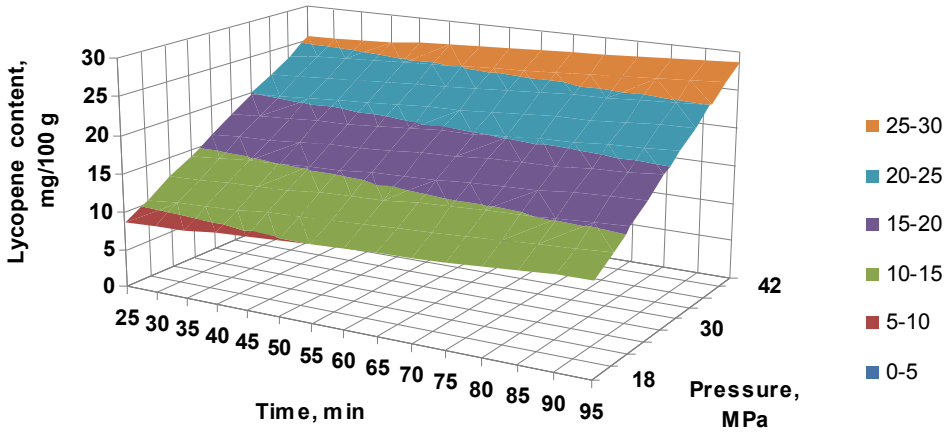
According to the mathematical model, at 75 °C a maximum lycopene content of 48.76 mg/100 g is obtained at P = 45 MPa and t = 95 min, and the minimum lycopene content of 28.58 mg/100 g at P = 18 MPa, t = 25 min (Figure 3b).

If the pressure is constant, namely for P_{min} = 15 MPa (Figure 4a), the minimum lycopene concentration is equal to 6.74 mg/100 g (35 °C and 25 min) and the maximum concentration is up to 29.89 mg/100 g (75 °C and 95 min).

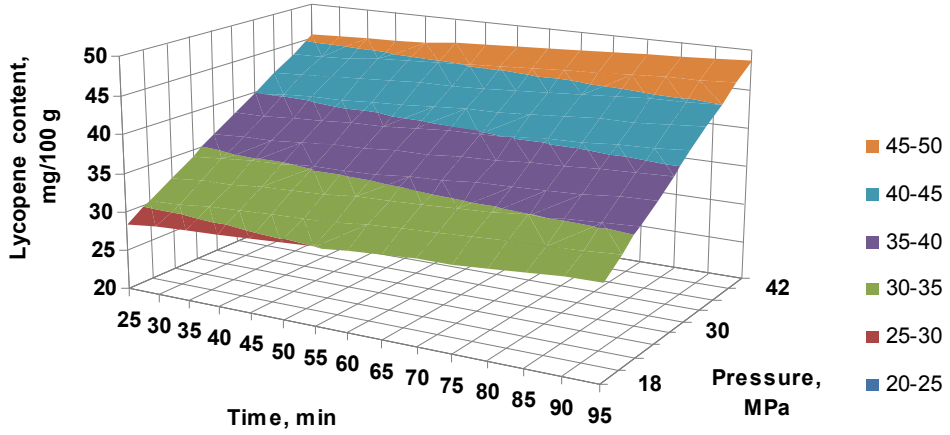
In the case when pressure is constant, for P_{max} = 45 MPa (Figure 4b), the minimum lycopene concentration is 25.61 mg/100 g (35 °C and 25 min) and the maximum concentration reaches 48.76 mg/100 g (75 °C and 95 min).

At a constant time of 25 minutes, the lycopene concentration would be at least 5.43 mg/100 g at 35 °C and 18 MPa, and at most 42.36 mg/100 g at 75 °C and 45 MPa (Figure 5a).

For the duration of the 120 minute constant extraction, according to the response area obtained according to the final equation, the minimum concentration of lycopene is 18.45 mg/100 g at 35 °C and 18 MPa and the maximum concentration is 55.38 mg/100 g at 75 °C and 45 MPa (Figure 5b).

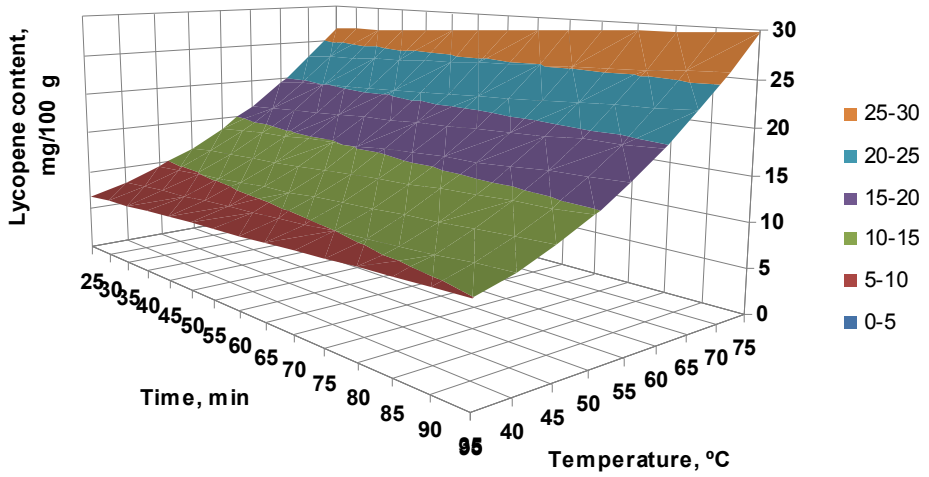


a



b

Figure 3. The response surface plot of tomato waste CO_2 extraction : lycopene content vs. extraction pressure and time at constant temperature
a – 35 °C; b – 75 °C



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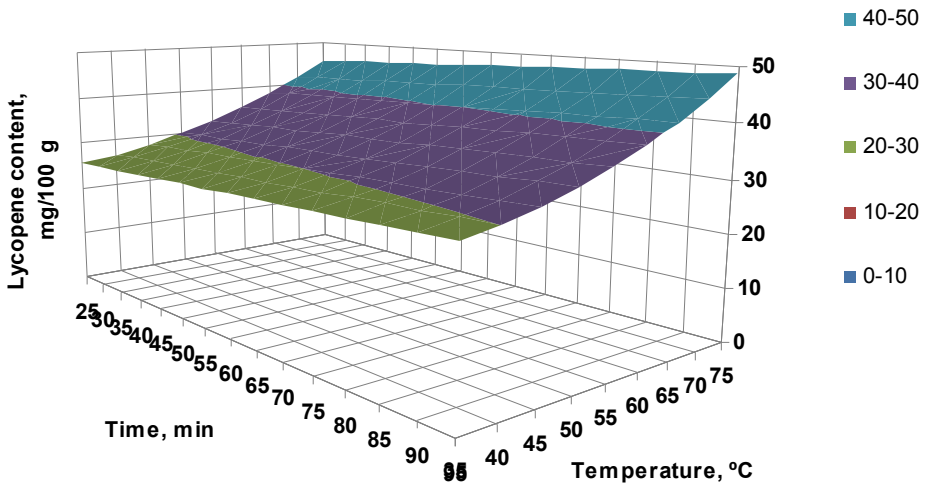
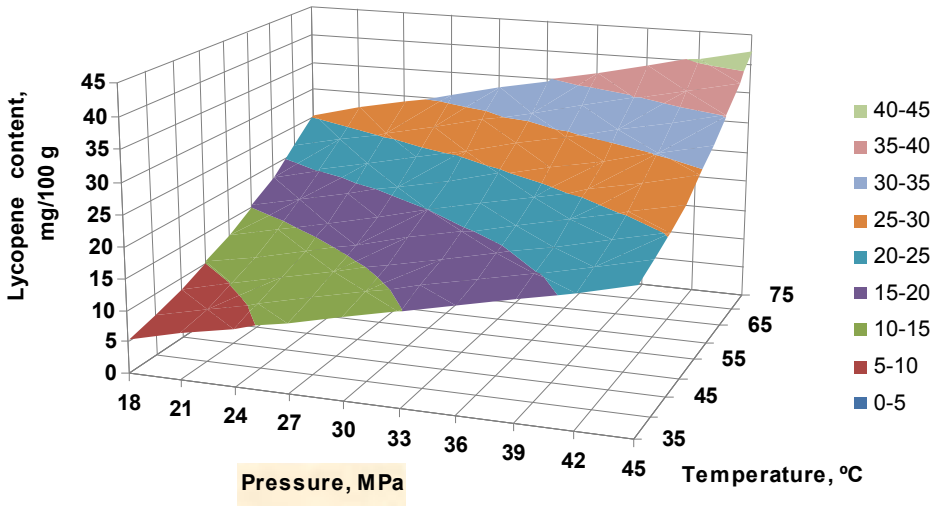
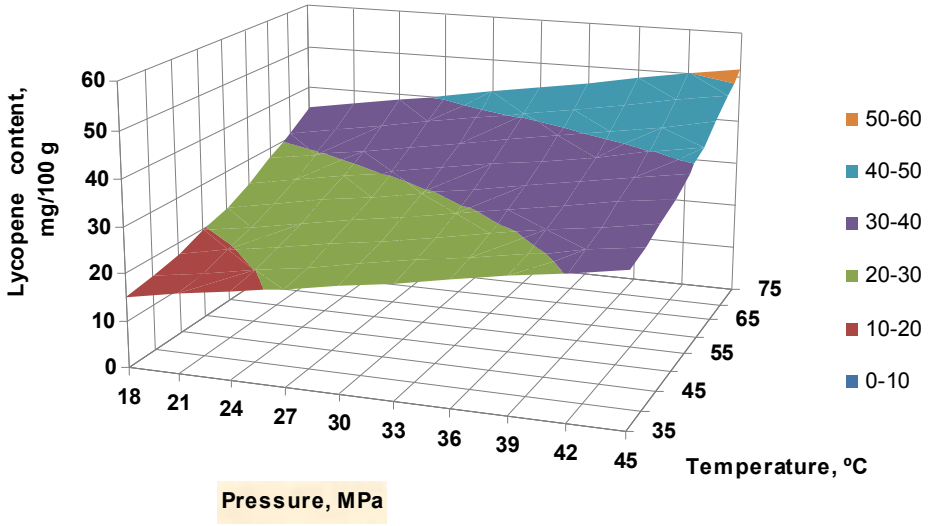


b

Figure 4. The response surface plot of tomato waste CO_2 extraction : lycopene content vs. extraction temperature and time at constant pressure
***a* – 15 Mpa; *b* – 45 MPa**



a



b

Figure 5. The response surface plot of tomato waste CO_2 extraction : lycopene content vs. extraction pressure and temperature at constant time
***a* – 25 min; *b* – 95 min**

The content of lycopene in the CO_2 extract from tomato waste varies between 10,80–47,12 mg/100 g, ie on average 28,96 mg/100 g of CO_2-extract, about 2–9 times higher than Recommended Daily Amount (RDA), 5–15 mg/day [6, 7].

In order to provide the human body with 15% of the RDA [17] of lycopene, a portion of the consumed product must contain at least 0.75 mg of lycopene.

Conclusion

Tomato waste can be used as a secondary raw material for the extraction of lycopene in liposoluble CO_2 extract.

For supercritical CO_2 extraction parameters: T=36–73 °C; P=18–42 MPa and t=24–96 min, the lycopene content in CO_2 fatty soluble extracts from tomato waste varies in the range from 10.80 to 47.12 mg/100 g.

The greatest influence on the extracting process of lycopene in CO_2 extracts from tomato waste has the temperature, followed by pressure, and the duration of the process has the least influence.

The final form of the second degree equation describing the CO_2 extraction of lycopene from tomato waste has been established:

$$\hat{Y} = 24,80 + 7,48(T-55)/15 + 6,29(P-30)/10 + 1,37(t-60)/30 + 1,66((T-55)/15)^2$$

The optimal parameters of supercritical CO_2 extraction of lycopene from tomato waste are temperature 60–75 °C, pressure 33–42 MPa and time 62–68 min.

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Application of hydrodynamic oscillations for activation of the hydrated lime slurry

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Abstract

Introduction. The purpose of this scientific work is to study the impact of the application of hydrodynamic oscillations for activation of the hydrated lime slurry in the production of sugar from sugar beets.

Materials and methods. General scientific methods, special methods, volume parametric imitation and visualization modelling methods, math modelling methods, optical microscopy, and ionometry were used for the researches.

Results and discussion. It is established that application of hydrodynamic oscillations for activation of the hydrated lime slurry in the production of sugar from sugar beets is very perspective.

It was established that the value of the linear speeds of a stream should be within 22 m/s for the first rotor and 24 m/s for the second rotor for intensification mass exchange processes between lime and water throughout the activating hydrated lime slurry.

The research studies demonstrated the increasing of the potential of hydrogen of the water prepared for the technology of the activating hydrated lime slurry for the processes of juice purification within 15%.

In general case was established that the decreasing of reduction-oxidation reaction which obtained throughout processing on an extent 210s, after that there is not large decreasing of the reduction-oxidation reaction.

The obtained data verify, that the lowest rank of reduction-oxidation reaction was observed in water which has been treating with application of the hydrodynamic oscillations. The common stage of decrease of reduction-oxidation reaction in evaluation with the initial makes 65%.

Conclusions. Application of hydrodynamic oscillations for activation of the hydrated lime slurry in the technological processes of purifying juice can greatly increase the capacity and replace the batch process for the continuous, can greatly reduce the duration of the process of activating mode, reduce power consumption

Introduction

Agriculture and food engineering are measured as one of the largest sectors worldwide with significant contribution to the economic development of the country.

The process for refining sugar beets consists of the dependable operations: washing, crushing, extraction, liming, carbonation, filtering, and addition of sulphur dioxide, concentrating, crystallizing and drying.

The most critical of these varieties of stages are:

- liming;
- carbonation;
- addition of sulphur dioxide.

Every of these stages have need of continuous control of potential of hydrogen, because it is important value which limits the velocity of the technological process of sugar production.

In recent years researches and technologists have turned their interest to employment of the innovative non-traditional technologies and methods in processing of the liquid mediums which consists of the water or water solutions.

Very actual to explain this setback is to use inexpensive methods that require commercial venture and allowing the use of existing reserves to reduce specific energy consumption of existing equipment due to the intensification of technological processes.

Analysis of scientific works

Sugar beet raw juice is polyconponent system that contains almost 99% of the original sugar and must be purified to eliminate the many other organics and minerals impurities that accompany it, so-called non-sugar particles [1].

Carbonation is the process in which remove impurities from the sugar solution of the sugar beet raw juice. The juice is purified using lime and carbonic acid.

Optimal purification is achieved through two stages of carbonation to avoid an uncontrollable form of rapid that can increase in single stage carbonation, but sometimes ccarbonation occurs in several stages. Secure pH control is necessary at each stage of the technological process to assure greatest removal of both impurities and calcium [2].

Strict process control, particularly of pH, must be maintained to avoid loss of sucrose in processing through its chemical hydrolysis to the unwanted sugars glucose and fructose [3].

.An adjunction of hydrated lime slurry into sugar beet raw juice coagulates colloid substances and precipitates non-soluble or hardly soluble substances [4].

The precipitate, called carbonation mud, contains fine crystals of $CaCO_3$ and aggregated or adsorbed non-sugars [5].

The chemical reaction is so high-speed. The process of carbonation has next form. For that reason, the sugar plants operate lime kilns where lime stone (calcium carbonate) is heated to create burnt lime (calcium oxide) and carbon dioxide.

$$CaCO_3 + \text{heat} \Rightarrow CaO + CO_2 \quad (1)$$

The lime is added to the sugar beet raw juice as lime milk or hydrated lime slurry. In the process, free calcium hydroxide precipitates are formed which connect the non-sugar particles.

$$CaO + H_2O \Rightarrow Ca(OH)_2 \quad (2)$$

Currently, the carbon dioxide is led into this mixture. The lime including the non-sugar particles stably precipitates and can be separated by filtration.

$$Ca(OH)_2 + CO_2 \Rightarrow CaCO3 + H_2O \quad (3)$$

This is the essence of carbonation. It is repeated in a second stage. Measurement of the electrical resistance of the solution indicates the residual lime content [6,7].

The calcium carbonate precipitate, including the impurities, is now removed in a pressure filtration stage using polypropylene filter cloth as supporting media and utilizing the calcium carbonate as a filter aid [8].

For coagulation to occur, the medium must be alkaline and produced by the medium or by the presence of alkalinizing agents such as calcium oxide (quick lime), calcium hydroxide sodium hydroxide, or sodium carbonate [9, 10].

These reagents and components are modifying the potential of hydrogen of the sugar beet raw juice.

There are many methods and processes of water treatment to obtain water and water solutions with necessary physical and chemical parameters and properties which require for the manufacturing.

They are including: acoustic treatment, the electromagnetic pulse effect of the low-frequency field, cavitations processing, emitting treatment (ultraviolet, ionizing, infrared), hydrodynamic effects.

The method of discrete-pulsed input of energy can power structural transformations in difficult liquid systems on micro- and nanolevel and gives possibility to initiate physical and chemical transformations in these complex systems.

The main effects of the discrete-pulsed input of energy are effects which connected with increase of velocity of association of a continuous phase, power of pressure of shift, cavitations, the effect of explosive boiling, collective effects in assembly of vials, crossness of an interphase surface in gas-liquid bubbly medium, action of hydrodynamic oscillations, alternating impulses of pressure.

A great number of mass industrial processes such as: crushing, dispersion, mixing, emulsification, homogenization, activating, etc. are exhausted in rotary pulse apparatus of cylindrical type.

In these types of apparatus the main effects of the discrete-pulsed input of energy are realise.

The purpose of this scientific work is to research the impact of the application of hydrodynamic oscillations for activation of the hydrated lime slurry using reagent-free method of treatment in the production of sugar from sugar beets.

Materials and methods

Materials

Water, water systems, carbon dioxide and hydrated lime slurry were used for experiments. The proportion of the hydrated lime slurry was wide-ranging by the technological regulations of the productions sugar from the sugar beets.

Experimental installation

The most important element of the pilot unit is a rotary pulsed apparatus in which liquids treat by hydrodynamic oscillations [11].

Sample preparation

Water and water solutions and hydrated lime slurry were prepared using the standard methods which described in [12]. Water, carbon dioxide and lime milk was used for activating of the hydrated lime slurry.

Water and lime milk gave in to processing by hydrodynamic oscillations previous to the industrial procedure of receiving of the hydrated lime slurry. Water treatment and activating of the hydrated lime slurry was spent in rotary pulse apparatus [13].

Liquid water solutions and hydrated lime slurry were passed throughout turning coaxial cylinders with cuts on a surface and small clearances between them, which reach $(500–100)\cdot10^{-6}$m instantaneously that permitted to spend this process by continuous approach.

Methods

General scientific methods and special methods were used for the analyzing of the results of research work.

The volume parametric imitation and visualization, modelling methods, math modelling methods were used for the prognosis of the physical and chemical parameters of the hydrated lime slurry and water solutions.

The ionometry and optical microscopy method were used for the researches.

Experimental investigations of liquid samples were carried out with using standard laboratory measurement procedure.

For the description of physical and chemical parameters of liquid samples of water and hydrated lime slurry which obtained throughout the experimental investigations, standard methods described in singular literature are used [14].

The scrutiny of change of potential of hydrogen and the potential of reduction-oxidation reaction of liquid samples of the hydrated lime slurry is carried out with use analogue pH-meter-millivoltmeter pH-150 M with special electrodes.

For the reception related data, liquid samples of water and hydrated lime slurry were analyzed not less than three times with the following statistical processing.

Results and discussion

The power of introductory processing of water with appliance of the hydrodynamic oscillations for activating hydrated lime slurry in the technology of production sugar from sugar beets was studied.

Throughout water treatment by hydrodynamic oscillations the potential of hydrogen and reactionary ability of water, calcium oxide and carbon dioxide varies.

All through the processing of water and activating hydrated lime slurry in the conditions of hydrodynamic oscillations characterized $\Delta P = 350$ kPa near an outside surface of an interior spinning rotor; $\Delta P = 250$ kPa near an outside stator surface; $\Delta P = 150$

kPa near an interior stator surface; ΔP = 200 kPa near an interior surface of an outside spinning rotor.

By the volume three-dimensional parametric imitation visualization modelling processes, mathematical and numerical modelling was found that the value of the linear speeds of a stream should be within 22 m/s for the first rotor and 24 m/s, for the second rotor, Figure 1.

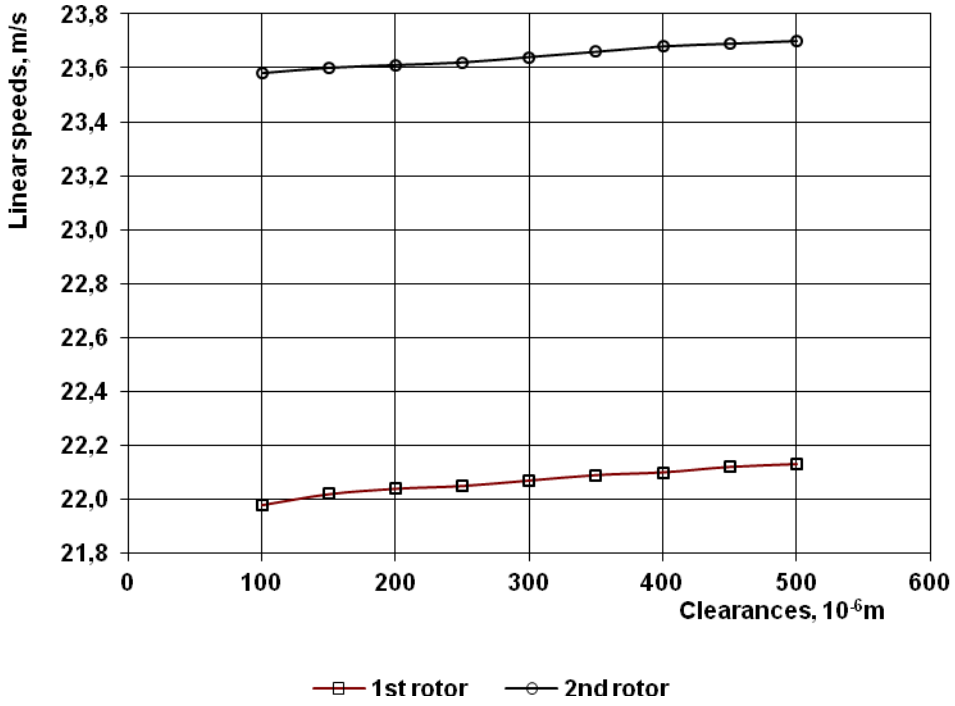

Figure 1. Profile of changes linear speeds of a stream from the clearances between coaxial cylinders

It was established that speeds of shift of a stream should be equal to $2{,}0 \cdot 10^5 s^{-1}$ for the first rotor and $2{,}5 \cdot 10^5 s^{-1}$ for the second rotor Figure 2. Such values of the speeds of shift of a stream provide intensive particle movement of the carbon dioxide in continuous phase – water.

The value of pressure of shift of a stream must be 220Pa for the first rotor and 230Pa, for the second rotor Figure 3.

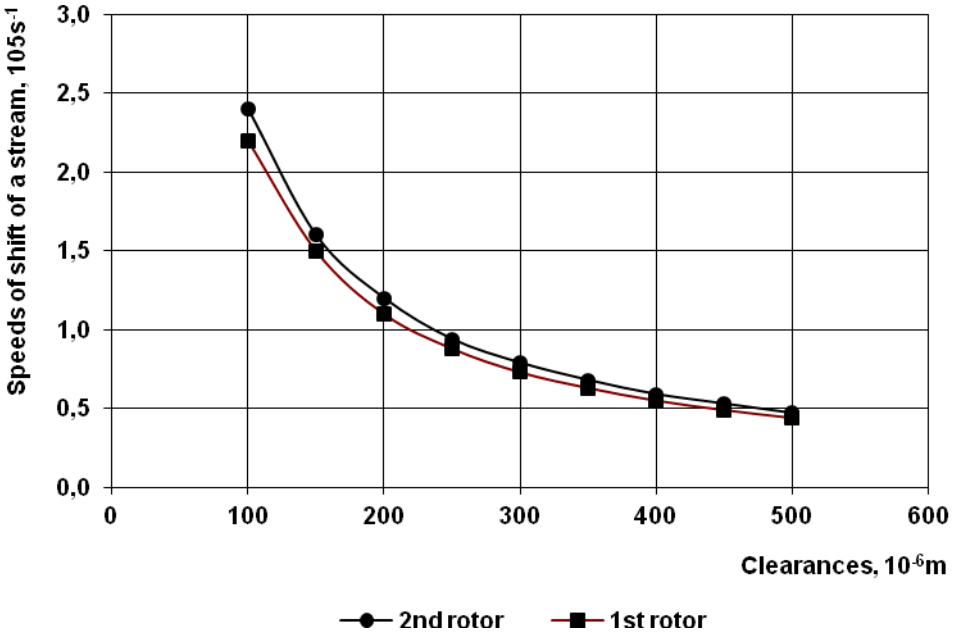

Figure 2. The profile of changes of speeds of shift of a stream from the clearances between coaxial cylinders

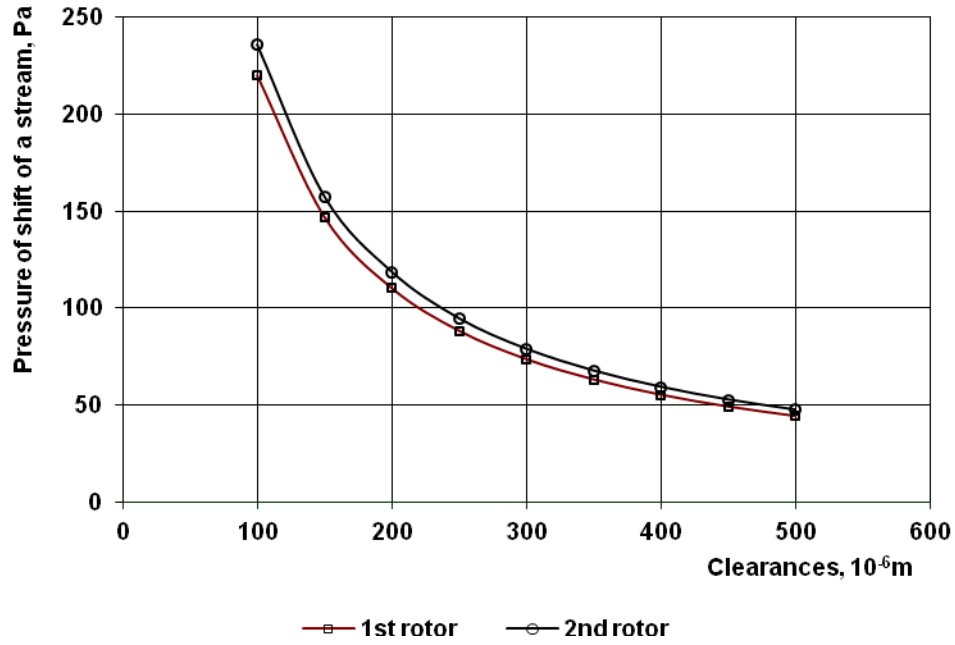

Figure 3. The profile of changes pressure of shift of a stream from the clearances between coaxial cylinders

These demanding hydrodynamic conditions give the possibility to treat water and water solutions with the initialization of the formation of structure and intermolecular interacting such as forming three-dimensional framework from the hydrogen bonds.

The nature and velocity of many physical and chemical processes which take place in such water systems transforms.

Besides, the activity of the water depends from the transformations and hydrogen bonds which can form between molecules. It is important for activation of the hydrated lime slurry

For shipping out of process of activation of water for the carbonating process hydrated lime slurry gave in to action during special time from 1s to 300s. The change of pH value during the processing by hydrodynamic oscillations is shown on the Figure 4.

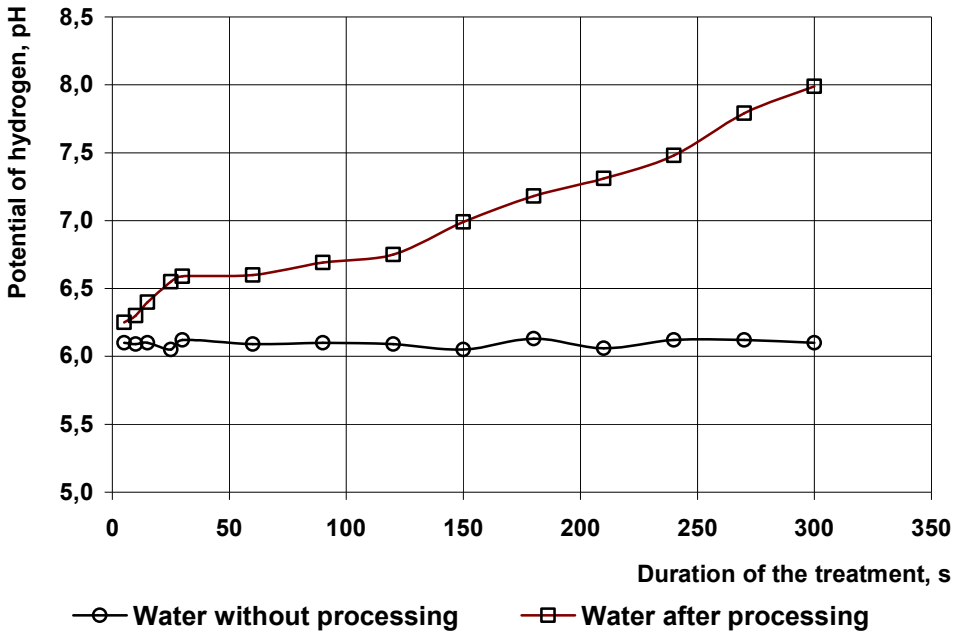

Figure 4. Change of potential of hydrogen during water processing by the hydrodynamic oscillations

The potential of hydrogen is shows concentration of free ions of hydrogen in water and water solutions and it is one of the major operational indicators of quality of water, in many compliments describes nature of chemical and another process which take place in water and in hydrated lime slurry.

The research studies demonstrated the increasing of the pH of the water prepared for the technology of the activating hydrated lime slurry for the processes of juice purification within 15%.

The significance of the potential of reduction-oxidation reaction is depending of the potential of hydrogen. It is the interrelated quantities of the water and hydrated lime slurry.

The potential of reduction-oxidation reaction depends from activity of oxidized form of material.

In this research employment the results of the investigation of the change of the potential of reduction-oxidation reaction is presented.

The decreasing of the potential of reduction-oxidation reaction of water in technological process of liming throughout experimental treatment in rotary pulse apparatus is shown on Figure 5.

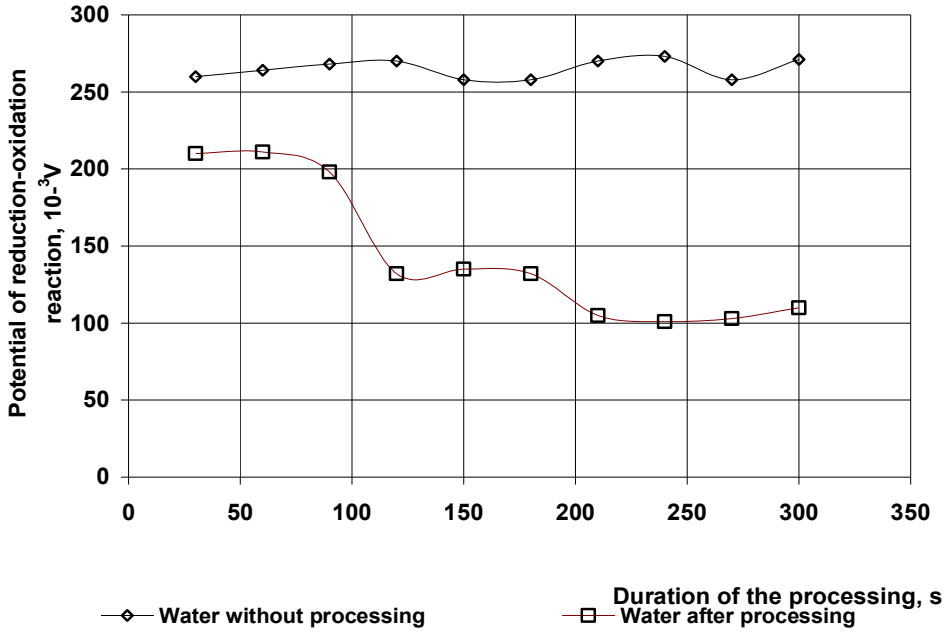

Figure 5. Investigation of the potential of reduction-oxidation reaction during the experimental water processing

A significance of reduction-oxidation reaction in the itinerary of processing with the appliance of the hydrodynamic oscillations depends from the duration of the processing and decreases on 25-65%.

During the activating hydrated lime slurry in the technology of production sugar from sugar beets the great value has change of a potential of hydrogen significance to initial value to processing.

The potential of hydrogen can greatly verify the velocity of itinerary of chemical reactions.

Appliance of the hydrodynamic oscillations in the technology of the production of sugar from sugar beets allow receiving the activated water and hydrated lime slurry with the definite substantial properties and parameters, assured value of a pH.

The alteration of physical and chemical properties and parameters of pure water and water solutions has been established during the processing with appliance of hydrodynamic oscillation.

It gives the possibilities to explain change of reactionary capability, outstanding to beginning of carrying over of a H^+ in associated liquids such as water and water solutions and configuration of a three-dimensional grating which formed by hydrogen bonds which in turn influences to the structural framework and a formation.

The experimental researches of the liquid examples of water solutions and hydrated lime slurry were carried out by research microscope system Zeiss Axio Imager Vario.

The samples were analyzed in automatic mode in straight light which passes through the examples of water solutions of the different types of water and hydrated lime slurry. Some of the examples were received by traditional technology and another was activated by the hydrodynamic oscillation in which water was exposed to processing and was not exposed to processing.

A significance of the reduction-oxidation reaction in the route of treatment in the conditions of hydrodynamic oscillations depends on dispensation duration.

In general case was established that the decreasing of reduction-oxidation reaction which obtained throughout processing on an extent 210s has been noted Figure 5, after that there is not large decreasing of the reduction-oxidation reaction.

The obtained data verify, that the lowest rank of reduction-oxidation reaction was observed in water which has been treating with application of the hydrodynamic oscillations. The common stage of decrease of reduction-oxidation reaction in evaluation with the initial makes 65%.

Conclusions

As a result of research, it was found that the application of hydrodynamic oscillations for activation of the hydrated lime slurry in the technological processes of purifying juice can greatly increase the capacity and replace the batch process for the continuous, can greatly reduce the duration of the process of activating mode, reduce power consumption.

The experimental and analytical studies have shown that activation of the hydrated lime slurry in rotary pulsed apparatus may be suitable for processing in food engineering especially for production sugar from sugar beets, where hydrodynamic oscillations are found to be a substitute to traditional tanks activating.

A complete study of experimental data showed that the use of hydrodynamic oscillations in the treatment of water and preparation hydrated lime slurry allows obtaining solutions with improved physical and chemical parameters.

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Suitability of the technical grape variety of the Northern Black Sea Coast in the traditional production for "Icewine"

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Abstract

Introduction. The purpose of the work was to study the mechanical composition and physical and chemical properties of grape varieties in the Northern Black Sea Coast to determine their feasibility in icewine production.

Materials and methods. Riesling, Rkatsiteli and Telti Kuruk, Marselan and Moldova grape varieties for 2015–2018 in vineyards of Shabo, Tairov and Kherson were studied on the average mass of grape clusters, the number of berries in the cluster, the weight of grape berries, the weight of the grape peel, the mass of pulp with juice according to the technique prof. Prostoserdov.

Results and discussion. On average, the highest average weight of clusters in varieties of Moldova and Marselan was observed, the smallest – in Telti Kuruk and Riesling. After the advent of technological maturity, the mass of clusters in all varieties decreased from the end of October to the month of December: an average of 0.95 times in the Shabo region, 0.92 times in the Tairov region and 0.90 times in Kherson. The greatest differentiation in the number of berries during the warm months ±4p. and ±6p. had Rkatsiteli and Telti Kuruk, respectively, the smallest – ±1p. Moldova and Marselan in Shabo. On grape plantations in the village of Tairov and the city of Kherson, a significant difference in the number of berries by grade was not noted and was ±1÷±3 pcs.

Rkatsiteli accumulated the largest amount of sugar among other varieties, whose mass concentrations reached in December, on average by regions, from 243–245.13 g/dm^3, and the smallest ones were in Telti Kuruk, which amounted to 179.5–182.7 g/dm^3. In the Riesling variety after heavy rainfall, the mass concentration of sugars decreased to an average of 30 g/dm^3 – in the Shabo region, to 25 g/dm^3 – in the v. Tairov, and to 22 g/dm^3 – in the Kherson region. The mass fractions of sugars of Telti Kuruk were smaller and in November were 180–182.7 g/dm^3, than Riesling, which had mass concentrations in the end of October in the ranges of 199.5-201.6 g/dm^3 during seasons of each year on vineyards of Shabo. The sugar accumulation of varieties during long-term maturing on the vine of the 3 regions during August-December of 2015-2018 were as follows: Rkatsiteli, Marselan, Moldova, Telti Kuruk, Riesling.

Conclusions. Riesling is not able to withstand a hard time on the vine after technological maturity, and the most suitable varieties were Marselan, Rkatsiteli and Moldova, which meet to the requirements that are needed for characteristic varieties for use in technology of icewines.

Introduction

Icewine is one of the most unique among another types of wines. Unlike all others, it is made from frozen grapes, the berries are cooled directly on the vine. Water freezes, and sugar and other dissolved substances remain. Due to this particular grape must is concentrated and then it is very sweet. To make one liter, you need about 30 kg of berries. Icewine is a special dessert wine which has the certain requirements, among which the prominent place belongs to the agricultural climatic conditions: late maturing grape variety, the harvest of that occurs mainly in the winter months at air temperature -7 °C.

Labor-intensive technology directly affects the release of wines, causing a high cost of goods and serves as the main reason for a limited comprehensive analysis of icewines. Today, Canada is the largest producer of icewine, but not the only one. It is also produced in Germany, Austria, Croatia, Luxembourg, Slovenia, Czech Republic, Hungary and the popularity of these unique wines is increasing every year [1].

Firstly, icewine was made from frozen Riesling. However, subsequent experiments allowed the selection of several more varieties of grapes. Austrians prefer Gruner Veltliner, Welschriesling and Gewürztraminer. Canadians use Vidal Blanc [2, 3, 12]. In the New World, icewine is produced from Merlot and Cabernet Sauvignon [2–11].

The availability of varieties to withstand adverse climatic conditions and the dynamics of their chemical composition for further use in technology of icewines in the scientific literature is almost absent. Only research on Canadian icewines is known from Riesling and Vidal Blanc, where the cool climate contributes to the larger size of the production of such wines [9–12].

The purpose of the work is to study the mechanical composition and physical and chemical properties of grape varieties in the Northern Black Sea Coast to determine their feasibility in the production of icewines.

Materials and methods

Materials

Experiments were carried out on white (Riesling, Rkatsiteli and Talti Kukur) and red (Marselan and Moldova) grape varieties. The research was conducted during 2015–2018 in vineyards of Shabo, Tairov and Kherson, part of the Northern Black Sea Coast. Conditions of experiment on the load of formation of bushes and age were regulated in the same range.

Methods

The mechanical composition, including the average mass of grape clusters (g), the number of berries in the cluster (pieces), the weight of grape berries (g), the weight of the grape peel (g), the weight of pulp with juice (g) were determined according to the complex method for evaluating grapes that expresses the ratio of mechanical and plastic elements of bunches and berries [4], [5]. The pH was determined using the pH meter S220 (Mettler-Toledo International Inc., Switzerland), the concentration of titrated acids (TA) according to general method [6].

Results and discussion

1. Mechanical composition of grape varieties

The monitoring of the mechanical composition of grapes, which has undergone changes under the influence of meteorological factors and soil conditions in the area where the vine grows, makes it possible to state the techno-chemical quality of the grapes before the onset of low temperatures for the production of icewines. Parameters such as the average weight of grape bunch (g) (AWGB), the number of berries in the cluster (pcs) (NB), the weight of grape berries (g) (WB), the weight of the grape peel (g) (WP), the weight of pulp with juice (g) (WPJ), are mostly significant in the study of variety suitability in the production of sweet wines that can predict the following criteria: the output of must from frozen grapes (%), the protection of berries by the skin from adverse conditions, the choice of the regime of pressing and processing, the direction of grape processing in general. The average and standard deviation of the mechanical composition of the grape cluster for 3 years of research during August-December 2015-2018 on the studied regions are given in Tables 1, 2.

Table 1

Indicators of mechanical composition of technical varieties of grapes in Shabo

Parameters	Month	Grape variety				
		Riesling	Rkatsiteli	Marselan	Moldova	Telti kuruk
1.AWGB (g)	08	84,7±2,08	166,7±1,53	194,7±0,58	255,3±1,53	109,3±0,58
	09	111,7±1,53	169,7±1,15	205,7±1,15	267,7±1,15	125,7±1,53
	10	97,3±4,16	165,3±4,73	212±2,65	265,3±4,04	120,7±3,06
	11		162,7±4,04	209±4,36	264±4,0	115,3±4,73
	12		158,3±5,51	203,3±4,04	254,3±4,04	104,7±3,51
2. NB (pcs)	08	58±2	90±2	102±4	146±1	95±1
	09	70±2	92±2	109,0±2	158±1	101±3
	10	42±2	88±4	115±2	154±1	99±6
	11		86±4	109±8	152±4	9±5
	12		83±4	104±12	146±6	84±4
3. WB (g)	08	79,4±2,2	159,5±1,6	187,0±1,0	246,9±1,4	103,1±0,7
	09	106,2±1,6	162,5±1,1	197,6±0,8	258,9±1,1	119,4±1,3
	10	62,0±4,2	158,4±4,7	204,0±3,0	256,7±3,8	114,8±3,0
	11		155,8±4,0	201,1±4,5	255,6±3,9	109,4±4,7
	12		151,8±5,4	195,9±4,0	246,1±4,1	98,8±3,4
4. WP (g)	08	6,8±0,5	6,8±0,5	9,3±0,3	9,2±0,2	7,2±0,3
	09	7,3±0,3	6,8±0,4	9,4±0,3	9,5±0,1	7,7±0,2
	10	6,3±0,7	6,9±0,5	8,8±0,2	9,0±0,2	6,9±0,3
	11		6,6±0,3	8,3±0,2	8,7±0,1	6,4±0,2
	12		6,1±0,3	7,7±0,3	8,1±0,6	6,3±0,3
5. WPJ (g)	08	71,7±2,9	149,1±8,8	169,4±7,5	233,7±4,1	94,6±0,2
	09	97,5±1,9	151,7±3,2	182,1±11,1	243,4±6,6	110,4±0,7
	10	83,9±3,5	149,8±4,9	193,9±3,6	245,7±4,8	106,6±3,4
	11		146,9±4,7	190,8±5,3	244,6±4,5	101,6±5,4
	12		142,7±7,2	184,8±3,1	236,4±3,7	87,8±7,2

According to its biological characteristics, the highest average mass of clusters among the varieties was observed in the varieties Moldova 265.3–277.7 g and Marselan 212–214 g, the smallest – in Telti Kuruk 104.7–109.3g and Riesling 80.0–84.7g, the Rkatsiteli variety was distinguished by the average masses of clusters compared to other 158.3–184.3g, regardless of region and month. After the advent of technological maturity, the mass of clusters in all varieties decreased from the end of October to December, on average 0.95 times in the Shabo region, 0.92 times – according to Tairov, 0.90 times – in Kherson.

Table 2

Indicators of mechanical composition of technical varieties of grapes in Tairov and Kherson

Parameters	Month	Grape variety					
		Riesling		Rkatsiteli		Moldova	
		Tairov	Kherson	Tairov	Kherson	Tairov	Kherson
1.AWGB (g)	08	81,7±0,6	80,0±3,6	175,3±1,5	181,0±1,0	268±1,0	267,7±4,5
	09	110,3± 1,5	112,0± 2,6	171±2,6	184,3±0,6	276,3±1,5	277,7±1,5
	10	94,7± 0,6	101,7± 11,8	169±3,0	176,3±1,5	271,7±2,1	272,0±2,6
	11			165,3±4,2	169,3±1,2	268±2,6	267,7±2,5
	12			157,7±3,8	159,3±1,2	259,7±5,5	259,3±4,5
2. NB (pcs)	08	60±2	59±5	96± 3	108± 3	149±1	156±3
	09	67±2	62±3	92± 2	111± 2	166±3	166±1
	10	41±2	48±3	88±3	103±1	162±3	161±1
	11			86±2	96±2	157±2	156±2
	12			80±2	87±2	148±1	147±2
3. WB (g)	08	76,4±0,5	74,8±3,4	168,2±1,5	173,9±1,0	259,5±1,1	259,2±4,5
	09	104,9±1,5	106,5±2,6	163,8±2,6	177,2±0,7	267,6±1,7	268,9±1,7
	10	59,4±0,6	66,4±11,8	162,0±3,0	169,4±1,6	263,0±2,3	263,3±2,9
	11			158,5±4,2	162,5±1,2	259,6±2,8	259,3±2,6
	12			151,1±3,8	152,8±3,7	251,5±5,6	251,1±4,6
4. WP (g)	08	7,1±0,1	6,9±0,1	7,4±0,1	7,2±0,1	9,6±0,2	9,3±0,2
	09	7,4±0,3	7,2±0,1	7,4±0,1	7,3±0,1	9,8±0,2	9,5±0,1
	10	6,8±0,4	7,1±0,1	7,0±0,3	7,1±0,1	9,6±0,1	9,6±0,1
	11			6,6±0,1	6,8±0,1	9,1±0,1	9,3±0,1
	12			6,1±0,1	6,4±0,3	8,7±0,2	8,8±0,1
5. WPJ (g)	08	69,3± 0,5	67,9± 3,3	160,8±1,4	166,6±0,9	249,9±1,0	249,9±4,4
	09	97,5±1,6	99,3±2,6	156,4±2,6	169,8±0,8	257,8±1,8	259,4±1,6
	10	82,6±0,4	89,3±11,8	155,0±2,7	162,3±1,6	253,4±2,3	253,7±2,8
	11			151,9±4,2	155,7±1,3	250,6±2,8	250,0±2,5
	12			145,0±3,8	146,4±3,9	242,8±5,6	242,4±4,6

The general reflection of the influence of precipitation on the mechanical structure of the cluster is found in the mass of grape berries, which depended directly on the number of berries. Thus, the greatest differentiation in the number of berries during the warm months of the autumn ±4 and±6ps had varieties of Rkatsiteli and Telti Kuruk respectively, the smallest –±1p Moldova and Marselan in vineyards of Shabo. On grape plantations in the village of Tairov and the city of Kherson, a significant difference in the number of berries

by cultivars was not noted and was ±1 ÷±3pcs. However, in November and December all varieties of these regions were characterized by a sharp decrease in the number of berries in the cluster, which was reflected directly in the lower mass of the cluster, which is due to overgrowing and the possible effect of the precipitation. Thus, the Rkatsiteli variety at the technological maturity of the berries in the cluster was 92 pcs in the Shabo and Tairov region and 103 g in Kherson, the weight of which was 162.5, 163.8 and 177.2 g, after the cold months – 83, 80 and 87 pcs with the corresponding weight of 151.8, 151.1 g and 152.8 g. The weight of berries in Moldova variety decreased from 258.9 – 263.3 g to 246.1 – 251.1 g with the number of berries 166 – 146 pcs to 147 – 148 pcs, respectively, on average over the years. Marselan and Telti Kuruk were characterized by the amount of berries in the cluster of 115 and 101 pcs with a weight of 204 and 119.4 g, and after prolonged stay on the vine, the number of berries was 104 and 84 pcs with a weight of 195.9 and 98.8 g. However, from September to October, the Riesling variety lost 28, 26 and 24 berries, the weight of which decreased by 44.2, 45.5 and 40 g, according to the regions of growing Shabo, Tairov and Kherson.

Also, it should be noted that the direct dependence of the influence of precipitation on the mechanical composition of the cluster reflects the stability of a certain variety of grapes to diseases and the effects of pests.

The largest weight of the skin was noted in red grape varieties – 9.0±0.7 g and 8.8±0.5 g in Moldova in all regions and Marselan respectively. The white varieties were characterized by the average weight of the skin, which varied from 6.0 to 7.3g in Riesling, from 6.1 to 7.4 g in Rkatsiteli, from 6.3 to 7.7 g in Telti Kuruk. With the continuation of the harvest period, the weight of the skin of the studied grape varieties became thinner, which made their weight lighter, on average, 0.3, 0.96, 1.25, 1.7 and 1.4g respectively, according to Riesling, Rkatsiteli, Moldova, Marselan and Telti Kuruk, and therefore more vulnerable to adverse climatic factors.

Despite the fact that the rainy season recorded for September-October of all three years, the parameters of the mechanical composition of grape varieties, Moldova and Marselan, did not change critically at the location of the first frosts compared with other varieties, indicating the probable first feasibility of using these varieties in icewine technology.

The conditionality of the studied varieties according to the statistic results of the cluster's mechanical composition during August-January 2015–2018 in the three regions is shown in this order Moldova, Marselan, Rkatsiteli, Telti Kuruk, Riesling (from the highest to the smallest).

2. Chemical indicators of grape quality

One of the most important factors of the suitability of a variety for the icewine production is the rapid accumulation of the sugar content of frozen berries and their initial concentration to freezing to determine the stages of maturation and oversaturation of this indicator.

The dynamics of the physicochemical properties of the grapes studied by the varieties shows that varieties accumulate sugar differently depending on the time and region of cultivation (Table 3.1–3.3)

Table 3.1

Dynamics of physical and chemical properties of grapes from Shabo

Parameters	Month	Riesling	Rkatsiteli	Marselan	Moldova	Telti Kuruk
Mass concentration of sugars, g/dm^3	08	143,53±9,5	180,67±5,5	195,37±4,7	187,77±0,9	137,63±1,8
	09	199,50±7,1	185,73±9,2	197,53±1,6	195,27±0,6	140,20±1,06
	10	171,5±13	192,10±10,25	223,80±3,1	220,97±1,7	160,30±1,2
	11		223,00±4,9	217,83±5,6	219,57±0,9	170,13±2,7
	12		243,07±4,27	237,77±1,1	236,60±1,1	181,00±1,7
Mass concentration of titrated acids, g/dm^3	08	8,47±0,25	7,70±0,1	8,20±0,06	8,07±0,1	9,00±0,17
	09	7,83±0,21	6,90±0,1	7,13±0,12	7,57±0,2	8,57±0,12
	10	6,70±0,17	6,50±0,26	6,27±0,12	6,77±0,15	7,00±0,10
	11		6,10±0,26	5,80±0,15	6,23±0,15	6,53±0,15
	12		5,80±0,3	5,53±0,06	5,63±0,03	6,03±0,06
pH	08	2,69±0,02	2,88±0,01	2,91±0,01	2,94±0,02	2,82±0,01
	09	2,71±0,03	2,96±0,02	2,97±0,02	3,12±0,01	2,89±0,02
	10	3,04±0,02	2,99±0,02	3,02±0,01	3,21±0,01	3,01±0,03
	11		3,07±0,02	3,10±0,02	3,24±0,02	3,12±0,01
	12		3,14±0,01	3,14±0,02	3,27±0,01	3,14±0,01

Table 3.2

Dynamics of physical and chemical properties of grapes from Tairov

Parameters	Month	Riesling	Rkatsiteli	Moldova
Mass concentration of sugars, g/dm^3	08	144,63±9,6	180,7±5,7	188,8±1,4
	09	200,6±7,4	186,3±9,4	196,2±1,6
	10	172,66±13	193,2±10,3	221,9±1,7
	11		224,0±5,1	220,3±0,5
	12		244,0±4,1	237,5±1,5
Mass concentration of titrated acids, g/dm^3	08	8,36±0,32	7,63±0,1	7,9±0,14
	09	7,73±0,3	6,8±0,2	7,4±0,13
	10	6,6±0,18	6,43±0,24	6,6±0,15
	11		6,03±0,23	6,1±0,12
	12		5,7±0,2	5,5±0,13
pH	08	2,72±0,1	2,85±0,01	2,87±0,01
	09	2,74±0,01	2,94±0,02	3,05±0,02
	10	3,07±0,02	2,95±0,01	3,14±0,02
	11		3,08±0,02	3,17±0,01
	12		3,15±0,01	3,2±0,02

Table 3.3

Dynamics of physical and chemical properties of grapes from Kherson

Parameters	Month	Riesling	Rkatsiteli	Moldova
Mass concentration of sugars, g/dm^3	08	145,7±9,78	181,7±6,4	189,5±1,9
	09	201,6±8,3	187,7±10,2	197,3±1,6
	10	173,3±14	194,2±10,8	222,9±1,5
	11		225,4±5,7	211,3±1,02
	12		245,3±4,05	238,4±1,9
Mass concentration of titrated acids, g/dm^3	08	8,5±0,4	7,8±0,15	8,2±0,1
	09	7,9±0,2	7,03±0,11	7,7±0,17
	10	6,8±0,1	6,6±0,25	6,9±0,1
	11		6,3±0,21	6,3±0,15
	12		5,7±0,21	5,7±0,13
pH	08	2,73±0,02	2,86±0,02	2,92±0,02
	09	2,75±0,03	2,94±0,01	3,13±0,02
	10	3,05±0,02	2,96±0,01	3,2±0,02
	11		3,1±0,02	3,24±0,01
	12		3,17±0,01	3,25±0,01

The highest concentration of sugars was observed in all studied varieties at the end of November: in Riesling 199.5, 200.6, 201.6 g/dm^3; Rkatsiteli 243.7, 244, 245.3 g/dm^3; in Moldova 236.6, 237.5, 238.4 g/dm^3; Marselan 237.7 g/dm^3 and Telti Kuruk 181 g/dm^3 in accordance with the regions of Shabo, Tairov and Kherson. In the red varieties of grapes, the rate of accumulation of sugar was slower, an average of 3–5 marks less during the months of October-November compared with white, but the mass concentration of sugar content was significantly higher, which is due to the late degree of berry maturation (Table 3.1–3.3).

Order of the grape varieties studied according to the accumulation of sugar during long maturation on the vine of the three regions during August-December 2015–2018 are Rkatsiteli, Marselan, Moldova, Telti Kuruk, Riesling.

Detailed monitoring of temperatures in December–January 2015–2018 in all regions made it possible to determine the grape harvesting time, which was frozen on the vine, which occurred in the early hours of the morning and made the complexity of the technological process to maintain the desired concentration of sugars – above 280 g/dm^3. It is precisely the achievement of the grapes of the specified condition that makes it possible to direct it to the production of icewines. Riesling has not shown tendency to long-term preservation of technological parameters on the vine during three seasons in three regions. The dynamics of the concentration of sugars in the studied varieties was not the same (Figures 1–3).

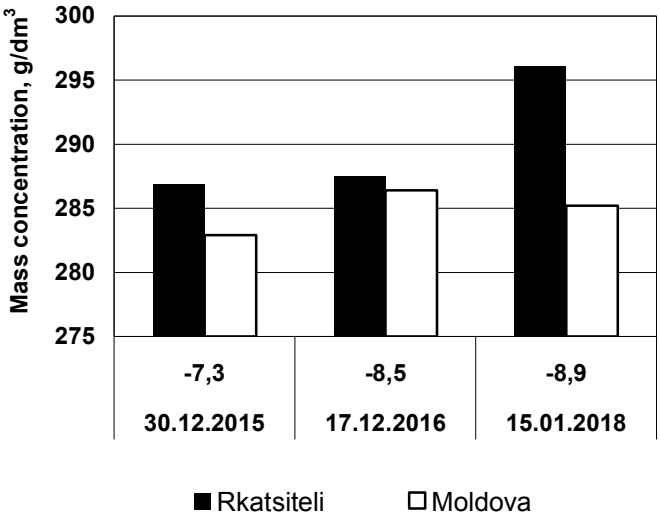

Figure 1. Dynamics of sugar concentration of varieties of Rkatsiteli and Moldova depending on the date and minus temperature in Tairov (2015–2018)

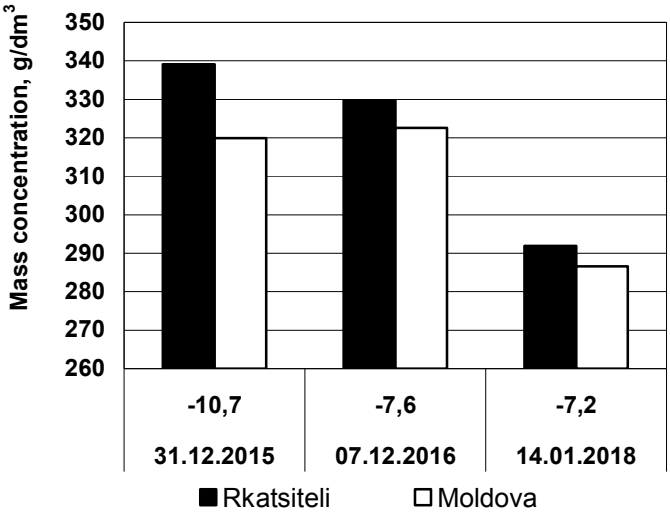

Figure 2. Dynamics of sugar concentration of varieties of Rkatsiteli and Moldova depending on the date and minus temperature in Kherson (2015–2018)

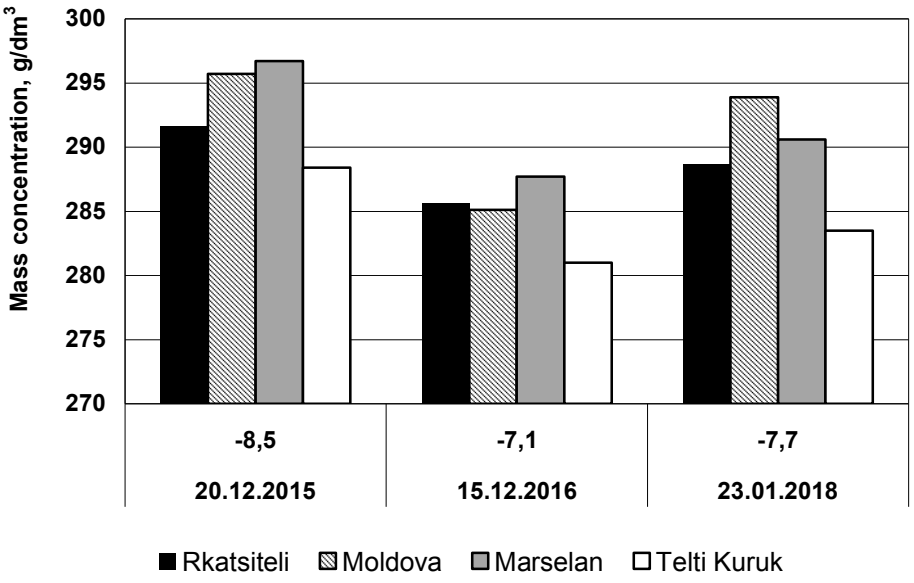

Figure 3. Dynamics of concentration of sugar of grape varieties, depending on the date and minus temperature in v. Shabo (2015–2018)

In December 2016, in the Tairov region, Rkatsiteli and Moldova had a mass concentration of sugar 287.5 and 286.4 g/dm^3, which is 4.1 and 9.3 g/dm^3 less than in 2015 in Shabo, although the grape harvest was carried out at the same temperature -8.5 °C. At -7.6 °C in 2016 and -7.2 °C in 2018, the Rkatsiteli variety, frozen in the vineyards of Kherson, showed a higher sugar content compared with the crop collected from the v. Shabo a week later of the same years by 13.5 and 11.6% and with a temperature difference of 0.6 and 0.5 °C respectively. The lower the temperature, the higher the accumulation of sugar was observed in the Moldova variety, however, in Kherson was the highest mass concentration of 322.6 g/dm^3 in 2016 when the thermometer was marked -7.6 °C, when -10°C, in 2015, and sugar content was lower – 319.9 g/dm^3.

Another red variety, Marselan, contained higher sugar in berries frozen on a vine compared to Moldova, but no significant difference was noted: 1 and 2.6 g/dm^3 more than 2016-2017 years of harvest. The native grape variety Telti Kuruk showed the lowest accumulation of mass concentrations of sugar among the studied varieties, which, on average, amounted to 284.3 g/dm^3 by years.

The concentration of titrated acids and pH values show a tendency with lower temperatures, higher pH values ($p \leq 0.01$, $p \leq 0.001$), and the mass concentrations of titrated acids did not differ significantly among all grape varieties ($p \leq 0.05$, n/s). This fact is explained by the distribution of constituent substances in the grape during prolonged maturation, where sugar concentrates more and the acid content decreases, therefore, even at low temperatures, slight increases in the parameters of this parameter are observed. Thus, the mass concentration of titrated acids of the Rkatsiteli variety was the same and amounted to 8.9 g/dm^3 at temperatures of -7.1, -7.3, -8.9, -10.7°C in different regions, and the pH values increased with decreasing temperatures. According to the mathematical treatment, a similar situation was also observed in the Marselan variety, where the content of titrated

acidity was found in the amount of 9.1-9.2 g/dm^3, and the active acidity had a growing direction, varying in the range of 3,58-3,78. In Shabo region, the varieties of Moldova and Telti Kuruk did not differ in terms of the values of the analyzed chemical parameters from the collection dates of 9.2 g/dm^3 and pH 3.67 and 8.6 g/dm^3 at pH 3,58, respectively, in each year (Table 4).

Statistic analysis has made it possible to conclude that it is precisely the stability of grapes to diseases and pests and biological peculiarities of grapes that significantly affect the chemical properties of grape varieties under consideration in traditional freezing.

Table 4

Mass concentration of titrated acids and pH of grapes, 2015-2018

Harvest	T, °C	Rkatsiteli		Moldova		Marselan		Telti Kuruk	
		TA	pH	TA	pH	TA	pH	TA	pH
Tairov									
30.12.2015	-7,3	8,9^a	3,62^b	8,7^a	3,48^a				
17.12.2016	-8,5	8,7^a	3,57^a	9^b	3,52^b				
15.01.2018	-8,9	8,9^a	3,76^c	9,2^b	3,74^c				
p-value		n/s	***	**	***				
Kherson									
31.12.2015	-10,7	8,9^a	3,73^c	9,2^a	3,67^c				
07.12.2016	-7,6	9^b	3,66^b	9,3^a	3,54^b				
14.01.2018	-7,2	9,1^b	3,62^a	9,3^a	3,45^a				
p-value		*	***	n/s	***				
Shabo									
20.12.2015	-8,5	8,9^a	3,62^b	9,2^a	3,66^a	9,1^a	3,78^c	8,5^a	3,56^a
15.12.2016	-7,1	8,8^a	3,57^a	9,2^a	3,67^a	9,2^a	3,58^a	8,6^a	3,58^a
23.01.2018	-7,7	8,8^a	3,61^b	9,3^a	3,67^a	9,1^a	3,63^b	8,6^a	3,58^a
p-value		n/s	*	n/s	n/s	n/s	***	n/s	n/s

Note:*,**,***– significance at p≤0.05, 0.01 and 0.001 respectively; n/s value is not significant.
Values for columns with the same letter do not differ significantly.

Conclusions

The peculiarities of the change in the quality of the mechanical composition of grapes, revealed during long maturation, made it possible to highlight the suitability of a particular variety to withstand adverse climatic conditions in a particular area, which is one of the key details for the production of icewines. The mass concentrations of titrated acids of all grapes after the onset of technological maturity had a direction to decrease, and the pH increased.

On the basis of the data presented, it can be stated that Riesling, in accordance with the climatic conditions of the Northern Black Sea Region, is not able to withstand a hard time on the vine after technological maturity, and therefore is not a perspective cultivar for the production of icewines in Ukraine. The most suitable varieties were Marselan, Rkatsiteli and Moldova, which according to their physicochemical parameters and mechanical composition meet the requirements that are needed for the characteristic varieties for use in technology of icewines.

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Анотації

Харчові технології

Вихід проміжних продуктів у драному процесі сортового помелу пшениці

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Вступ. З метою визначення виходу проміжних продуктів подрібнення досліджено процес крупоутворення при помелі пшениці в сортове борошно.

Матеріали і методи. На перших трьох драних системах відбиралися проміжні продукти подрібнення під вальцями і просіювалися з метою визначення режиму роботи, потім проходові фракції просіювалися на ситах з метою визначення виходу окремих фракцій продуктів. Результати досліджень подавалися як залежність «загальний добуток – вихід фракції».

Результати і обговорення. Вихід усіх продуктів подрібнення на першій драній системі залежно від режиму подрібнення має нелінійний характер. На другій драній системі лінійний характер має лише залежності виходу дрібної крупки та дунстів, а вихід крупної та середньої крупки, а також борошна має нелінійний характер. На третій драній системі (крупній) вихід продуктів залежить від режиму подрібнення. Всі продукти подрібнення, крім дрібної крупки, мають нелінійний характер. На третій драній системі (дрібній) лінійні залежності виходу продуктів мають лише дунсти та борошно, решта продуктів мають нелінійний характер.

При збільшенні загального добутку проміжних продуктів подрібнення від 29,4% до 56,6% на першій драній системі спостерігався екстремум виходу крупної крупки при 40,0%. На другій драній системі при збільшенні загального добутку проміжних продуктів подрібнення від 46,5% до 72,0% спостерігався екстремум виходу середньої крупки при 60,0%. На третій драній системі (крупній) при загальному добутку проміжних продуктів подрібнення від 11,9% до 40,6% спостерігався екстремум виходу дунстів при 35,5%. При збільшенні загального добутку проміжних продуктів подрібнення на третій драній системі (дрібній)від 22,6% до 47,9% спостерігався екстремум виходу дрібної крупки при 46,4%. Отримані екстремуми є оптимальними значеннями виходів продуктів трьох драних систем.

Висновки. Залежності виходу окремих фракцій продуктів подрібнення зерна пшениці дають змогу розрахувати кількісні баланси сортових помелів.

Ключові слова: *борошно, подрібнення, пшениця, вальці, млин, вихід.*

Застосування відходів сагової пальми і нанокремнезему із золи рисового лушпиння як гібридного композитного біонанонаповнювача для харчової пластикової упаковки

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Вступ. У результаті сезонного збору врожаю утворюються тисячі тонн сільськогосподарських відходів, таких як порошок із рисового лушпиння (Oryza sativa) (RHA) і відходи саго (Metroxylon sago sp.) (SP. Ці відходи мають відносно високий вміст кремнію й целюлози та можуть бути використані як біокомпозити для розкладання пластику.

Матеріали тіметоди. Нанокремнезем із RHA був отриманий методом золь-гель, а SP – методом кислотного промивання. Експеримент проводився з допомогою тесту на тиск при занурені у воду та поглинання теплоти з використанням мікрохвильової печі.

Результати і обговорення. Сформований зразок містить зшивання гібридного наповнювача з матрицею PLA (полімолочної кислоти), яка ефективно покращує твердість і щільність у PLA (61%). Це виявлено у поєднанні нанокремнезему з SPW-волокном і PLA (60:20:20). При випробуванні відбувалося поглинання води модифікованими зразками, що свідчать про незначну водостійкість з ефективним сполученням кремнезему: кількість волокон SPW 20:10. Ця комбінація має складний бар'єр, який перешкоджає проникненню молекули води в матричну сполуку. Під час випробовування теплопровідності всі модифіковані біокомпозити мали більш високу температуру, ніж стандартна PLA, але несуттєво. Можна стверджувати, що це спричинено композицією нанокремнезему, яка демонструє чудову теплоізоляцію та повільну термодесорбцію під час теплового впливу, що накопичується в полімерній матриці та розподіляє підвищену температуру в модифікованих біокомпозитах, якщо порівняти з чистою PLA.

Висновки. Незважаючи на те, що потрібні додаткові дослідження аспектів безпечності, можна високо оцінити можливість використання відходів сільського господарства для формування екологічно чистої упаковки для продуктів харчування та напоїв. Окрім того, отриманий гібридний композит дасть змогу зменшити використання звичайних пластмас і пінопласту як контейнера з точки зору загальних пластичних фізико-хімічних характеристик.

Ключові слова: *нанонаповнювач, харчова упаковка, біопластик, відходи саго, відходи.*

Вплив ферментативної модифікації крохмалю рисового борошна на якість хліба для хворих на целіакію

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Вступ. Науково обґрунтовано доцільність застосування ферментів з амілолітичною активністю для модифікації вуглеводного складу рисового борошна з метою покращення якості безглютенового хліба.

Матеріали і методи. Крохмаль рисового борошна гідролізували за допомогою двох амілаз, а саме: грибної α-амілази та глюкоамілази. Загальну кількість цукрів визначали йодометричним методом. Вміст декстринів визначали за їх здатністю осаджуватися при різних концентраціях етилового спирту в розчині. Перебіг мікробіологічних процесів у тісті досліджували за його газоутворювальною здатністю волюмометричним методом і загальною кислотністю методом титрування.

Результати і обговорення. Використання α-амілази в кількості 0,005% та глюкоамілази – 0,03% до маси рисового борошна призводить до накопичення цукрів

в кількості 5,5-6%, які необхідні для інтенсифікації перебігу мікробіологічних процесів у тісті. З метою проведення більш повного гідролізу крохмалю доцільно готувати напівфабрикат-гідролізат з 50% рисового борошна від його рецептурної кількості вологістю 65% з подальшим замішуванням тіста на його основі. Для накопичення моно- та дицукридів у кількості, яка є оптимальною для активної життєдіяльності дріжджів і покращення газоутворення в тісті, тривалість гідролізу крохмалю рисового борошна при приготуванні напівфабрикату-гідролізату становить 2 год.

Продукти гідролізу крохмалю рисового борошна, утворені внаслідок його ферментативної модифікації α-амілазою та глюкоамілазою, а саме: моно- та дицукриди, інтенсифікують процес бродіння тіста, про що свідчить збільшення кількості виділеного CO_2 на 57,8% та кислотності на 0,6 град порівняно із контрольним зразком, внаслідок чого готові вироби характеризуються покращеними структурно-механічними показниками якості. Підвищення кількості декстринів у тісті впливає на уповільнення процесу ретроградації крохмалю при зберіганні готових виробів.

Висновки. Проведення гідролізу крохмалю рисового борошна за допомогою амілолітичних ферментів при приготуванні хліба для хворих на целіакію сприяє інтенсифікації мікробіологічних процесів у тісті, покращенню показників якості готових виробів тіподовженню терміну зберігання ними свіжості.

Ключові слова: *целіакія, хліб, гідроліз, крохмаль, α-амілаза, глюкоамілаза.*

Моделювання ефективності процесу мікрофільтрації під час пом'якшення, поліпшення видалення нецукрів і чистоти цукрового бурякового соку

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Вступ. Метою дослідження є визначення найкращої конфігурації штучної нейронної мережі. Розроблено різні мережі з номерами нейронів від 2 до 20. Їх середні квадратичні помилки, квадратичні нормалізовані похибки, абсолютні похибки та коефіцієнти кореляції досліджувались для різних правил навчання та функцій передачі.

Матеріали і методи. Моделювали потенціал мікрофільтраційного процесу зі зменшенням твердості, поліпшенням чистоти та відмовою від цукрового бурякового соку штучною нейронною мережею (ANN), з таким параметрами: температура (30 та 60 °C) трансмембранний тиск (1, 1,75 і 2,5 бар) і час (звичайні часові інтервали від 1 до 60 хвилин). Моделювання ANN проводилося за допомогою прорамного пакета Neurosolution software v6 для визначення найкращого типу транспортної функції, правил перевірки та прикладних відсотків для стадій навчання, валідації й тестування.

Результати і обговорення. Найкращою була нейронна мережа з одним прихованим шаром за методом Левенберга з функцією дотичної передачі, яка включала 8 нейронів. Це дало змогу досягти максимального коефіцієнта кореляції для твердості відповідно до температури, тиску та часу. Нейронна мережа з одним прихованим шаром, у тому числі 4 нейронами із сигмоїдною передавальною функцією за методом Левенберга, мала найменшу помилку і найбільшу r для зміни

чистоти. Нейронна мережа з одним прихованим шаром, яка включала 2 нейрони за методом Левенберга та функцію передачі дотичної домішки, мала найнижчу похибку та найвищу кореляцію для відсотка відмови від цукру. Моделювання проводилось із різними відсотками даних для навчання. Найкраща кореляція прогнозування за всіма параметрами (мутність, чистота, неприєднання цукру) отримана за умови, коли 60% даних використовувались для навчання, 35% з них – для перевірки та 5% – для тестування. Також отримано кореляцію експериментальних даних з прогнозованими значеннями моделі. Згідно з отриманими моделями, ANN одержав дані з належною кореляцією з експериментальними даними твердості, чистоти та неприєднання цукру з відповідними коефіцієнтами кореляції 0,987, 0,980 та 0,981. Розглянуло чутливість моделі до вхідних даних. Найкращою моделлю чутливості є модель для прогнозування мутності, чистоти та відмови від цукру, не пов'язана з часом.

Висновок. Найкращим правилом мережі для прогнозування твердості, чистоти та відмови від цукру є правило Левенберга. Модель спрогнозувала твердість, чистоту та відсоток відмови від цукру за різними операційними моделями, оскільки модельні дані демонстрували високу кореляцію з експериментальними даними.

Ключові слова: *цукор, буряк, мікрофільтрація, нейронна мережа, Левенберг, тангенс.*

Функціональні продукти і препарати в системній концепції здоров'я

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Вступ. Проведені аналітичні й експериментальні дослідження з наукового обґрунтування функціональних продуктів і препаратів у новій системній концепції здоров'я.

Матеріали і методи. Досліджувались ненасичені жирні кислоти, роль холестерину, системна концепція здоров'я, соняшникова і лляна олії, олійні композиції і продукти, антиокислювальні препарати. Кінетику окиснення олій при температурній обробці характеризували середньою швидкістю зміни їх показників (пероксидних і кислотних чисел). Для оцінки летких сполук використано хроматографічний метод.

Результати і обговорення. За результатами дослідження ролі поліненасичених жирних кислот омега-3 та омега-6 у рослинних оліях і функціональних продуктах, а також проблеми холестерину в активній життєдіяльності та здоров'ї людей різних вікових груп запропонована система комплоексної терапії індивідуального оздоровлення людей (KTIOL), яка полягає в інтегрованому виборі чинників в індивідуальній профілактиці, лікуванні та реабілітації.

Препарат KTIOL-BF (1%) знижує середню швидкість окиснення соняшникової олії при 150 °С (3 год) у12,2 раза, при 200 °С (6 год) у 13,6 раза, середня кислотність олії знижується в 9 і 2,2 раза відповідно. За аналогічних умов середня швидкість окиснення льняної олії зменшується в 1,4 та 1,5 раза відповідно. Кислотність олії практично не знижується. Соняшниково-льняна олійна композиція KTIOL-LS2 з 1% KTIOL-BF при 20–25 °С зберігається 6 місяців. За компонентним складом майонез без холестерину і лактози на основі цієї олії відноситься до дієтичної групи.

На основі аналізу газохроматографічних профілей олійної композиції КТІОЛ-ЛС2 висловлено гіпотезу щодо можливого зменшення кількості летких сполук у ній як за рахунок складу олії, так і за рахунок взаємодії окремих летких інгредієнтів.

Висновки. Спеціальні продукти на основі соняшниково-льняної компзиції KTIOL-LS2 покращують фізіологічний стан людей різних вікових груп при виникненні вікозалежних і супутніх патологій.

Ключові слова*: продукти, препарати, система, концепція, здоров'я.*

Термічні, структурні і зв'язувальні властивості бразильського імбирного (Zingiber officinale Roscoe) крохмалю

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Вступ. Нетрадиційні джерела крохмалю – цікаві промислові альтернативи, кожна з яких має певні властивості. Досліджено термічні, морфологічні, структурні та зв'язувальні характеристики крохмалю імбиру.

Матеріали і методи. Імбирний крохмаль був екстрагований водним процесом, а його характеристики визначалися термогравіметрією/похідною термогравіметрією, диференціальною сканувальною калориметрію, швидким віскоамілографічним аналізом, сканувальною електронною мікроскопією і рентгенівською порошковою дифрактометрією.

Результати і обговорення. Для зразків крохмалю було виявлено аналогічну термостійкість і три втрати маси. Виявлено більш високі температури переходу та ентальпію желатинізації для комерційного зразка, який був пов'язаний з більш довгими амілопектиновими ланцюгами завдяки кристалічності B-типу. Крохмаль, отриманий із "солодкого" імбиру, показав найвищу пікову і кінцеву в'язкість, пов'язану з найменшою температурою желатинізації, що є цікавим результатом для харчових технологій, на додачу до низької енергії, необхідної для желатинізації. Еліпсоїдальна форма і тріщини на поверхні гранул нівелювалися мікроскопією, а діаметр гранул комерційних зразків був найменшим. Дифракція типу A отримана для крохмалів "Солодкий" і "Форте", тоді як комерційний крохмаль був представлений поверхнею типу B. Найбільшу відносну кристалічність виявлено в імбирного крохмалю "Форте".

Висновки. Комерційні зразки крохмалю порівняно з відомими різновидами мають інші характеристики. Виявлені цікаві властивості, що підкреслюють різноманітність «солодкого» імбиру.

Ключові слова: *крохмаль, імбир, патоутворення, желатинізація.*

Механізм трансформації протонів у процесі створення водно-спиртових сумішей

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Вступ. Метою публікації є вивчення механізмів трансформації протонів етанолу (спирту етилового ректифікованого – СЕР) і води (води питної) в процесі створення

водно-спиртових сумішей (ВСС) за допомогою ^{1}Н ЯМР спектроскопії.

Матеріали і методи. *^{1}Н ЯМР* аналіз проводився з використанням: Фур'є-*ЯМР*-спектрометра Bruker Avance II – 400 МГц; спеціального капіляра з ацетоном-d_6 (атомна частка дейтерію – 99,88%; хімічний зсув δ=2,75 ppm); ампул №507-НР високого розділення; дозатора; СЕР; води питної; ВСС із СЕР і питної води.

Методика виконання: за допомогою мірної піпетки готували 0,3 мл ВСС із заданою міцністю (40,0 ± 0,2) %об. Необхідний для роботи системи LOCK'a – дейтерієвій стабілізації ЯМР спектрометра дейтеророзчинник (ацетон-d_6) – зовнішній стандарт, який відокремлений від досліджуваної речовини, вносили до ампули в капілярі спеціальної форми; запис спектрів ^{1}Н ЯМР і обробку даних проводили відповідно до інструкції, що додається до Фур'е-ЯМР-спектрометра Bruker Avance II (400 МГц).

Результати і обговорення. Встановлені принципово нові концепції в процесі створення ВСС, які безпосередньо залежать від часу контакту СЕР з водою. Як результат, підтверджено наявність складного динамічного процесу досягнення рівноваги ААМ із застосуванням питної води з pH=7,01 та СЕР. У той же час pH отриманого ААМ – 8,32. У перші 48 год при постійній концентрації спирту (міцність ВСС – 39,94 %об) і термостатуванні системи (t=23,5 ºС), швидкість обміну гідроксильного протону етанолу (*EtOH*) знаходиться в проміжній області, з можливістю роздільного спостереження сигналів. В інтервалі від τ=48 до 120 год за рахунок перебудови структури системи протонний обмін прискорюється і, починаючи з 120 год, спостерігається тільки один загальний сигнал рухливих протонів несиметричної форми. Величина хімічного зсуву сумарного сигналу $\delta_{EtOH+H2O}$=4,74 ppm (τ=120 год.) починає поступово зростати і переходить в «слабкіші поля» до величини $\delta_{EtOH+H2O}$=4,81 ppm (τ=312 год).

Висновки. Завдяки дослідженню визначено фундаментально нові особливості процесу створення ВСС, які залежать від часу контакту питної води і СЕР.

Ключові слова: *етанол, вода, суміш, ^{1}Н ЯМР, стабілізація.*

Оптимізація робочих параметрів надкритичної вуглекислотної екстракції лікопену з відходів промислового томату

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Вступ. Томатні відходи можуть бути використані як вторинна сировини для одержання ліпорозчинних екстрактів. Лікопен, будучи ліпофільним з'єднанням з антиоксидантними властивостями, що виявлене в томатах, може бути екстрагований із застосуванням надкрикритичного діоксиду вуглецю з відходів, отриманих під час промислової переробки томатів.

Матеріали і методи. Томатні відходи, отримані під час виробництва томатного соку, були зібрані на фабриці АО «Орхей-Віт», м. Орхей, Республіка Молдова. Використовуючи повний факторний ортогональний метод експериментального проектування, створено матрицю планування в реальних змінних. У результаті отримано 15 режимів екстракції шляхом зміни параметрів: температура (36–73 °С), тиск (18–42 МПа) і час (24–96 хв). Вміст лікопену визначався спектрофотометричним методом за довжини хвилі 502 нм.

Результати і обговорнення. Первинно томатні відходи висушувались (від початкового вмісту вологості 80,0% до кінцевого 6,5%). Щоб збільшити контактну

поверхню з діоксидом вуглецю, томатні відходи були подрібнені. Зразки CO_2-екстрактів із томатних відходів отримано за різних параметрів екстракції в лабораторних умовах. Концентрацію лікопену приймали за вихідний фактор. Було встановлено остаточну форму рівняння регресії другого порядку, що характеризує процес CO^2-екстракції лікопену в жиророзчинній фракції з томатних відходів. Рівняння регресії дало змогу оптимізувати результат, використовуючи метод градієнтного поглинання. Таким чином було визначено оптимальні параметри екстракції біоактивного з'єднання – лікопену. Графічно представлена ділянка поверхні реакції описується поліномом другого ступеня, що характеризує процес CO_2-екстракції лікопену з відходів томатів за постійних параметрів: тиску, температури і часу.

Висновки. CO_2-екстракти з томатних відходів багаті на лікопен з концентрацією від 10,8 до 47,1 мг/100 г. Оптимальними параметрами екстракції лікопену з відходів томатів є температура 60–75 °С, тиск 33–42 МПа і час екстрагування 62–68 хв.

Ключові слова: томат, відходи, суперкритичний, CO_2-екстракція, ліпокен.

Застосування гідродинамічних осциляцій для процесу активації вапняного молока

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Вступ. Представлено дослідження впливу застосування гідродинамічних осциляцій для процесу активації вапняного молока при виробництві цукру з цукрових буряків.

Матеріали і методи. Під час досліджень використовувались загальнонаукові методи, спеціальні методи, тривимірне об'ємне параметричне імітаційне моделювання та візуалізація, математичне моделювання, чисельний експеримент, оптична мікроскопія, метод потенціометричних вимірювань, а саме: іонометрія.

Результати і обговорення. В результаті комплексних аналітичних досліджень визначено шляхи удосконалення процесу вапнування дифузійного соку під час виробництва цукру.

Застосування гідродинамічних осциляцій для процесу активації вапняного молока при виробництві цукру з цукрових буряків є надзвичайно перспективним.

Встановлено, що для забезпечення інтенсифікації масообмінних процесів, які відбуваються між вапном і водою під час активації вапняного молока, а також оброблення водних розчинів з метою зміни фізико-хімічних параметрів та ініціювання структурних перетворень в них, величина лінійної швидкості потоку повинна становити близько 22м/с для першого ротора і близько 24м/с для другого ротора.

Під час експериментальних досліджень встановлено зміну водневого показника води підготовленої за технологією для процесу активації, з використанням гідродинамічних осциляцій, при проведенні активації вапняного молока, в процесі очищення дифузійного соку, що становить 15%.

Зниження величини окисно-відновного потенціалу під час оброблення води та водних розчинів досягає максимального значення при тривалості процесу

оброблення – 210с, при подальшому обробленні значних змін окисно-відновного потенціалу не відбувається.

Найбільшого зниження величина окисно-відновного потенціалу сягає під час оброблення із застосуванням гідродинамічних осциляцій і становить 65% порівняно з початковим значенням.

Висновки. Застосування гідродинамічних осциляцій для активації вапняного молока в технологічному процесі очищення дифузійного соку може значною мірою підвищити продуктивність, замінити періодичний процес оброблення на безперервний, скоротити тривалість процесу активації, зменшити витрати вапняного молока, знизити енерговитрати.

Ключові слова: *вода, гідратований, вапняк, тиск, осциляція.*

Придатність технічних сортів винограду Північного Причорномор'я для виробництва традиційним шляхом вин «Icewine»

Вікторія Остапенко, Наталія Каменева
Одеська національна академія харчових технологій, Одеса, Україна

Вступ. Метою статті є дослідження механічного складу та фізико-хімічних властивостей сортів винограду Північного Причорномор'я для визначення доцільності їх використання у виробництві крижаних вин .

Матеріали і методи. Рислінг, Ркацителі і Тельти курук, Марселан і Молдова протягом 2015-2018 років на виноградниках с. Шабо, Таїрова і Херсону були досліджені за основними показниками механічного складу винограду, включаючи середню масу грона винограду, кількість ягід у гроні, масу ягід винограду, масу шкірочки винограду, масу м'якоті із соком за методикою проф. Простосердова. Також визначили pH, масову концентрацію титрованих кислот і цукрів відповідно до прийнятих методик.

Результати і обговорення. Найбільша середня маса грона серед сортів спостерігались у сортів Молдова і Марселан, найменші – у Тельти курук і Рислінг, сорт Ркацителі відзначився середніми масами грон порівняно з іншими незалежно від регіону і місяця. Після настання технологічної зрілості маса грон у всіх сортів зменшувалася, починаючи з кінця жовтня і до грудня місяця: у середньому в 0,95 раза по регіону Шабо, у 0,92 раза – по району Таїрова та у 0,90 раза – по Херсону. Найбільші диференціації у чисельності ягід під час теплих місяців осені ±4шт і ±6шт мали сорти Ркацителі і Тельти курук відповідно, найменші – ±1шт Молдова і Марселан на виноградниках с. Шабо. На виноградних плантаціях у селищі Таїрова і місті Херсоні значна різниця у кількості ягід за сортами не спостерігалася і складала ±1÷±3шт.

Сорт Ркацителі накопичував найбільше цукру серед інших сортів, масові концентрації якого сягали у грудні, в середньому по регіонах, від 243-245,13 г/дм^3, найменші – у Тельти курук, що становили 179,5-182,7 г/дм^3. У сорту Рислінг після значних опадів масова концентрація цукрів зменшилась у середньому до 30 г/дм^3 – у регіоні Шабо, до 25 г/дм^3 – у с. Таїрова, і до 22 г/дм^3 – на виноградниках Херсону. Масові частки цукрів Тельти куруку були менші і в листопаді місяці складали 180-182,7 г/дм^3, ніж у Рислінгу, що мав масові концентрації у кінці жовтня у діапазонах 199,5–201,6 г/дм^3 протягом сезонів кожного року на виноградниках с. Шабо.

Вищезгадані сорти за накопиченням цукру протягом тривалого дозрівання на лозі трьох регіонів під час серпня-грудня 2015–2018 рр. розташувалися таким чином: Ркацителі, Марселан, Молдова, Тельти курук, Рислінг.

Висновки. Рислінг не здатний витримати тривалий термін на лозі після технологічної зрілості, а найбільш придатними сортами виявилися Марселан, Ркацителі і Молдова, які за своїми фізико-хімічними показниками і механічним складом відповідають вимогам до характерних сортів, що використовуються у технології крижаних вин.

Ключові слова: *крижане вино, виноград, гроно, склад, Північне Причорномор'я.*

Instructions for authors

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The Editorial Board of scientific periodical
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Requirements for article:
Language – English.
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   - Introduction
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Шановні колеги!

Редакційна колегія наукового періодичного видання «**Ukrainian Food Journal**» запрошує Вас до публікації результатів наукових досліджень.

Вимоги до оформлення статей

Мова статей – англійська.

Мінімальний обсяг статті – **8 сторінок** формату А4 (без врахування анотацій і списку літератури)**.**

Стаття виконується в текстовому редакторі Microsoft Word 2003, в форматі *.doc.

Для всіх елементів статті шрифт – **Times New Roman**, кегль – **14**, інтервал – 1.

Всі поля сторінки – по 2 см.

Структура статті:

1**.** УДК**.**
2. **Назва статті.**
3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озерянко).
4. *Установа, в якій виконана робота.*
5. Анотація. **Обов'язкова** структура анотації:
   - Вступ (2–3 рядки).
   - Матеріали та методи (до 5 рядків)
   - Результати та обговорення (пів сторінки).
   - Висновки (2–3 рядки).
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Пункти 2–6 виконати англійською і українською мовами.

7. Основний текст статті. Має включати такі обов'язкові розділи:
   - Вступ
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За необхідності можна додавати інші розділи та розбивати їх на підрозділи.

8. Авторська довідка (Прізвище, ім'я та по батькові, вчений ступінь та звання, місце роботи, електронна адреса або телефон).
9. Контактні дані автора, до якого за необхідності буде звертатись редакція журналу.

Рисунки виконуються якісно. Скановані рисунки не приймаються. Розмір тексту на рисунках повинен бути **співрозмірним** (!) тексту статті. **Фотографії можна використовувати лише за їх значної наукової цінності.**

Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

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Скорочені назви фізичних величин в тексті та на графіках позначаються латинськими літерами відповідно до системи СІ.

В списку літератури повинні переважати англомовні статті та монографії, які опубліковані після 2000 року.

Правила оформлення списку літератури

В Ukrainian Food Journalвзято за основу загальноприйняте в світі спрощене оформлення списку літератури згідно стандарту Garvard. Всі елементи посилання розділяються **лише комами**.

1. Посилання на статтю:

Автори А.А. (рік видання), Назва статті, Назва журналу (курсивом), Том (номер), сторінки.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

1. Приклад:
   Popovici C., Gitin L., Alexe P. (2013), Characterization of walnut (Juglans regia L.) green husk extract obtained by supercritical carbon dioxide fluid extraction, *Journal of Food and Packaging Science, Technique and Technologies,* 2(2), pp. 104–108.

2. Посилання на книгу:

Автори (рік), Назва книги (курсивом), Видавництво, Місто.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

Приклад:

2. Wen-Ching Yang (2003), *Handbook of fluidization and fluid-particle systems*, Marcel Dekker, New York.

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Приклади:

1. (2013), *Svitovi naukovometrychni bazy*, available at: http://www1.nas.gov.ua/publications/q_a /Pages/scopus.aspx
2. Cheung T. (2011), *World's 50 most delicious drinks [Text]*, Available at: http://travel.cnn.com/explorations/drink/worlds–50-most-delicious-drinks–883542

Список літератури оформлюється лише латиницею. Елементи списку українською та російською мовою потрібно транслітерувати. Для транслітерації з української мови використовується паспортний стандарт, а з російської – стандарт МВД (в цих стандартах використовуються символи лише англійського алфавіту, без хвостиків, апострофів та ін).

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УДК 663/664

Ukrainian Food Journal публікує оригінальні наукові статті, короткі повідомлення, оглядові статті, новини та огляди літератури.

Тематика публікацій в Ukrainian Food Journal:

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Мікробіологія	Економіка та управління
Фізичні властивості харчових продуктів	Автоматизація процесів
Якість та безпека харчових продуктів	Упаковка для харчових продуктів

Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв'язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

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CABI full text (2014)
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Universal Impact Factor (2014)
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European Reference Index for the Humanities and the Social Sciences (ERIH PLUS) (2014)
Directory of Open Access Journals (DOAJ) (2015)
InfoBase Index (2015)
Chemical Abstracts Service Source Index (CASSI) (2016)

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Інструкції для авторів та інша корисна інформація розміщені на сайті
http://ufj.ho.ua

Редакційна колегія

Ukrainian Food Journal in 2017. Statistics.

1. Number of the articles

Total number	Original research articles	Review articles
55	53	2

2. Topics of the articles

Food Technology	Biotechnology and Microbiology	Processes and Equipment of Food Production	Economics and Management
44	1	5	3

3. Geography of authors

State of authors	Number of the articles	%
Ukraine	35	63,6
Bulgaria	2	3,6
Moldova	3	5,5
Brazil	2	3,6
Nigeria	2	3,6
Pakistan	1	1,8
India	2	3,6
Bangladesh	1	1,8
Turkey	1	1,8
Iran	2	3,6
States of the author team		
Australia, Indonesia	1	1,8
Bulgaria, Ukraine	1	1,8
Ukraine, Poland	2	3,6

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