ISSN 2313–5891 (Online)
ISSN 2304–974X (Print)

Ukrainian Food Journal

Volume 7, Issue 1
2018

Kyiv **Київ**

2018

Ukrainian Food Journal is an international scientific journal that publishes innovative papers of the experts in the fields of food science, engineering and technology, chemistry, economics and management.
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Ukrainian Food Journal включено у перелік наукових фахових видань України з технічних наук, в якому можуть публікуватися результати дисертаційних робіт на здобуття наукових ступенів доктора і кандидата наук (Наказ Міністерства освіти і науки України № 1609 від 21.11.2013)

Editorial office address:

National University
of Food Technologies
Volodymyrska str., 68
Ukraine, Kyiv 01601

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Scientific Council of the National University of Food Technologies recommends the Journal for printing.
Minutes № 9, 29.03.2018

Рекомендовано вченою радою Національного університету харчових технологій.
Протокол № 9 від 29.03.2018 р.

Ukrainian Food Journal publishes the original research articles, short communications, review papers, news and literature reviews.

Topics:

Food engineering	Food nanotechnologies
Food chemistry	Food processes
Food microbiology	Economics and management
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Periodicity of the journal – 4 isues per year.

Studies must be novel, have a clear connection to food science, and be of general interest to the international scientific community.

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Index Copernicus (2012)
EBSCO (2013)
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Contents

Antioxidant properties of candy caramel with plant extracts

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Keywords:

Caramel
Antioxidant
Polyphenolic
Ascorbic acid
Coulometry

Article history:

Received 21.01.2018
Received in revised form 27.02.2018
Accepted 29.03.2018

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DOI: 10.24263/2304-974X-2018-7-1-3

Abstract

Introduction. An investigation of the antioxidant properties of the candy caramel samples based on the sugar replacers of maltitol and isomaltol, enriched with ascorbic acid and biologically active substances of water extracts of dried leaves of *Menthae Piperitae* and flowers of *Matricariae chamomilla L.* was carried out.

Materials and methods. The total antioxidant capacity (TAC) and total content of polyphenolic compounds (TPC) of candy caramel samples were determined by galvanostatic coulometric titration with electrogenated bromine and by spectrophotometry using the Folin-Ciocalteu reagent. The results were expressed as milligrams of gallic (GAE) or ascorbic (AAE) acids per gram of the sample (SW). The amount of ascorbic acid in the final product was determined by galvanostatic coulometry with electrogenerated iodine.

Results and discussion. The total antioxidant capacity of the aqueous extracts of of *Menthae piperitae* and flowers of *Matricariae chamomilla L.* was 40.0 and 23.3 mg of GAE / g SW, respectively, and the total content of polyphenols was 54.5 and 17.1 GAE / g SW.

It is shown that samples of candy caramel based on sugar substitutes with the addition of plant extracts contain from 48 to 66% of the initial mass of ascorbic acid.

Based on the experimental data of the caramel samples with the variation of the recipe ingredients, the correct values of the total polyphenol content for the two candy caramel samples in the presence of interfering compounds were determined that are 408 mg GAE/100 g of the sample for caramel based on maltitol and *Matricariae chamomilla L.* extract and 222 mg GAE/100 g sample for caramel based on isomaltol and *Menthae piperitae* extract.

A positive correlation between the values of the total antioxidant capacity of TAC and the total content of polyphenols TPC for the samples was obtained.

Conclusions. The obtained results indicate the prospects of technologies for enriching the candy caramel on sugar replacers with natural biologically active substances with antioxidant properties for the production of diet-functional food systems.

Introduction

Confectionery products can not be attributed to healthy eating foods, because they have a low nutritional value. Among the wide range of confectionery products, candy caramel is in great demand among the Ukrainian population, especially in children, due to high organoleptic indicators and low price. Due to these factors, the volume of its production increases with each passing year. Almost all types of candy caramel, which are offered by a modern production, have no functional ingredients. The main raw material during the production of candy caramel is white crystalline sugar and caramel molasses, the glycemic index of which is quite high, therefore, candy caramel which is made according to the traditional technology cannot be consumed by patients with diabetes mellitus.

There is a need for the use of sugar substitutes of the new generation to reduce the glycemic index of candy caramel - polyols (isomaltitol, maltitol, eritritol, lactitol) that have lower caloric content in comparison with sugar, lower glycemic index, have prebiotic properties and causing no tooth decay, especially isomaltitol and maltitol [1, 2].

Among these polyols, known in the Ukrainian market is isomaltitol and maltitol. Isomaltitol has a fairly low hygroscopicity, and because of this you can significantly extend the term of storage of caramel products. Isomaltitol doesn't have any harmful effects on the teeth, since it causing no caries, doesn't increase glucose and insulin levels in the blood, and has a reduced caloric content. Maltitol is a polyol obtained by means of hydrolysis of maltose, has anti-crystalline properties. Important for the usage in food technologies, physicochemical and other characteristics of these substances are given in the Table 1.

Table 1

Parameters of polyols

Polyol	Sweetenary, unit	Energy, kcal/g	Glycemic index, %	Melting point, °C	Solubility in water (20 °C), %
Isomaltitol	0.5–0.6	2.4	9±3	142–150	24.5
Maltitol	0.9	2.4	36	144–152	65.0

Technologies of caramel production using maltitol and isomaltitol are used in world practice, but such products contain high-glucose molasses or artificial sweeteners [3,4].

Antioxidants are important components of a healthy nutrition due to their ability to block a harmful effect on the human body of free radicals. These substances are essential components of all tissues and cells of living organisms. That is why their usage in the technologies of production of functional food products is a modern trend of the food industry development. According to the abstract and citation database Web of Science Core Collection, the number of publications devoted to the research of antioxidant activity of food systems has increased over the course of 20 years in an exponential relation. Thus, the number of sources which have in their title, in the abstract or in the keywords a combination of words "food&antioxidant" reaches about 25307.

In recent years, interest in the antioxidant properties of substances of natural origin has grown [5]. This is due to the fact that the best sources of antioxidants are plants, in particular medicinal ones, which contain them in the form of related compounds complexes [6]. These complexes include phenolic compounds (flavonoids, isoflavonoids, tannins, etc.), vitamins (C, E, A), carotenoids [7, 8], which are able to prevent free radical oxidation

of biological structures of the organism, slowing down aging processes and development of pathological changes.

The usage of plant extracts in confectionery products technologies is not a new practice. However, the technology of full replacement of water on the aqueous extract is a new and interesting solution in the enrichment of candy caramel [9].

In this study, water extracts of chamomile and peppermint were preferred, the chemical composition of which is quite rich in the presence of antioxidants, and the extracts have satisfactory organoleptic indicators. Dried *Matricaria chamomilla L.* flowers (MCF) are traditionally used in medical practice. From a pharmacological point of view, this product is a selective inhibitor of COX-2 with anti-inflammatory activity [10], demonstrates antimicrobial, antioxidant, antiplatelet and chemopreventive effects [11, 12]. The antioxidant effect of MCF is associated with the content of essential oil (not less than 0.3%), which includes chamazulene, prochamazulene, other terpenes and sesquiterpenes [13], as well as the presence of polyphenolic compounds [14, 15].

Menthae piperitae folia (MPF) contains essential oil (2-3%), which includes menthol, pinene, limonene, felandren, cineol and other terpenoids. In addition, flavonoids, ursolic and oleanolic acids, betaine, carotene, hesperidin, tannin substances, organic acids, trace elements can be found in the mint leaves [6]. According to [16-21], extracts of MP demonstrate analgesic, antibacterial, antiviral, choleretic and antinociceptive activity, antioxidant and antiallergic effects.

Among natural antioxidants the most common is ascorbic acid (AA), which can not only prevents free radical oxidation, but also takes part in the synthesis of collagen, promotes adsorption of iron and excretion of cholesterol [22].

Thus, the developed technology of candy caramel on the basis of sugar substitutes with the adding of ascorbic acid and extracts of MPF or MFC allow to provide in this product dietary and functional properties. Among the latest, the most important are antioxidant properties, the results in the researches of which are the purpose of this publication.

Materials and methods

Materials

The following chemicals used in this study are as follows: potassium bromide, potassium iodide, sodium hydroxide, sodium carbonate (Reachim, Russia); Sulphur acid and hydrochloric acid (Sumychimprom, Ukraine); gallic acid (Sigma Aldrich, USA); ascorbic acid (China). All the chemicals used in this experiment were of analytical grade, except for ascorbic acid, which were of pharmaceutical grade (British Pharmacopeia).

For manufacture of the candy caramel isomaltitol (Isodeco, Italy), maltitol (Intenson, Poland) and fructose (Vitamin, Ukraine) was used.

The synthesis of Folin-Ciocalteu reagent was done according to the procedure [23]. All the chemicals used in this procedure were of analytical grade. For analysis 2 M solution was used.

For preparation of the solutions distilled water with electric conductivity no more 0.55 mS/m was used.

Preparation of *Menthae piperitae* folia and *Matricaria chamomilla L.* flores extracts

Dried samples of *Menthae piperitae* folia and *Matricariae chamomilla L.* flores (Liktravi, Ukraine) were purchased from the local pharmacy.

During the experiment, it was found that the liquid-solid phase extraction for the ratio of dried plant material (*Menthae piperitae* folia or *Matricariae chamomilla L.* flores) to the solvent mass (water) (S/L) 1:10 has a maximum yield.

For process of extraction important parameter is the particle size of the raw material. It was established that the maximum yield of soluble solids during extraction was obtained for the particle size of 1-3 mm.

When investigating the effect of temperature and duration of extraction, experimental data were obtained at room temperature and in thermostat conditions. Additional studies have shown that the best transition of dry matter occurs during heat treatment near 100 ° C (97-98 ° C) for 12-15 minutes and subsequent storage of the extract for 120-150 minutes in room conditions.

Thus, the exact weighting of the crushed powder of the sample (10.0 g) was boiled from 100 ml of water for 12-15 min. Subsequently, extractions were performed by maceration for 120-150 min at room temperature. The mixture was filtered using a paper filter. The content of soluble solid in the finished extracts did not exceed 5°Bx.

The extracts obtained were used to produce caramel, as well as to study their antioxidant capacity and the content of polyphenolic compounds. Between the experiments, samples were stored in a frozen state at -18 °C.

Manufacture of candy caramel with plant extract

Candy caramel was produced by innovative technology, the features of which were as follows:

- it was proposed to completely replace the water with extracts of plant material (*Menthae piperitae* folia or *Matricariae chamomilla L.* flores), taking into account the amount of soluble solids of the extract;
- a mixture of isomaltol-fructose (85:15, w/w) and maltitol-fructose (90:10, w/w) was used;
- mass fractions of *Menthae piperitae* folia and *Matricariae chamomilla L.* flores extracts in the caramel content were respectively 30% and 10% by weight of the sugar substitute-fructose mixture;
- the so obtained syrup was added to the content of soluble solids 98 °Bx;
- to provide candy caramel the necessary organoleptic properties and increase the antioxidant activity at the stage of cooling the caramel mass at a temperature of 80-85 °C was added to the caramel ascorbic acid in the amount of 2% to the mass of samples.

Preparation of caramels aqueous solutions

Determination of antioxidant properties of caramel with the addition of plant extracts was carried out using aqueous solutions. From five to eight grams of candy caramel was accurately weighed and was triturated in a porcelain mortar with 10-20 ml of water. Then transferred quantitatively to a pre-weighed conical flask. After addition of distilled water in a ratio 1:10 (w/w) and weighed the solution.

The effect of the caramel`s components on its the antioxidant properties was studied using the following eight types of candy caramel samples (Table 2).

Table 2

Candy caramel samples

Abbreviation of sample	Basic compounds of samples		
	Sugar substitutes	Extract	Ascorbic acid
K1	maltitol	–	–
K2		*Matricaria chamomilla L.* flores	–
K3		–	present
K4		*Matricaria chamomilla L.* flores	present
K5	isomaltitol	–	–
K6		*Menthae piperitae* folia	–
K7		–	present
K8		*Menthae piperitae* folia	present

Determination of physico-chemical parameters

The electric conductivity was measured by conductometer CEL-1M2 (Analitpribor, Georgia). Total soluble solids based on the degree of brix (°Bx) was by using a refractometer URL (Avtomatika, Armenia) according [24].

The pH and temperature of solutions was determined by 692 pH/Ion Meter (Metrohm, Swizz) with Combined LL pH glass electrode with Pt 1000 temperature sensor (Metroohm, Swizz).

If necessary, the solutions were kept at a constant temperature using the thermostat 1TZH-0.03 (Russia). The temperature in this device was maintained at an accuracy of 0.2 °C and determined by the sensor SM60-Pt1000 (Yokogawa Europa, Holland) with a precision of 0.1 °C.

The samples were weighed on laboratory scales balance CBA-300-0.005 (T-Scale, China) with accuracy of 5 mg and on analytical laboratory scales balance VLR-200 (Gosmetr, Russia) with accuracy up to 0.1 mg.

Determination of Ascorbic Acid

The amount of ascorbic acid in solutions of caramel samples was determined by the coulometry with electrogenerated iodine [25]. The electrogeneration of iodine was performed using a PU-1 (ZIP, Belarus) potentiostat in a 0.1 M solution of KI in an phthalate buffer solution (pH=4,01), this was performed on a platinum electrode SM29-PT9 (Yokogawa Europa, Holland) under a constant current of 2.0-5.0 mA.

The end┐ point of titration was established a potentiometric method with two platinum EPV-1 (ZIP, Belarus) and silver chloride EVL-1M3.1 (ZIP, Belarus) electrodes.

Monitoring and experimental data recording (electromotive force-time) was performed electronically with the help of PhCh Data logger device (Arduino Uno microcontroller with

ADS1115 16-bit analog-to-digital converter and automatic timer relay) and PhCh Graph software.

Validation of method for the determination of AA was carried out according to [26].

The concentration of AA m (mg/100g sample) in candy caramels was established by the equation:

$$m = \frac{100ItM}{nFm_{al}}$$

where I is current strength, t is the time of the titration end-point, M is the molar weight of AA, F is Faraday's constant 96500 C/mole, n is the number of electrons, participating in the reaction, m_{al} is the weight of the aliquot portion of the solution.

Determination of the Total Antioxidant Capacity

TAC of simples was determined by the reaction with electronegative bromine as [26, 27] using the same method that was detailed for ascorbic acid. The experimental data of coulometric titration were used to calculate the TAC(q) as the electricity quantity Q, spent for titration per 100 g of the sample and it were calculated by expression:

$$TAC(q) = \frac{100\ Itm_{sol}}{m_{al}m_{sam}}$$

where m_{sam} is the weight of the sample (dry powder of plant or candy caramel), m_{sol} is the total weight of the solution for candy caramel or of the extract for powder of plant.

The total antioxidant capacity (3) is expressed in units of ascorbic acid, recalculated per 100 g of sample. Values of TAC in ascorbic acid equivalent (mg AAE/100 g sample) were calculated by expression:

$$TAC = \frac{TAC(q) - a}{b}$$

where a and b are parameters of linear regression Y=a+bX on series working standard solutions of ascorbic acid or gallic acids in water.

For aqueous solutions of AA the coefficients of the linear regression were determined in [28].

To calculate the experimental values of TAC in the equivalent of the mass of gallic acid (GA) as a reference, a coulometric titration of standard aqueous solutions of gallic acid at a concentration of 10-1000 μg/g by electrogenerated bromine was conducted as a reference (Table 3).

Table 3

Linear regressions Y=a + b·X on series working standard solutions of gallic acid in water (coulometry)

Regression parameters	Data
Range, mg/kg	10-1000
Regression equation:	$Y=a+bX$
Slope, b	2.2693
Intercept, a	0.2567
Regression coefficient, r	0.9998
Standard deviation of the analytical signal, σ	1.269
Limit of detection, mg/kg	1.8
Limit of quantitation, mg/kg	5.6

The obtained dependence is linear with a high coefficient of correlation of 0.9998 and an slope of the curve of 2.2693, which, with an accuracy of 0.18%, corresponds to the theoretical value of 2,2686 for gallic acid according to the Faraday law.

Determination of the Total Phenolic Content

The concentration of phenolic compounds in samples was estimated using a modified spectrophotometric Folin-Ciocalteu method according Singleton and Rossi [29] with the transition from volume to weight of the aliquot portion. Briefly, 0.1 g of extract, standard or blank solution was mixed with 0.5 g of Folin-Ciocalteu's reagent and 2 g water. A sample of extracts was previously diluted in 10 times. After 8 min, 1.5 g of sodium carbonate 20% (w/w) solution was added to the mixture and adjusted to 10 g with distilled water. Mixture was incubated for 30 min in thermostat at 45 °C temperature. Finally, measurement of absorbance was carried out in spectrophotometer SF-46 (Lomo, Russia) at wavelength of 765 nm against a blank sample.

Gallic acid was used as a standard. The TPC values were expressed as mg of gallic acid equivalents (GAEs) per g of dry weight (SW) of plant. A 1000 mg/kg stock solution of gallic acid was prepared by dissolving 0.1 g of gallic acid in 100 g of distilled water. Working standard solutions of gallic acid at five different concentration levels (25, 50, 100, 250, and 500 mg/kg) were prepared by dilution of the stock solution.

The gallic acid calibration curve was constructed in the range of 25–500 mg/kg and used to calculate linear regression models (Table 4).

Statistical analysis

One-way analysis of variance (ANOVA) was carried out on the experimental results. Determination of the experimental values were done for a number of parallel measurements (n=4). The difference of parameters were tested by Student's t-test. A $p < 0.05$ was considered as statistically significant. All results were presented as mean value ± confidence interval. The data was analyzed by using OriginPro v.8 (OriginLab Corp., USA) statistical software.

Table 4

Linear regressions Y=a + b·X on series working standard solutions of gallic acid in water (The Folin–Ciocalteu method)

Regression parameters	Data
Range, mg/kg	25-500
Regression equation:	*Y=a+bX*
Slope, b	0.00104
Intercept, a	- 0.00262
Regression coefficient, r	0.9993
Standard deviation of the analytical signal, σ	0.0031
Limit of detection, mg/kg	0.25
Limit of quantitation, mg/kg	0.76

Results and discussion

Ascorbic acid amount in candy caramel simples

Table 5 shows us experimental data on the amount of ascorbic acid in candy caramel samples.

According to the technological process, 2000 mg of ascorbic acid were added to the samples at the stage of cooling the caramel mass at a temperature of about 40 °C. For comparative analysis, samples of caramel with ascorbic acid and with the addition (K4, K8) or without addition (K3, K7) of chamomile and mint extracts were prepared.

According to the data on the Table 4, despite the usage in the technological process of the manufacturing of high-temperature caramel, there are about 50% of the initial number of ascorbic acid remained in samples.

Table 5

Ascorbic acid amount in candy caramel samples (n=4, P=0.95)

Sample	Added according recipe, mg	Founded in experiment, mg	RSD, %	Residue amount, %
K3	2000	1179 ± 15	1.7	59.0%
K4	2000	1100 ± 13	2.0	55.0%
K7	2000	1325 ± 16	2.3	66.3%
K8	2000	953 ± 9	1.5	47.6%

It is known that ascorbic acid is a very volatile and thermolabile substance and is easily oxidized by oxygen in aqueous solutions to dehydroascorbic acid [30]. A more complex mechanism occurs in dehydrated food systems [31], which include caramel. Therefore, the result is quite satisfactory. Further researches on the stability of ascorbic acid in the food caramel matrix over time will allow us to assess the prospect of caramel production as a prophylactic agent enriched with the required amount of vitamin.

Antioxidant properties of plant extract

One of the conditions for using the Folin-Ciocalteu spectrophotometric technique is the need for experimental values of optical density in the range that does not exceed the value of optical density of a standard solution with maximum concentration. That is, in our case, 0.6 for a solution of gallic acid at a concentration of 500 μg/g. During the usage for calculations of standard solutions with a concentration above 500 μg/g, the graduated graph of the optical density dependence on the concentration of gallic acid becomes nonlinear. During the analyzing objects when it comes to determining the total content of polyphenols, this circumstance should not be logically significant. Indeed, if we have a similar nonlinear dependence for a plant sample, we calculate the standard procedure with allowance for the nonlinearity of the standard curve.

For a more detailed study of this issue, the procedure for defining TPC has been modified. Thus, for a peppermint extract, instead of a single sample weighing 0.1 g in the standard TPC determination procedure given above, 6 samples with a mass in the range of 0.06-0.35 g were used, and for the chamomile extract, respectively, 3 samples with a mass in the range of 0.15-0.35 g. The results are shown in Figure 2

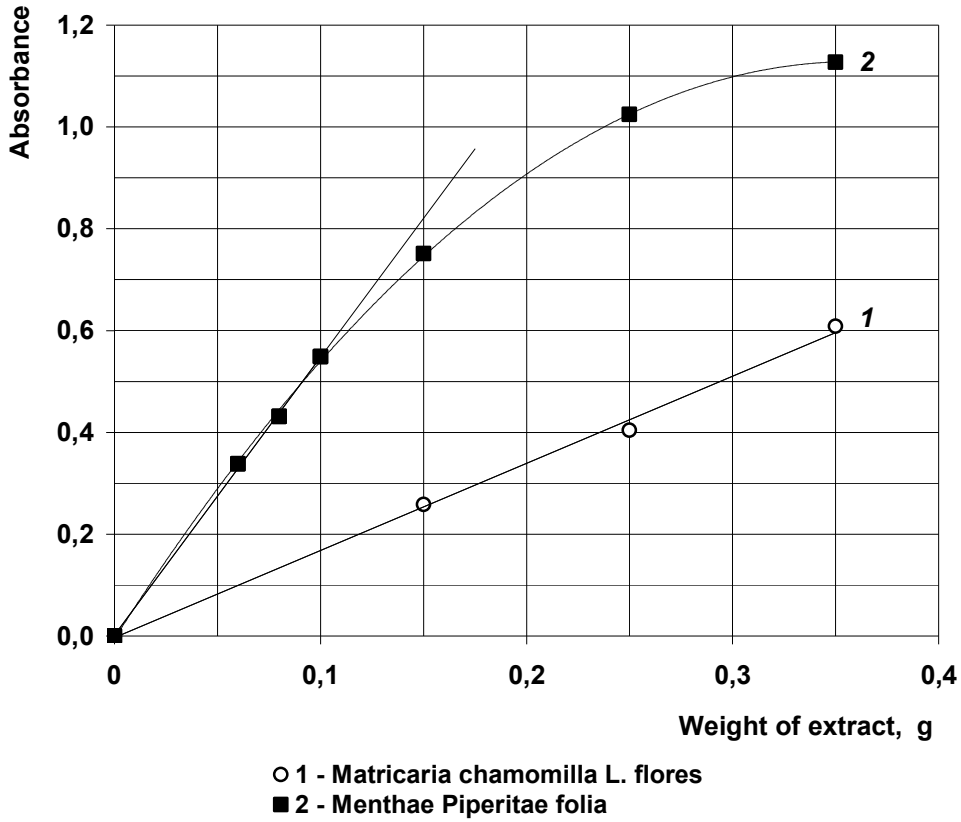

Figure 2. Dependence absorbance of solution from weight of extracts in reaction with Folin-Ciocalteu reagent

As can be seen from Figure 2, for the chamomile extract, all samples have an optical density in the range of the linearity of the graduated graph to a value of 0.6. The calculated TPC values for each of the 3 samples were obtained in the range of 15.8-16.9 mg GAE/g SW with an average value of 16.5 mg GAE/g SW. Approximation of the obtained linear regression dependence with the inclusion of zero concentration allows obtaining a value of 17,1 mg GAE/g SW. This value is more statistically substantiated than the average value of several measurements or even a single one.

In the case of peppermint extract, a nonlinear dependence of optical density on the sample mass after 0.1 g was obtained. During the calculation of the TPC under the standard procedure, even with the application of a nonlinear graduated graph, we obtain the concentration for the same sample in the range of 31.3–55.0 mg GAE/g SW, which is hardly a satisfactory procedure. We have some uncertainty about the size of the TPC sample and its dependence on the size of the sample extract mass in the determination procedure. During the usage of only a linear dependence, i.e. for a peppermint extract, it is 3 of 6 points in the range of 0.06-0.1 g and it has a TPC value in the range of 52.6-55.0 mg GAE/g SW. During the approximation of the linear regression dependence, we obtain a value of 55.0 mg GAE/g SW.

Thus, in order to obtain the correct values of the TPC of plant extracts, we have a modification of the spectrophotometric procedure of determining the total content of polyphenols from the Folin-Ciocalteu reagent, which includes the following:

1. Application of several samples of the test object instead of one with the variation of the ratio of the Folin-Ciocalteu reagent: the reducing agent (polyphenols of a sample), with the verification of the linearity of the analytical signal in the operating range of sample concentrations;

2. The usage of the samples mass in the procedure, whose optical density of solutions does not exceed the maximum optical density of the linear range of the graduated graph for the standard solution;

3. Approximation of the dependence of the linear regression curve (with the inclusion of a zero value) for obtaining statistically substantiated values of TPC.

Table 6 shows us TAC and TPC data for mint and chamomile extracts.

Table 6

Total antioxidant capacity, total polyphenols and flavonoids in *Matricaria chamomilla L.* flores and *Menthae piperitae* folia extracts (n=4, P=0.95)

Extract	TAC		RSD, %	TPC, mg GAE/ g SW	RSD, %
	mg AAE/ g SW	mg GAE/ g SW			
Menthae piperitae folia	83.3±2.4	40.0±0.8	1.6	54.5±0.8	1.6
Matricaria chamomilla L. flores	48.4±1.6	23.3±0.5	2.5	17.1±0.6	1.3

The values of TAC for comparability in the subsequent discussion of the results are presented with the usage of two referential substances - ascorbic and gallic acids. The obtained value of TPC 17.1 mg GAE/g SW for aqueous extract (1:10 w/w) of Matricaria chamomilla L. corresponds properly to the values of 14.697 and 17.8 mg GAE/g

SW, according to [14, 15], respectively. Also, there is satisfactory data comparability on the total antioxidant capacity of TACs aqueous infusions of these plant samples that were obtained also by the method of coulometric titration [32]. The values of TAC, expressed in terms of the amount of electricity without the usage of referential substance, given by the authors are 0.46 and 0.87 kC/100 ml infusion, compared to 0.53 and 0.91 kC/100 ml obtained in this work for MCF and MPF, respectively.

According to the data on the Table 2, the peppermint extract has high antioxidant properties of 72, 1% of the equivalent of ascorbic acid (mg AAE/g SW) and 71.8% of the equivalent of gallic acid (GAE/g SW) compared with the same extract of MCF. The content of polyphenols in the extract of MCF is 2.9 times less than in the extract of MPF. This is due to the presence in the mint the content of substances that are stronger antioxidants compared with the chemical composition substances of MCF.

Antioxidant properties of candy caramels

The results obtained from TAC and TPC for solutions of caramel samples are given in Table 7. According to the data on the Table 7, the antioxidant properties of TAC and TPC for the investigated samples of candy caramel vary in the same way as in the variety of samples of caramel based on maltitol (K1-K4) and in a variety of samples of caramel based on isomaltol (K5-K8). The various mechanisms of oxidative-reduction reactions, simulating the action of radical oxidation are used in these methods of study of antioxidant properties. Thus, in the determination of the TAC, the oxidation reaction with electrogenerated bromine [25], occurs, while in the determination of the TPC, a Folin-Ciocalteau reagent consisting of a mixture of molybdenum tungstic heteropoly compounds in which molybdenum and tungsten, being in a state of oxidation of 6+, form molybdenum tungstic heteropoly anions with an average state of oxidation of metals from 5 to 6 during the reaction with the reducing agent [33]. Despite the different mechanism of action of the reactions on which these methods of evaluation of antioxidant properties of systems are based, there is a rather high positive correlation between the data obtained (Figure 3). This indicates that the coulometric determination methodology for TACs is sufficiently adequate for these purposes in the studied food systems. This conclusion can be made taking into account the fact that there aren`t almost any alternatives in application of the spectrophotometric technique with the Folin-Ciocalteau reagent in relation to the definition of polyphenols as antioxidants.

Table 7

Antioxidant properties of candy caramel samples (n=4, P=0.95)

Sample of candy caramel	TAC		RSD, %	TPC, mg GAE/ 100 g simple	RSD, %
	mg AAE/ 100 g simple	mg GAE/ 100 g simple			
K1	*53 ± 4*	*14 ± 3*	2.4	*97 ± 5*	1.5
K2	178 ± 2	75 ± 5	2.6	132 ± 4	1.7
K3	1781 ± 56	603 ± 10	2.8	*1041 ± 10*	1.2
K4	1680 ± 64	857 ± 10	3.1	*1546 ± 13*	1.5
K5	41 ± 8	8,6 ± 2	3.6	24 ± 2	1.3
K6	365 ± 9	165 ± 11	2.5	332 ± *9*	1.4
K7	1825 ± 15	872 ± 15	2.1	*1340 ± 23*	1.5
K8	1874 ± 16	895 ± 12	1.9	*1586* ± 19	1.6

However, it is necessary to make a significant remark regarding the presented in Table 7 data. The values for K1 and K4 samples are not consistent with the general values of antioxidant capacity and polyphenols content, were selected in italics. Also, for samples K3, K4, K6 and K7 the correction is required in the amount of the total content of polyphenols.

Indeed, samples that are made on the basis of fructose and sugar substitutes (K1 and K4 only) have the minimum values of TAC and TPC which are associated with the oxidation of these substances. During the determination of TPC, these substances cannot be attributed to compounds of phenolic nature, and as in the case of reduced sugars, metal ions, ascorbic acid, etc., are considered to be concomitant substances, as indicated in the methods of determination the total content of polyphenols by reaction Folin-Ciocalteu [34]. In the presence of such substances in complex food systems, correction should be made for their presence during the determination of the TPC value of the entire system [23]. Thus, the selected values of the TPCs of the K1 and K4 systems, which actually do not have any polyphenolic nature in, are corrective for the TPC of other systems, given that these systems are included in other as subsystems. The same applies to TAC, given that the components of these samples are not antioxidants.

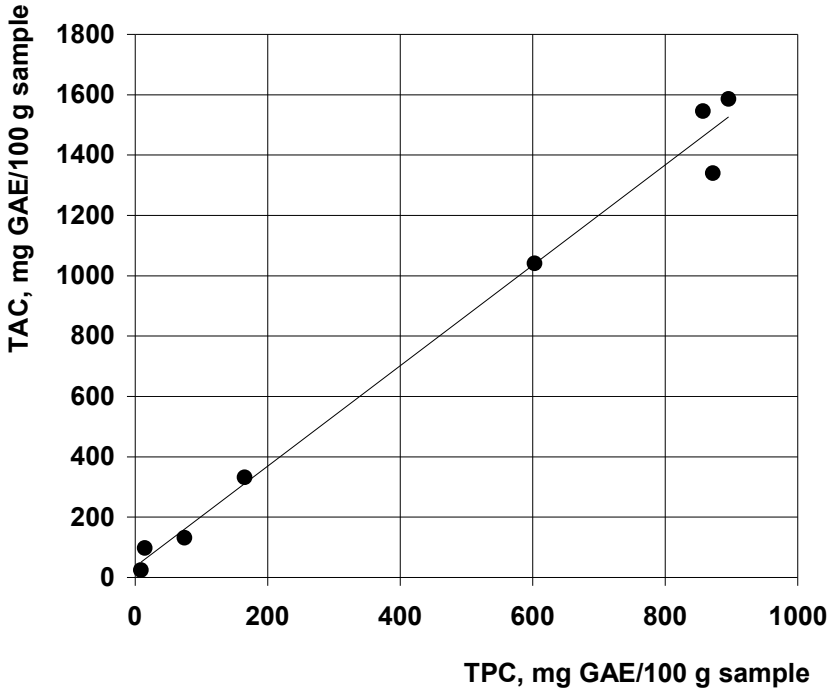

Figure 3. Correlation plots for TAC vs. TPC of candy caramel samples

For caramel samples K3, K4, K7 and K8, ascorbic acid which is present in the formulation and makes its contribution to the TAC value as an antioxidant is not a substance of the phenolic nature, which also needs correction for the determined values of TPC caramel.

Taking into account the foregoing, after making the necessary corrections, we obtain the following values of TPC for samples of the final product 408 and 222 mg GAE/100 g of the sample for caramel K4 and K8, respectively. These results indicate that despite the higher value of TPC for the peppermint extract and its higher content in the mass of the corresponding caramel, less value was obtained for the content of polyphenols for a caramel sample that is based on this extract compared to chamomile extract samples. An explanation of the obtained patterns in the values of TPC for these samples should be sought in the tread mechanism of the interaction of ascorbic acid with polyphenols; an issue requires more detailed researches than at the level of integral values of TAC and TPC.

For samples of caramel K2 and K6, in which there is no ascorbic acid, there is a reverse trend, namely, a higher content of polyphenols in caramel based on mint. This corresponds to the values of TPCs of aqueous extracts, and samples K2 and K6 were enriched by them.

Conclusion

The following conclusions can be drawn, based on the obtained results:

1. As a result of the study of antioxidant properties of mint and chamomile extracts, it was found that the peppermint extract has a larger antioxidant capacity of 40 versus 23.3 mg GAE/g SW due to the higher amount of polyphenolic compounds. This is evidenced by the higher value of the total content of polyphenolic compounds of 54.5 and 17.1 GAE/g SW, respectively.

2. Determination of the content of ascorbic acid in samples of candy caramel indicates that, despite the application in the technological process of manufacturing the high temperatures caramel, it was remained from 48 to 66% of the initial number of ascorbic acid in the samples. This fact is the basis for the application of this technology for the production of vitamin-rich caramel, and its use for prophylactic purposes.

3. Investigation of caramel samples with variation of the recipe components allowed us to determine the correct values of the total content of polyphenolic compounds for two samples of candy caramel: 408 mg GAE/100 g sample for caramel based on maltitol and chamomile extract and 222 mg GAE/100 g for caramel based on isomaltol and peppermint extract.

4. The procedure of spectrophotometric determination of the total content of polyphenolic compounds in plant objects was modified for the purpose of obtaining statistically substantiated results.

References

1. Kay O'Donnell, M. K. (Ed.) (2012), *Sweeteners and sugar alternatives in food technology* (2nd ed.), Oxford, UK: Wiley-Blackwell.
2. Nabors L. O. B. (2004), *Alternative sweeteners*, *Agro Food Industry Hi-Tech*, *Vol. 15*. doi:10.1017/CBO9781107415324.004
3. Zumbé A., Lee A., Storey D. (2001), Polyols in confectionery: the route to sugar-free, reduced sugar and reduced calorie confectionery, *British Journal of Nutrition*, 85(S1), pp. S31. doi:10.1079/BJN2000260
4. Hartel R. W., von Elbe J. H., Hofberger R. (2018), *Confectionery Science and Technology*, Cham: Springer International Publishing. doi:10.1007/978-3-319-61742-8

5. Charles D. J. (2013), *Antioxidant properties of spices, herbs and other sources*, *Springer 4* (Vol. 9781461443). doi:10.1007/978-1-4614-4310-0
6. Marta C.T. Duarte, M. R. (Ed.) (2015), *Therapeutic Medicinal Plants: From Lab to the Market*, Boca Raton: CRC Press. doi:10.3402/ljm.v7i0.16205
7. Banjarnahor S. D. S., Artanti N. (2014), Antioxidant properties of flavonoids, *Medical Journal of Indonesia*, 23(4), pp. 239–244. doi:10.13181/mji.v23i4.1015
8. Procházková D., Boušová I., Wilhelmová N. (2011), Antioxidant and prooxidant properties of flavonoids, *Fitoterapia*, 82(4), pp. 513–523. doi:10.1016/j.fitote.2011.01.018
9. Mazur L., Dorochovich A., Savchuk S. (2016), Use of phyto-tea extracts in the production of candy caramelIn , *Scientific achievements of youth - solving problems of human nutrition in the XXI century: materials of 82 international scientific conference of young scientists postgraduates and students, Kiyiv, NUCHT* , p. 163.
10. Srivastava J. K., Pandey M., Gupta S. (2009), Chamomile, a novel and selective COX-2 inhibitor with anti-inflammatory activity, *Life Sciences*, 85(19–20), pp. 663–669. doi:10.1016/j.lfs.2009.09.007
11. McKay D. L., Blumberg J. B. (2006), A Review of the bioactivity and potential health benefits of chamomile tea (Matricaria recutita L.), *Phytotherapy Research*, 20(7), pp. 519–530. doi:10.1002/ptr.1900
12. Munir N., Iqbal A. S., Altaf I., Bashir R., Sharif N., Saleem F., Naz S. (2014), Evaluation of antioxidant and antimicrobial potential of two endangered plant species Atropa belladonna and Matricaria chamomilla., *African journal of traditional, complementary, and alternative medicines : AJTCAM*, 11(5), pp. 111–7. doi:http://dx.doi.org/10.4314/ajtcam.v11i5.18
13. Sazegar M. R., Banakar A., Bahrami N., Bahrami A., Baghbani M., Nematolahi P., Mottaghi M. (2011), Determination of the Antioxidant Activity and Stability of Chamomile (Matricaria chamomilla L .) Extract in Sunflower Oil, *World Appl. Sci. J.*, 12(9), pp. 1500–1504.
14. Seddik K., Dalila B., Saliha D., Saliha D., Smain A., Noureddine C., Lekhmici A. (2013), Polyphenols and antioxidant properties of extracts from Mentha pulegium L. and Matricaria chamomilla L., *Pharmacognosy Communications*, 3(2), pp. 35–40. doi:10.5530/pc.2013.2.8
15. Harbourne N., Jacquier J. C., O'Riordan D. (2009), Optimisation of the extraction and processing conditions of chamomile (Matricaria chamomilla L.) for incorporation into a beverage, *Food Chemistry*, *115*(1), pp. 15–19. doi:10.1016/j.foodchem.2008.11.044
16. Noue T. I., Ugimoto Y. S., Asuda H. M., Amei C. K. (2002), Antiallergic Effect of Flavonoid Glycosides Obtained from Mentha piperita L ., *Biol. Pharm. Bull.*, 25(2), pp. 256–259.
17. Taher Y. A. (2012), Antinociceptive activity of Mentha piperita leaf aqueous extract in mice Yousef, *Libyan Journal of Medicine*, 1, pp. 7–11. doi:10.3402/ljm.v7i0.16205
18. Barbalho S. M. (2017), Properties of mentha piperita : a brief review, *World Journal of Pharmaceutical and Medical Research*, 3(1), pp. 309–313.
19. Meenatchisundaram S., Parameswari G., Sunny D., Brinda M., Subbraj T. (2009), Pharmacological Activities of Mentha piperita- Mini Review, *Ethnobotanical Leaflets*, 13, pp. 213–215.
20. *Assessment report on Mentha x Piperita L.; Folium; EMEA/HMPC/193910/2007* (2008), London.
21. Neves J. M., Gomes L. R., Moutinho C., Matos C., Neves J. M., Teixeira D. M. (2013), Antispasmodic activity of aqueous extracts from Mentha x piperita native from Trás-

osMontes region (Portugal), *International Journal of Indigenous Medicinal Plants*, 29(1), pp. 1167–1174.
22. Parsons E. (Ed.) (2016), *Ascorbic Acid: Properties, Synthesis and Applications*, Nova Science Publishers.
23. Singleton V. L., Orthofer R., Lamuela-Raventós R. M. (1999), [14] Analysis of total phenols and other oxidation substrates and antioxidants by means of folin-ciocalteu reagentIn , *Methods in Enzymology* (pp. 152–178). doi:10.1016/S0076-6879(99)99017-1
24. *AOAC Official Methods of Analyisis of AOAC International* (2000), (17th editi.), Gaithersburg: MD.
25. Ziyatdinova G. K., Nizamova A. M., Budnikov G. K. (2010), Galvanostatic coulometry in the analysis of natural polyphenols and its use in pharmacy, *Journal of Analytical Chemistry*, 65(11), pp. 1176–1180. doi:10.1134/S1061934810110146
26. Gubskyi S., Nikitin S., Evlash V., Nemirich O. (2015), Iodine content determination in dried talli of laminaria by galvanostatic coulometry, *Ukrainian Food Journal*, 4(2), pp. 320–327. doi:10.13140/RG.2.1.4488.6485
27. Gubsky S., Artamonova M., Shmatchenko N., Piliugina I., Aksonova E. (2016), Determination of total antioxidant capacity in marmalade and marshmallow, *Eastern-European Journal of Enterprise Technologies*, 4(11(82)), pp. 43. doi:10.15587/1729-4061.2016.73546
28. Evlash V., Gubsky S., Aksonova E., et al. (2016), Determination of ascorbic acid amount in gelatin aqueous solutions by galvanostatic coulometry using electrogenerated bromine, *Industrial Technology and Engineering*, 18(1), pp. 22–31.
29. Singleton V. L., Rossi J. A. (1965), Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents, *American Journal of Enology and Viticulture*, 16(3), pp. 144 LP-158.
30. Yuan J.-P., & Chen F. (1998), Degradation of Ascorbic Acid in Aqueous Solution, *Journal of Agricultural and Food Chemistry*, 46(12), pp. 5078–5082. doi:10.1021/jf9805404
31. Kirk J., Dennison D., Kokoczka P., Heldman D. (1977), Degradation of ascorbic acid in a dehydrated food system, *Journal of Food Science*, 42(5), pp. 1274–1279. doi:10.1111/j.1365-2621.1977.tb14477.x
32. Lapin A. A., Borisenkov M. F., Karmanov A. P., Berdnik I. V., Kocheva L. S., Musin R. Z., Magdeev I. M. (2007), Antioxidant properties of vegetable products origins, *Khimija Rastitel'nogo Syr'ja*, *2*, pp. 79–83 (in Russian).
33. Agbor G. A., Vinson J. A., Donnelly P. E. (2014), Folin-Ciocalteau Reagent for Polyphenolic Assay Description of Folin Ciocalteau Reagent, *International Journal of Food Science Nutrition and Dietetics*, 3(38), pp. 147–156. doi:10.19070/2326-3350-1400028
34. Wrolstad R. E., Acree T. E., et al. (Eds.) (2003), *Current Protocols in Food Analytical Chemistry*, John Wiley & Sons, Inc.

Effects of different holding types and times on quality attributes of oil obtained from olives belonging to Akhisar Region, Turkey

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Keywords:

Olive
Akhisar
Properties
Oxidative
Stability
Quality

Article history:

Received 18.02.2018
Received in revised form 23.03.2018
Accepted 29.03.2018

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DOI: 10.24263/2304-974X-2018-7-1-4

Abstract

Introduction. In this study, it was aimed to determine the effects of different holding types and times on quality attributes of oil obtained by extraction using Abencor system.

Materials and methods. Edremit and Uslu types of olives which are widely grown in the region of Akhisar, constitute the main material of the study. These two kinds of olives were filled into plastic boxes or nylon sacks. After waiting for 0, 7, 14, 21 days, oils were extracted by using Abencor system. Free fatty acid, peroxide value, UV absorption values (at 232 and 270 nm), the amount of total phenol, refractive index, the amount of total chlorphyll and carotenoid contents, fatty acid composition and color values were determined in olive oil samples. Oxidative stabilities and sensorial properties of olive oils were also examined.

Results and discussion. The results indicated that loss in quality of the samples, especially the Uslu variety, holded in sacks. Total phenol content of olive oils were decreased excessively during the holding time for both types of samples. Although the majority of the chemical parameters fell within the limits established by the Legislation. Chlorophyll and carotenoid contents ranged, respectively from 0.7 to 8.69 mg/kg and from 0.7 to 3.44 mg/kg for Edremit olive oil and from 0.93 to 2.17 mg/kg and from 0.96 to 1.49 mg/kg. Oleic (C18:1), linoleic (C18:2), palmitic (C16:0) and stearic (C18:0) acids found as predominant fatty acids in all samples. Oil samples obtained from Edremit variety on the first day of holding and the 7th day of the holding period in sack were classified as extra virgin olive oil. Also oil obtained from Uslu variety on the first day of the holding period showed the caracteristics of extra virgin olive oil according to the sensorial properties. Whereas other samples were classified as virgin olive oil. The initial Induction Period (IP) of Edremit and Uslu olive oils were 3.9 and 3.8 h. For Uslu variety, it was observed a decrease during holding period at each holding types until 21 th day. For Edremit variety, it was not observed a significant decrease during holding period.

Conclusion. According to the results, the chemical parameters analysed in the different samples are within the limits established by the legislation, but vary during the holding period and according to the variety.

Introduction

Olive is a typical plant of Mediterranean countries grown in Aegean, Marmara, Mediterranean and South East Anatolian regions of Turkey. Spain is leading the field in olive oil production and olive growing. Italy, Greece and Turkey follow Spain in olive oil production, respectively. The share of our country in world olive oil production is 5,8 %. With mentioned the positive effects of olive oil on health by the experts, its consumption gradually increase in countries with high level of income. Greece continues to lead the ranking with 12.8 kg per capita per year. It is followed by Spain (11.3 kg), Italy (11.3 kg), Portugal (10.5 kg), Cyprus (5.5 kg), Luxemburg (3.2 kg), Malta (3 kg), France (1.7 kg) and Turkey (1.4 kg) [IOOC, 2015]. Period among the planting of olive tree and serving the olive and olive oil to consumer includes extensive processes such as cultural applications like using appropriate variety, planting and pruning and the other processes like harvesting, transportation, pressing and holding. These processes directly affect both olive and olive oil quality and the amount of product which might be obtained in the future.

In this study, it was aimed to determine the effects of different holding types and times on quality attribute of oil obtained after the pressing. Edremit and Uslu type olive cultivars which are widely grown in the region of Akhisar, Turkey that constitute the main material of the study are harvested in 2012-2013 crop season. Their maturation index was indicated. Then these two kinds of olives filled into boxes and nylon sacks and after waiting for 0, 7, 14, 21 days, oils were extracted by using Abencor system. Free fatty acid, peroxide value, UV absorption values (232 and 270), the amount of total phenol, refractive index, color values, the amount of total chlorophyll and carotenoid contents, fatty acid composition were determined as analytical criteria in olive oil samples. The results of the analyses were compared with the criteria given in the Communication for Edible Olive Oil and Olive Pomace of Turkish Food Codex and International Olive Council Legislation and scientific researches [Anon 2014; IOC 2015]. In addition, sensory properties and oxidative stability were evaluated as quality criteria. Up to our knowledge there are rather limited studies about determination the effects of holding times and types on olive oil quality so it's invented that these results elucidate to researchers.

Materials and Methods

Materials

Edremit and Uslu varieties of olive which are widely cultivated in Akhisar Region of Manisa/Turkey were used. Olives were manually harvested randomly as 10 kg for each variety at 2012 and 2013 harvest season. Harvested samples for each variety were put into plastic boxes (53x37x31 cm) and nylon sacks (60x90 cm) and were kept inside of them for 0, 7, 14 and 21 days (Figure 1 and Figure 2). Samples were randomly taken from the plastic boxes or nylon sacks for each analysis period. Then they were crushed by Abencor system at Institute of Olive Researches, Bornova/Izmir. They were filtered and filled into the dark-bottles and kept at 4°C until being analyzed. Each of the analyses were repeated three times for each smple.

Figure 1. Olive samples holded in plastic boxes

Figure 2. Olive samples holded in nylon sacks

Maturation index

The MI of olive fruits was determined according to the method given in by Vinha *et al.* [2005]. MI was calculated after visual colour inspection over a hundred randomly chosen olives, according to the following formula: MI=(a x 0)+(b x 1)+(c x 2)+(d x 3)+(e x 4)+(f x 5)+(g x 6)+(h x 7)/100. Where a, b, etc. are the number of olives in each of the seven colour classes from dark green to dark black.

Olive oil extraction by Abencor system

Oil was extracted using an Abencor laboratory mill (Polat Machinery Inc.), simulating commercial oil extraction systems. Extraction process consisted of the following steps: fruit

crushing and malaxation for 60 min at 35 ± 1°C, two rounds of centrifugation, 60 s each at 3000 rpm, with 100 mL water added between rounds. After centrifugation, oils were decanted, filtered, transferred into amber glass bottles and holded at 4 °C until analysed.

Determination of physical characteristics

Color valuesof the olive oil samples were determined in terms of L*, a*, and b* criteria using Lovibond PFX880-Tintometer [AOCS 1993a]. The optical path lenght of the glass cell was 1" for extra virgin olive oil. The refractive index values of the samples were carried out using method of Turkish Standard 4960 EN ISO 6320 by Abbe Refractometer at 20°C [Anon, 2010].

Determination of quality criteria

The samples were analyzed after each holding times and types. Acidity (% as oleic acid) and peroxide value (meq O_2/kg) of the virgin olive oil samples were carried out according to the method reported by AOCS [1993b]. and Salvador et al. [2000]. UV specific extinctions of *K*232 and *K*270 were determined by Anon [2014]. Chlorophylls and carotenoids were determined colorimetrically following the method [Morello *et al*. 2004; Beltran *et al*. 2005]. The maximum absorption at 670 nm is related to the chlorophyll fraction and at 470 nm is related to carotenoid fraction.

Total phenol content

Total polyphenol content was analyzed as described [Gutfinger, 1981]. The phenolic compounds were isolated from a solution of oil in hexane by extraction with a water/ methanol mixture (60:40, v/v). The Folin–Ciocalteau reagent was added to a suitable aliquot of the combined extracts, and the absorption of the solution was measured at 725 nm. The results were evaluated in terms of gallic acid as mg GA/kg oil.

Fatty acid composition

Fatty acid compositions of the oil samples were determined by GC [AOCS, 1997]. Methyl esters were prepared by vigorous shaking of a solution of each olive oil sample in n-hexane (0.2 g in 5 mL) with 0.5 mL 2 N methanolic potassium hydroxide solution. Chromatographic analysis was performed on a Agilent Technologies 6890N Gas Chromatograph (*Hewlett-Packard Company, Wilmington, DE, USA*), equipped with a capillary column (Agilent 122-2362: 60 m x 0.25 mm x 0.25 μm), an injector split-splitless and a FID detector. The carrier gas was nitrogen, with a flow rate of 25 ml/mn. Initial oven temperature was 170°C, raised at 2°C/min to 210 °C and hold for 15 min. The temperatures of the injector and the detector were held at 250 °C. Fatty acids were identified by comparing retention times with those of standard compounds.

Measurement of oxidative stability

An automated Metrohm Rancimat apparatus model 743 (Metrohm, Switzerland) capable of operating over a temperature range of 50–200°C was used for induction period determination of oil samples. Fourteen oil samples were analyzed in the equipment at the same time. For oxidative stability measurement, each oil sample (3.0±0.1 g) was weighted

into the reaction vessel glassware. The conductimetry cells were filled with deionized water up to 90 ml. Air was flown through the heated oil at different rates, depending on the temperature. The flow rate of air was 20 l/h used for 120°C. Although this equipment (Model 743 Metrohm) presents a cleaner system of procedure, the glassware was rigorously cleaned between each run to avoid any contamination that would catalyze the peroxidation [Anwar *et al*. 2003; Mateos *et al*. 2006].

Sensory profile analysis

Sensory analysis was carried out by a panel of 10 selected trained judges of the Olive Oil Research Institute, Эzmir, Turkey, coordinated by a panel head [IOOC, 2010]. The sensory sessions were conducted in a sensory room equipped with 10 boots. Panellists evaluated olive oil samples as their negative and positive properties on a scale from 0 to 5.

Statistical Analysis

The data was analyzed utilizing the PROC MIXED procedure of SAS [SAS, 2000]. To find the treatment combination, means including all treatment combinations (holding time, holding types) for each olive variety were generated using the PROC MIXED procedure and these were compared to a control.

Results and Discussion

Physical caracteristics of olive oil samples

According to the different holding types and times, physical caracteristics of olive oils obtained from Edremit and Uslu varieties which were harvested at the maturation index of 3.75 and 4.5 respectively, are given in Table 1 and 2.

L*, a* and b* values of olive oils were ranged between 19.9-85.81, 2.53-12.64 and 30.33-92.8, respectively. After holding period of the olive samples, L*, a* and b* values of the olive oils increased at both type (Table 1-2). As regards to the statistical results, the interaction of holding types and times was found significantly important for L*, a* and b* values at Edremit variety while it was found significantly important only for L* and b* values at Uslu variety ($p<0,0001$). The holding conditions and holding times of olives after harvest, cultivar, soil, climate conditions, degree of ripeness and irrigation can affect color, smell, taste and stability of oils [Kritsakis, 1998]. So, there are differences between initial and subsequent color values of olive oil samples.

One of the physical purity criteria is refractive index values for natural olive oils. Refractive index values of the samples wereamong 1,4696-1,4708. When compared with initial values, there were a slight decrease for each variety due to the holding types and times (Table 1-2).

Table 1

Least squares means of holding times and holding types on color values (L, a*, b*) and refractive index (RI) value for Edremit variety olive oil [a]

Source of variation	L	a*	b*	RI (nD 20° C)
Holding times, week				
0	85,79	12,09	80,09	1,4704a
7	82,49	6,56	50,02	1,4702b
14	37,49	5,2	50,73	1,4698c
21	45,53	6,07	60,81	1,4697c
P-value	<0,001	<0,0001	<0,0001	0,0002
holding types				
box	66,33	9,44	76,21	1,4699
sack	59,32	5,52	44,61	1,47
P-value	<0,0001	<0,0001	<0,0001	0,24
holding timesxholding types				
0/b	85,77f	12,12g	80,07d	1,4704
0/s	85,81f	12,06g	80,1d	1,4703
7/b	80,86e	11,61f	92,8e	1,47
7/s	84,12f	1,52a	71,24c	1,4704
14/b	55,09d	7,87e	71,13c	1,4698
14/s	19,9a	2,53b	30,33a	1,4698
21/b	43,62b	6,16d	60,84b	1,4696
21/s	47,44c	5,98c	60,77b	1,4697
P-value	<0,0001	<0,0001	<0,0001	0,06

Within columns, means with different letters differ *(P<0.05)*.

[a] Letters were not assigned to main effect lsmeans when interaction was significant

Table 2

Least squares means of holding times and holding types on color values (L, a*, b*) and refractive index (RI) value for Uslu variety olive oil [a]

Source of variation	L	a*	b*	RI (nD 20° C)
Holding times, week				
0	85,29	12,6a	82,19	1,4705
7	77,13	10,19b	73,63	1,4707
14	80,19	10,02b	74,81	1,4703
21	80,54	10,26b	74,68	1,4701
P-value	0,0006	0,0004	<0,0001	0,11
Holding types				
box	83,24	10,91	78,22	1,4704
sack	78,33	10,63	74,43	1,4703
P-value	0,0001	0,16	0,0001	0,0002
Holding timesxholding types				
0/b	85,35e	12,64	82,2f	1,4706d
0/s	85,22e	12,56	82,17f	1,4704c
7/b	84,4e	10,72	74,65c	1,4706d
7/s	69,86a	9,67	72,61b	1,4708e
14/b	83,64de	10,02	78,95e	1,4702b
14/s	76,73b	10,03	70,68a	1,4704c
21/b	79,55c	10,26	77,1d	1,4704c
21/s	81,53cd	10,26	72,25ab	1,4698a
P-value	0,0001	0,15	0,003	0,001

Within columns, means with different letters differ *(P<0.05)*.

[a] Letters were not assigned to main effect lsmeans when interaction was significant

Quality criteria of olive oil samples

According to the quality indices (free fatty acids, peroxide value and UV absorption parameters, K232 and K270), all samples were in line with the limit values for EVOO, OO and RFOO set by the Turkish Food Codex on Olive Oils and Olive Pomace Oils [Anon, 2014].

As seen in Table 3 and Table 4, FFA of Edremit and Uslu type olive oils increased constantly during holding time. In Edremit variety, FFA increased to 2.7 % from 0.62 % and for Uslu variety it reached upto 1.33% from 0.25% at the end of holding period in sacks. Regarding the influence of holding conditions, interaction of holding types and

holding times affect FFA content of Edremit olive oil variety ($p<0.0001$) whereas in Uslu olive oil variety only holding times affect FFA content ($p<0.0001$).It is thought that the reason of the high free fatty acidity of the oil was arised from the mechanical injury of the olives during harvest and the harms occurred during 21-days holding period.

Table 3

Least squares means of holding times and holding types on some analytical criteria and total phenol content for Edremit variety olive oil [a]

Source of variation	FFA (% as oleic acid)	PV ($meqO_2/kg$)	K232 ($E^{\%1}1cm$)	K270 ($E^{\%1}1cm$)	Total chlorophyll (mg/kg)	Total carotenoid (mg/kg)	Total phenol (mg/kg GA)
Holding times, week							
0	0,62	4,88	1,69	0,06a	0,61	0,67	251,43
7	0,74	4,94	1,3	0,06a	6,59	2,77	87,28
14	1,6	3,4	1,7	0,18b	4,37	2,22	62,77
21	2,05	3,81	1,85	0,15c	4,21	2,25	44,27
P-value	<0,0001	<0,0001	0,16	<0,0001	<0,0001	<0,0001	<0,0001
Holding types							
box	1,06	3,98	1,48	0,1a	3,48	1,85	113,22
sack	1,44	4,54	1,78	0,12b	4,4	2,1	109,64
P-value	<0,0001	0,0007	0,13	0,03	0,001	0,015	0,21
Holding timesxholding types							
0/b	0,61a	4,83a	1,68	0,06	0,7a	0,7a	235,03f
0/s	0,62a	4,93a	1,7	0,06	0,52a	0,64a	267,83g
7/b	0,75c	4,9a	0,9	0,41	4,5b	2,11b	100,13e
7/s	0,73b	4,99a	1,7	0,82	8,69c	3,44c	74,39d
14/b	1,47e	3,11d	1,7	0,18	4,43b	2,34b	64,48c
14/s	1,73f	3,69c	1,7	0,18	4,3b	2,1b	61,06bc
21/b	1,41d	3,08d	1,67	0,13	4,31b	2,28b	53,26b
21/s	2,7g	4,55b	2,03	0,17	4,1b	2,22b	35,28a
P-value	<0,0001	0,0034	0,33	0,18	0,001	0,0005	0,001

Within columns, means with different letters differ *($P<0.05$).*

[a] Letters were not assigned to main effect lsmeans when interaction was significant

FFA: Free fatty acid, PV: Peroxide value

It is thought that free fatty acid values of the sample increased due to the activity of lipolytic enzymes in the olive fruit. The activity of this enzyme is influenced from fruit quality, climate conditions, maintenance requirements olives and process conditions [Mateos *et al*. 2006].

The effect of holding time and container type on quality of extra virgin olive oil have reported by Mendez and Falquй [2007]. According to their findings, the acidity of olive oil samples increased to 0.38% from 0.25% at the end of 6-month holding period in plastic containers. It is thought that the differences among the results of the researches with literature data depend to a number of factors as olive harvest time, applied technology, preservation and holding conditions of olives.

Table 4

Least squares means of holding times and holding types on some analytical criteria and total phenol content for Uslu variety olive oil [a]

Source of variation	FFA (% as oleic acid)	PV ($meqO_2/kg$)	K232 ($E^{\%1}1cm$)	K270 ($E^{\%1}1cm$)	Total chlorophyll (mg/kg)	Total carotenoid (mg/kg)	Total phenol (mg/kg GA)
Holding times, week							
0	0,25a	6,09c	2,06	0,13a	1,04a	1	174,8a
7	0,47b	9,08a	2,27	0,14a	1,97b	1,22	69,82b
14	1,11c	8,28ab	1,9	0,17ab	1,58ab	1,02	59,37c
21	1,31d	8b	2,62	0,23b	2,1b	1,37	20,22d
P-value	<0,0001	0,0015	0,12	0,04	0,03	0,007	<0,0001
Holding types							
box	0,78	8,19b	2,38	0,17	1,54	1,02	81,74
sack	0,79	7,53a	2,05	0,16	1,8	1,29	80,37
P-value	0,46	0,04	0,15	0,48	0,18	0,003	0,64
Holding times-xholding types							
0/b	0,28	6,39	2,1	0,13	0,93	0,96b	177,33
0/s	0,22	5,79	2,02	0,12	1,14	1,04b	172,26
7/b	0,48	9,49	2,37	0,15	1,76	1,13bc	71,48
7/s	0,47	8,68	2,18	0,14	2,17	1,3cd	68,16
14/b	1,09	8,66	2,37	0,2	1,41	0,72a	60,87
14/s	1,14	7,9	1,42	0,14	1,76	1,33cd	57,88
21/b	1,28	8,24	2,67	0,22	2,1	1,26c	17,26
21/s	1,33	7,76	2,57	0,24	2,14	1,49d	23,18
P-value	0,43	0,95	0,36	0,56	0,89	0,05	0,5

Within columns, means with different letters differ *(P<0.05)*.

[a] Letters were not assigned to main effect lsmeans when interaction was significant

The peroxide value underwent a significant increase up to the 7th day of holding for both variety, then slowly decreased up to the 21th day in box and sack, probably due to the fact that the newly formed oxidation products were further converted to secondary ones (Table 3-4). But nevertheless, they did not exceed the legal limit of ≤20 meqO_2/kg for extra virgin olive oil set by the Anon [2014] and IOC [2015]. According to the statistical results, the interaction of holding types and holding times was found important for Edremit olive oil variety ($p<0.05$, Table 3), whereas for Uslu olive oil variety, the effect of holding times and holding types were found significantly important ($p<0.05$, Table 4). The peroxide value of Edremit and Uslu type olive oils from different regions and different harvest period have identified. Their peroxide value was changed between 3,01–8,05 meq O_2/kg and 4,52–8,16 meq O_2/kg, respectively [Yavuz, 2008]. It was observed that these values are similar to the values in our study. It is known that oxygen in the aircausesa rise in peroxide value. Heat and light accelerate these oxidative chemical reactions. Therefore, olives and olive oils should not be exposed to the oxygen for a long time and should be kept in dark places at 10–15 °C [Allalout *et al*. 2009].

The initial values of the coefficients K232 and K270 are between 1.68 and 0.06 for Edremit variety and 2.12 and 0.12 for Uslu variety, within the limits permitted by the International Olive Council Legislation [IOC, 2015]. In Table 3 and 4, it can be seen that the effect of different holding times and holding types did not significantly affect the changes in K232 value of both type($p>0.05$). But it was found that holding types and holding times had separately significant importance on the changes in K270 value of Edremit olive oil, whereas only the effect of holding times on K270 value was found significantly important for Uslu olive oil ($p<0.05$). K270 value of Uslu olive oil was slightly exceeded the legal limit of ≤2.60 for virgin olive oil as required by IOC at 21th day of holding [IOC, 2015] (Table 4). This occur due to the increase in the number of compounds resulting from the degradation of the hydroperoxides, which is confirmed by an increase of K270 value [Yavuz, 2008].

The natural pigments contents of the oils are important for the quality parameters because they correlate with colour and play a key role as a factor of sensorial acceptability among consumers. Virgin olive oil has a color changing among green-yellow to gold, depending on the variety and the stage of maturity [Salvador *et al*. 2000]. They undergo during fruit ripening and oil holding so they could be considered as a product freshness indicator [Allalout *et al*. 2009]. As shown in Table 3 and Table 4, Chlorophyll and carotenoid contents ranged, respectively from 0.7 to 8.69 mg/kg and from 0.7 to 3.44 mg/kg for Edremit olive oil and from 0.93 to 2.17 mg/kg and from 0.96 to 1.49 mg/kg.

These results are in agreement with the findings of which reported that the chlorophylls and carotenoids contents ranged, respectively from 0.05 to 1.52 mg/kg and 2.03 mg/kg for Moroccan cultivars [Tanouti *et al*. 2011]. It should be noted that the values found for the two pigments were low. This can be attributed to the geographical origin, olive cultivar, fruit ripeness, soil and climatic condition and the processing procedures [Psomiadou and Tsimidou, 2001]. Generally, oils obtained in irrigation regime had higher levels of chlorophyll pigments that non-irrigated one. However, the content of carotenoids was less affected by water supply [Baccouri *et al*. 2008]. Chlorophyll and carotenoid contents of Edremit olive oils have been identified as 0.95–6.73 mg/kg and 1.51–5.13 mg/kg, respectively. They reported that their contents decreased as maturation index increased [Yorulmaz *et al*. 2013].

The effect of interaction of the type of holding types and holding times significantly affected the changes in chlorophyll and carotenoid contents of Edremit variety ($p<0.001$, Table 3), whereas for Uslu variety while the interaction of holding types and holding times

affected the carotenoid content ($p<0.05$, Table 4). For chlorophyll content, only the effect of holding times was found statistically important ($p<0.05$, Table 4).

Total Phenol content of olive oil samples

The amount of total phenolic compounds in virgin olive oil is an important factor when evaluating its quality, given that the natural phenols improve its resistance to oxidation, and to certain extent, are responsible for its bitter taste [Baccouri *et al*. 2008]. The concentration of total phenols ranged between 35.28–267.83 mg/kg and 17.26–177.33 mg/kg for Edremit and Uslu olive oil varieties, respectively (Table 3–4).The higher concentrations of total phenol were found at the beginning of holding for both types. Then total phenols underwent a decrease during holding period. The literature reports that their decrease is due to the decomposition process and the oxidative activity of these compounds [Morello *et al*. 2004]. The most significant decrease of total phenol content occurred during holding in plastic boxes for both types.

Generally, total phenol content of olive oils was lower according to the literature reports. The characteristics of olive and olive oils during ripening have been examined and they found total phenol content between 550.33–810.98 mg/kg in Edremit olive oil [Yorulmaz *et al*. 2013]. In another study, total phenol content of "Bosana" extra virgin olive oil was found between 248-409 mg/kg oil during 16 months of holding under the light and dark [Del Caro *et al*. 2006]. Total phenol content of Edremit virgin olive oils were found between 89.2–128.7 mg/kg harvested in 2005 [Andjelkovic *et al*. 2009]. This results showed similarity with our results. These differences of total phenol content of virgin olive oils are depending to the variety, climatic conditions, maturity index, irrigation, time and type of harvesting, holding and processing technology [Boskou, 1996].

According to the statistical analyses results, it was determined that the interaction of holding types and holding times affected the changes in total phenol content of Edremit olive oil ($p<0.001$, Table 3). On the other hand, only holding time was found statistically important on the changes in total phenol content of Uslu olive oil ($p<0.0001$, Table 4).

Fatty acid composition of olive oil samples

The major fatty acids found in Edremit and Uslu olive oils had oleic (C18:1), linoleic (C18:2), palmitic (C16:0) and stearic (C18:0) acids. These predominant fatty acids were ranged in all samples between 70.05–71.97 %, 10.22–12.13 %, 12.40–13.87 %, 2.01–2.62 %, respectively. The distribution of fatty acids in the samples was in agreement with the Turkish Food Codex on Olive Oils and Olive Pomace Oils [TFC, 2014/53]. Palmitoleic (C16:1), heptadecanoic (C17:0), heptadecenoic (C17:1), linolenic (C18:3), arachidic (C20:0) and gadoleic (C20:1) acids were determined in low amounts.

In Edremit and Uslu virgin olive oils, total SFA, MUFA and PUFA were almost stable due to the different holding types and times as seen in Table 5 and Table 6. The samples showed the lowest total PUFA (10.7–12.05 % for Edremit, 12.16–12.67 % for Uslu) and the highest total MUFA (71.80–73.32 % for Edremit, 71.31–71.99 % for Uslu). As for that total SFA, it varied between 15.77–16.42 % for Edremit and 15.34–16.26 % for Uslu (Table 5–6). Fluctuations in total SFA, MUFA and PUFA contents observed in olive oil samples are related to holding conditions (Table 5–6). The holding times did not affect their contents in both types. The effect of the intereaction of holding time and type was found statistically important on the changes of total MUFA and PUFA contents of Edremit olive oil ($p < 0.05$, Table 5), whereas holding time caused significant effect for SFA and PUFA

contents and also interaction of holding time and type was found important on the changes of total MUFA contents of Uslu olive oil ($p < 0.05$, Table 6).

The fatty acid profiles of our samples were also in good agreement with values obtained for the same varieties in some other studies [Allalout et al. 2009;Yorulmaz *et al*. 2014]. Some characterization of Turkish olive oils have been investigated by Yorulmaz *et al*. [2014]. As they reported, average oleic, linoleic, palmitic and stearic acids of Uslu and Edremit olive oils were 72.34–71.57%, 10.18–10.37%, 12.65–12.98% and 1.70–2.25%, respectively. the total SFA, MUFA and PUFA contents in different cultivars of Spanish and Greece olive oils have been identified as 14.22–20.18%, 61.24–76.61% and 8.82–13.56%, respectively [Allalout *et al*.2009]. Total SFA, MUFA and PUFA contents were 15.5 %, 73.3 % and 8.6 % in different cultivars [Mendez and Falquй, 2007]. Total SFA, MUFA and PUFA contents of Edremit olive oil were 12.59 %, 74.29 % and 8.93 %. They also indicated the major fatty acid as oleic acid (72.78 %) in Edremit olive oil [Matthaus and Цzcan, 2011]. The fatty acid composition of olive oil varies widely depending on the cultivar, maturity of the fruit, altitude climate and several other factors [Matthaus and Цzcan, 2011]. Various factors such as harvest period, cultivar and origin affect the formation of the main fatty acids of olive oil in different ways [Bruni *et al*. 1994].

Table 5

Least squares means of holding times and holding types on total fatty acids composition (*Totals* SFA, MUFA and PUFA) for Edremit variety olive oil [a]

Source of variation	Totals		
	SFA (%)	MUFA (%)	PUFA (%)
Holding times, week			
0	16,38	71,86	11,81
7	15,91	72,96	11,02
14	16	72,07	11,88
21	16,1	72,19	11,62
P-value	0,18	0,0003	<0,0001
Holding types			
box	16,15	72,41	11,43
sack	16,1	72,13	11,73
P-value	0,44	0,01	0,0005
Holding timesxholding types			
0/b	16,42	71,8a	11,9de
0/s	16,34	71,92a	11,72c
7/b	15,93	73,32d	10,7a
7/s	15,89	72,59c	11,33b
14/b	15,81	72,16b	11,94de
14/s	16,2	71,97a	11,82cd
21/b	16,43	72,34b	11,19b
21/s	15,77	72,04ab	12,05e
P-value	0,07	0,05	0,0003

Within columns, means with different letters differ *(P<0.05)*.

[a] Letters were not assigned to main effect lsmeans when interaction was significant

SFA: Saturated fatty acids, MUFA: Monounsaturated fatty acids, PUFA: Polyunsaturated fatty acids

Table 6

Least squares means of holding times and holding types on total fatty acids composition (*Totals* SFA, MUFA and PUFA) for Uslu variety olive oil [a]

Source of variation	Totals		
	SFA (%)	MUFA (%)	PUFA (%)
Holding times, week			
0	15,77ab	71,84	12,48ab
7	16,21a	71,47	12,29b
14	15,43b	71,81	12,61a
21	15,44b	71,9	12,62a
P-value	0,03	0,004	0,02
Holding types			
box	15,69	71,8	12,55
sack	15,73	71,7	12,48
P-value	0,83	0,14	0,15
Stoarge timesxholding types			
0/b	15,68	71,93cd	12,6
0/s	15,86	71,75bc	12,36
7/b	16,26	71,31a	12,41
7/s	16,15	71,62b	12,16
14/b	15,34	71,97cd	12,62
14/s	15,51	71,64b	12,6
21/b	15,49	71,99d	12,57
21/s	15,39	71,8bcd	12,67
P-value	0,84	0,02	0,2

Within columns, means with different letters differ *(P<0.05)*.

[a] Letters were not assigned to main effect lsmeans when interaction was significant

Oxidative Stability of olive oil samples

The Rancimat method is an accelerated stability test that provides very useful information about the resistance of oil to oxidation [Beltran *et al*. 2005]. In Figure 3 is given the changes of IP values at 120°C for Edremit and Uslu olive oils obtained according to the different holding types and holding times. The initial IP of Edremit and Uslu olive oils were 3.9 and 3.8 h. For Uslu variety, it was observed a decrease during holding period at each holding types until 21 th day. At 21th day, there was a slight increase from 1.8 h to 2.1 h in box and 1.9 h to 2.7 h in sack. This caused that nonhomogenous sampling. For Edremit variety, it was not observed a significant decrease during holding period.

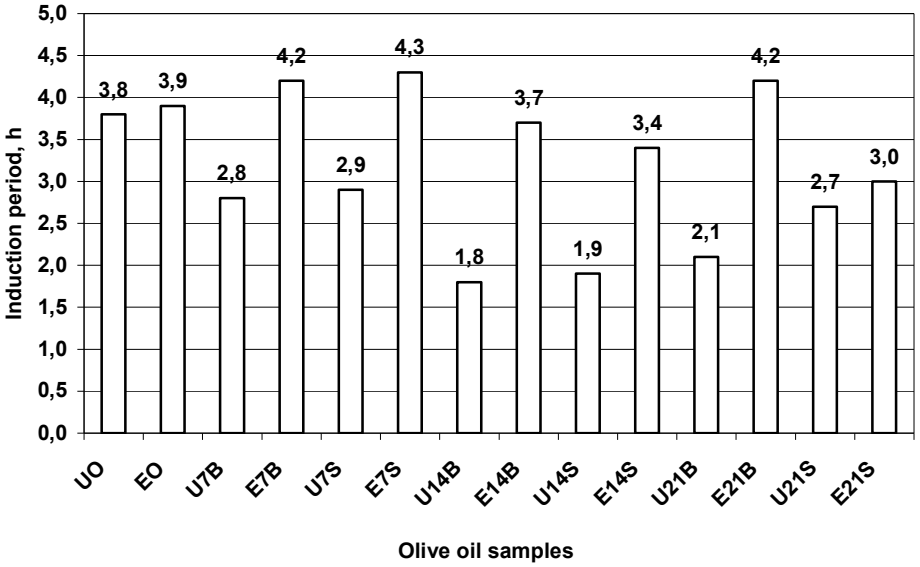

Figure 3. Changes of induction period (hour) of Edremit and Uslu Olive Oil Varieties according to the different storage types and times

UO – Uslu variety first day of harvest
EO – Edremit variety at first day of harvest
U7B – Uslu variety holded at 7 days in box,
E7B – Edremit variety holded at 7 days in box
U7S – Uslu variety holded at 7 days in sack
E7S – Edremit variety holded at 7 days in sack
U14B – Uslu variety holded at 14 days in box
E14B – Edremit variety holded at 14 days in box
U14S – Uslu variety holded at 14 days in sack
E14S – Edremit variety holded at 14 days in sack
U21B – Uslu variety holded at 21 days in box
E21B – Edremit variety holded at 21 days in box
U21S – Uslu variety holded at 21 days in sack
E21S – Edremit variety holded at 21 days in sack

IP of Frantoio cultivar olive oil was determined 3.7 h at 120°C [Mateos *et al*, 2006]. This finding is similar with our initial IP results. As the ripening occurs, the oil stability decreases according to the results described previously [Gutierrez *et al*, 1999].

Sensory Profile of olive oil samples

According to the results of sensory evaluation, two positive attributes of Uslu olive oil as fruitiness and pungency was found higher at 0th day. On the other hand, negative attributes as fusty-humid and winey of Uslu olive oil were found higher at 14th day holding in box (Table 7). All olive oil samples were located at mature index.

Table 7

Negative and Positive Sensorial Properties of Edremit and Uslu olive oil varieties according to the different holding times and holding types

Variety	Holding Times (week)	Holding Types	Negative properties					
			Muddy Sediment	Fusty-humid	Winey	Wet Wood	Rancid	Others
Uslu	0	-	-	-	-	-	-	-
	7	box	-	2	-	-	1,9	-
	14	box	0,75	2,5	3,2	-	-	-
	21	box	3,3	2	-	-	-	-
	7	sack	-	-	2,5	-	-	-
	14	sack	3	-	1	-	-	-
	21	sack	2,7	1,25	2,5	-	-	-
Edremit	0	-	-	-	-	-	-	-
	7	box	-	1,5	-	-	-	-
	14	box	-	2,4	-	-	-	-
	21	box	2	-	-	-	-	-
	7	sack	-	-	-	-	-	-
	14	sack	2,25	-	2	-	-	-
	21	sack	-	2,5	3	-	-	-

Variety	Holding Times (week)	Holding Types	Positive properties			
			Fruity	Bitter	Pungent	Maturity
Uslu	0	-	3,5	0,5	2	mature
	7	box	2,15	-	1,3	mature
	14	box	1,5	-	-	mature
	21	box	1,4	-	-	mature
	7	sack	2	-	1,3	mature
	14	sack	1,4	-	1,6	mature
	21	sack	1,85	-	-	mature
Edremit	0	-	2,75	-	1,5	mature
	7	box	2,45	-	1,5	mature
	14	box	2	0,5	-	mature
	21	box	2	-	-	mature
	7	sack	3,1	1	1,5	mature
	14	sack	2	-	-	mature
	21	sack	1,5	-	-	mature

According to the Table 8, while Edremit olive oil at initial day of holding, 7th day in sack and Uslu olive oil at initial day of holding were taken a part of extra virgin olive oil, other samples were classified as virgin olive oil according to the IOOC Method [IOOC, 2010]. Fruity score ranged from 1.4 to 3.5 for both olive oil samples. Fruit score were determined score as from 1.8 to 3.2 in Cornicabra virgin olive oils [Salvador *et al*. 2000]. Generally, muddy-sediment occurred at the latest holding times as 14th and 21th day for

both types. One of the negative attributes wet wood was not perceived in any sample (Table 7). Additionally, intensity of rancid was only determined in Uslu olive oil on 7th day of holding at box.

Table 8

Limits established for Median of defect and fruity attribute (IOC, 2015)

	Median of defect	**Median of the fruity attribute**
Extra virgin olive oil	Me=0	Me>0
Virgin olive oil	0<Me≤3.5	Me>0
Ordinary virgin olive oil	3.5<Me≤6.0	
Lampante virgin olive oil	Me>6	

The sensory caracteristics of bitterness and pungency are due to the activation of taste receptors and trigeminal nerve endings associated with taste buds in fungiform papillae, sensitive to chemical stimuli. In virgin olive oils, these sensations are related to the presence of phenolic compounds and can persist for rather long times after deglutition, showing a clear after-effect that can greatly vary among olive oils in intensity and duration and might affect consumer acceptance [Nieto *et al*. 2010].

Researches showed that the main reason of quality reduction in the olives which are holded before being processed is the increase in acidity and peroxide number [Cimato, 1990; Garcia *et al*. 1996].

Conclusion

The evaluation of the influence of holding types and times of olives on quality parameters and oxidative stability of olive oils is important for exhibit the requirement to not holding olives long time at inconvenient conditions. This study is also of great interest to the local industrial sector and consumers. Quality criteria of olive oils becomes much closer or exceeds the upper legal limits due to negative factors such as harvesting olives at inappropriate maturity index, the long holding period until processing, transport stage after harvesting. In addition to these, producer awareness has also effect on changes of olives quality criteria. Therefore, harvest should be made with appropriate methods and then olives transport to the place of processing and be holded in properly packaged without losing time. At this point, it is not the right approach to say that olive producers has the same consciousness in each region.

Post-harvest transport stage is the stage that showed the most increase the amount of free fatty acidity and oxidation as a result ofthe continued respiration in fruit and hydrolytic degradation.

According to the results, the chemical parameters analysed in the different samples are within the limits established by the legislation, but vary during the holding period and according to the variety. With respect to holding type, the acidification and oxidation of the olive oil increase during holding in sack. When compared two types of olives, Edremit variety has higher quality than Uslu variety in terms of phenolic compounds, peroxide value and thereby oxidative stability. The scores of positive sensorial properties of Edremit variety are higher, as well.

It is seen that the traditional olives holding methods using generally at villages and towns are not suitable for stability and quality of olive oils obtained from these olives. As a consequence, oxygen and light induce a rapid deterioration in sacks and boxes. Likewise, acidification, loss of phenolic compounds, oxidative rancidity and sensorial quality is favoured. However, olives should be holded at concrete and smooth surfaced panes or under plastic bedstead for not more high than 10-12 cm, after harvesting up to one or two months at maximum. The most important issue for the holding of olive is to provide getting the air and not be crushed.

Acknowledgement
The authors thank to Scientific Research Projects Coordination Unit of Celal Bayar University, Project No 2013-093, for financial support.

References

1. Allalout A., Krichene D., Methenni K., Taamalli A., Oueslati I., Daoud D., Zarrouk M. (2009), Characterization of virgin olive oil from Super Intensive Spanish and Greek varieties grown in northern Tunisia, *Scientia Horticulturae*, 120, pp. 77–83.
2. Anon. (2010), *Turkish Standard Animal and vegetable fats and oils*, Determination of refractive index, TS 4960 EN ISO 6320.
3. Anon. (2014), *Turkish Food Codex of Olive Oil and Olive Pomace Oils Report*, Report No: 2014/53.
4. Anwar F., Bhanger M.I., Kazi T.G. (2003), Relationship between Rancimat and Active Oxygen Method values at varying temperatures for several oils and fats, *Journal of the American Oil Chemists Society,* 80, pp. 151–155.
5. Andjelkovic M., Acun S., Hoed V.V., Verhi R., Camp J.V. (2009), Chemical Composition of Turkish Olive Oil-Ayvalk, *Journal of the American Oil Chemists Society*, 86, pp. 135–140.
6. AOCS (1993a), *Official Methods and recommended practices of the American Oil Chemists Society*, 3rd edn, Color Method Cc 13b–45.
7. AOCS (1993b), *Official Methods and Recommended practices of the American Oil Chemists Society*, Free Fatty Acids Method Ca 5a–40.
8. AOCS (1997), *Official Methods and Recommended practices of the American Oil Chemist Society*, Preparation of Methyl Esters of Fatty Acids Method Ce 2–66.
9. Baccouri O., Guerfel M., Baccouri B., Cerretani L., Bendini A., Lercker G., Zarrouk M.. ben Miled D.D. (2008), Chemical composition and oxidative stability of Tunisian monovarietal virgin olive oils with regard to fruit ripening, *Food Chem*istry 109, pp. 743–754.
10. Beltran G., Aguilera M.P., Del Rio C., Sanchez S., Martinez L. (2005), Influence of fruit ripening process on the natural antioxidant content of Hojiblanca virgin olive oils, *Food Chemistry*, 89, pp. 207–215.
11. Boskou D. (1996), *Olive Oil: Chemistry and Technology*, In Boskou D (ed), AOCS Press, Champaign, pp. 101–120

12. Bruni U., Cortesi N., Fiorino P. (1994), Influence of agricultural techniques, cultivar and area of origin on characteristics of virgin olive oil and on levels of some of its minor components, *Olivae*, 53, pp. 28–41.
13. Cimato A. (1990). Effect of agronomic factors on virgin olive oil quality, *Olivae,* 31, pp. 20–31.
14. Del Caro A., Vacca V., Poiana M., Fenu P., Piga A. (2006), Influence of technology, holding and exposure on components of extra virgin olive oil (Bosana *cv*) from whole and de-stoned fruits, *Food Chemistry*, 98, pp. 311–316.
15. Garcıa J.M., Seller S., Perez-Camıno M.C. (1996), Influence of Fruit Ripennig on Olive Oil Quality, *European Journal of Lipid Science and Technology*, 144, pp. 3516–3520.
16. Gutfinger T. (1981), Polyphenols in Olive Oils, *Journal of the American Oil Chemists Society*, 58, pp. 966–968.
17. Gutierrez F., Jimenez B., Ruiz A., Albi M.A. (1999), Effect of olive ripeness on the oxidative stability of virgin olive oil extracted from the varieties Picual and Hojiblanca and on the different components involved, *European Journal of Lipid Science and Technology*, 47, pp. 121–127.
18. IOC (2015), *Trade Standard Applying to Olive Oils and Olive- Pomace O*ils, COI/T.15/NC No 3/Rev, 10 November 2015.
19. IOOC (2010), *Sensory Analysis of Olive Oil Method for the Organoleptic Assessment of Virgin Olive Oil*. IOOC/T.20/Doc. No 15/Rev. 3.
20. IOOC. (2015), *World Olive Oil Figures*. Statistical Series. Consumption.
21. Kiritsakis A.P. (1998), *Olive Oil From The Tree to The Table*. *Second Edition*, pp. 88-93.
22. Mateos R., Uceda M., Aguilera M.P., Escuderos M.E., Maza G. (2006), Relationship of Rancimatmethod values at varying temperatures for virgin olive oils, *European Food Research Technology*, 223, pp. 246–252.
23. Matthaus B., Ozcan M.M. (2011), Determination of Fatty Acid, Tocopherol, Sterol Contents and 1,2-and 1,3-Diacylglycerols in Four Different Virgin Olive Oil, *Journal of Food Processing and Technology*, 2(4), pp.1-4.
24. Morello J.R., Motilva M.J., Tovar M.J., Romero M.P. (2004), Changes in commercial virgin olive oil (cv Arbequina) during holding, with special emphasis on the phenolic fraction, *Food Chemistry,* 85, pp. 357–364.
25. Mendez AI, Falquй E. (2007). Effect of holding time and container type on the quality of extra-virgin olive oil, *Food Control.* 18,521–529.
26. Nieto L.M., Hodaifa G., Pena J.L.L. (2010), Changes in phenolic compounds and Rancimat stability of olive oils from varieties of olives at different stgaes of ripeness, *Journal of the Science of Food and Agriculture*, 90, pp. 2393–2398.
27. Psomiadou E., Tsimidou M. (2001), Pigments in Greek virgin olive oils: Occurrence and levels, *Journal of the Science of Food and Agriculture,* 81, pp. 640–647.
28. SAS. (2000), *SAS User's Guide*. Cary, NC: SAS Institute, Inc.
29. Salvador M.D., Arand A.F., Alonso S.G., Fregapane G. (2000), Quality characteristics of Cornicabra virgin olive oil*, Research on Advanced Oil Chemistry*, 1, pp. 31–39.
30. Tanouti K., Elamrani A., Caid H.S., Tahani N. (2011), Quality of Olive Oils Produced in east of Morocco, *Electronical Journal of Environmental Agriculture and Food Chemistry*, 10(7), pp. 2439–2450.

31. Vinha A.F., Ferreres F., Silva B.M., Valentao P., Gonçalves A., Pereira J.A., Oliveira M.B., Seabra R.M., Andrade P.B. (2005), Phenolic profiles of Portuguese olive fruits (*Olea europaea* L.): Influences of cultivar and geographical origin, *Food Chem*istry, 89(4), pp. 561–568.
32. Yavuz H. (2008), *Determination of Some Quality and Genuineness of Turkish Olive Oils*. *Master thesis*, Ankara University Graduate School of Naturel and Applied Sciences Department of Food Engineering.
33. Yorulmaz A., Erinç H., Tekin A. (2013), Changes in Olive and Olive Oil Characteristics During Maturation, *Journal of the American Oil Chemists Society*, 90, pp. 647–658.
34. Yorulmaz A., Yavuz H., Tekin A. (2014), Characterization of Turkish Olive Oils by Triacylglycerol Structures and Sterol Profiles, *Journal of the American Oil Chemists Society,* 91, pp. 2077–2090.

Influence of sweeteners on rheological and qualitative indicators of ice cream

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Keywords:
Ice cream
Sugar
Molasses
Polyols
Rheology

Article history:

Received
14.12.2017
Received in
revised form
12.03.2018
Accepted
29.03.2018

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DOI:
10.24263/2304-974X-2018-7-1-5

Abstract

Introduction. The research was conducted to determine the influence of sweeteners on the rheological and qualitative characteristics of ice cream.

Materials and methods. Mixtures of cream-based ice cream and aromatic ice cream with sugar, a mixture of molasses (glucose-fructose syrup and molasses caramel), erythritol and sorbitol, as well as their compositions were investigated . Rheological characteristics were studied by rotational viscometry.

Results and discussions. The viscosity of creamy and aromatic ice cream increased in the case of a complete replacement of sugar by syrup starch. The ability to restore the structure of such systems during measurements in the mode of gradual decrease of the rate of displacement increased and ranged from 110.3% to 112.4%, which corresponds to reopectic behavior. However, the effective viscosity of ice-cream with polyols decreased compared to control, and the restoration of the structure of these systems was only 46.8 and 55.9%. In the case of combining a mixture of molasses with erythritol or sorbitol in equal ratios in cream-based ice cream, an increase in the effective viscosity for the degree of regeneration of the structure was recorded 81.9 and 87.0%, respectively.

A certain correlation was found between the effective viscosity and the physical and chemical parameters of ice cream. Thus, in the range of recommended values of effective viscosity of mixtures of ice cream of different chemical composition, the loss rate was not less than 60% of the periodic production method. It should be noted a slight decrease in the loss of ice cream in the case of the use of stomach molybdenum, which can be compensated by its combination with polyols.

The highest defilement was found in samples of ice cream with erythritol and sorbitol, and the lowest – in the case of a mixture of molasses . The combination of erythritol with a mixture of molasses was the highest technological effect.

The resistance to melting of cream ice cream with polyols declined to 44.1 min. with erythritol, and 45.2 min with sorbitol and raised for ice cream with a mixture of molasses up to 54.1 min. (control – 48.2%). For aromatic ice cream a similar pattern has been obtained.

Conclusions. The use of polyols and patch compositions makes it possible to adjust the degree of sweetness of the finished product and to formulate the specified physical and chemical characteristics of the mixtures and ice cream.

Introduction

The processes of formation and stabilization of the structure of ice cream are significantly influenced by the physical and chemical characteristics of the mixtures subject to further thermo mechanical treatment. The content of fat, sugar, dry skim milk and the stabilizer of the structure determine the technological properties of the mixtures and the quality indices of the finished product. Within certain species of ice cream groups there are certain requirements for the range of the content of each of these components, in particular, to the mass fraction of sugar. It is the presence of fat, sugar, dry skim milk and the stabilizer of the structure determines the technological properties of the mixtures and determines the quality indices of the finished product.

Within certain species of ice cream groups there are certain requirements for the range of the content of each of these components, in particular, to the mass fraction of sugar. Thus, its content in milk-based ice cream is usually not less than 14–15.5%, and in ice-cream aromatic and fruit-berry – about 25–28%. Thus, sugar serves not only as an intensive sweetener, but also adds dry matter to the composition of the product, which accounts for a percentage of their total content of about 35% for sealants, about 50% for dairy ice cream and up to 80–85% for aromatic and fruit and berry ice cream. Therefore, the purpose of the study is a comparative analysis of the technological efficiency of sweeteners of different origin for use in the composition of ice cream and aromatic sugar free [1, 2].

Literature review

It is important for consumers demanding organoleptic parameters and composition of ice to reduce its sweetness and glycemic index. Therefore, partial or complete replacement of sugar by other sweeteners for the preservation of the characteristic of the product of organoleptic and physical indicators of quality is an urgent task in the field of ice cream production. Sorbitol, xylitol, maltitol, erythritol, isomalt and other polyols are a good alternative to sugar, characterized by a moderate degree of sweetness, effectively affect the cryoscopic temperature of the product, are stable and soluble in water, are well digested, give the foodstuff a cooling effect [3].

Thus, according to the results of organoleptic evaluation of ice cream with polyols, a rather pleasant moderate sweetness of such a product without sugar (Maltisweet) was noted, compared with the excessive sweetness of the traditional composition of ice cream [4]. At the same time, consumption of polyols per day more than 20 g often leads to gastrointestinal disorders, diarrhea, bloating and other complications. Therefore, according to Codex Alimentarius, a product containing polyols should be marked accordingly with respect to the possible mitigating effect [5].

According to the recommendations of the American Dietetic Association, the consumption of sorbitol in quantities greater than 50 g, mannitol – in excess of 20 g, and isomalt – more than 40 g per day is considered superfluous. At the same time, there are no restrictions for laktitol, maltotol and erythritol. Of course, the daily requirement of polyols depends on age, weight, and the state of human health. Older people suffering from diabetes suffer from constipation, so restrictions on the use of polyols are individual and different for each person [6].

More known in the composition of ice cream as a sweetener molasses starch. It is obtained by sequential cleavage of macromolecules of starch by enzymatic hydrolysis to the desired carbohydrate composition and dextrose equivalent. Functional characteristics of molasses and syrups vary depending on the dextrose equivalent, which is directly related to the degree of hydrolysis of starch in the production process.

According to the results of previous studies, the authors found the expediency of using in the composition of ice cream a composite mixture of high-soluble molasses of the brand HFCS-42 (glucose-fructose syrup) and molasses of low degree of sucrose HFCS-30 (carbohydrate molasses) for the ratio of 30:70. Such mixture provides a proper degree of sweetness (0.7 units) and at the same time essentially structure mixtures of ice cream in the presence of higher sugars in the low-soluble molasses. The effective viscosity of mixtures of creamy ice cream with the specified composition of patches reached 1085.45 mPa·s, and mixtures of aromatic ice cream – 291.6 mPa·s, which are the recommended values for these types of ice cream [7].

Rheological characteristics of mixtures of ice cream of various composition, as well as the influence of individual components and technological regimes on the viscosity of mixtures were the subject of study since the 20-ies of the last century. Rheological characteristics of mixtures of ice cream of various composition, as well as the influence of individual components and technological regimes on the viscosity of mixtures were the subject of study since the 20-ies of the last century. So, F.F. Sherwood, H.L. Smallfield, G.D. Turnbow and K.W. Nielson describes the influence of technologically important parameters (temperature and duration of pasteurization, maturation of mixtures, pressure and temperature of homogenization, chemical composition of mixtures, etc.) on the rheological characteristics of mixtures for the production of classical ice cream on a milk basis [8, 9]. But, given the progressive changes in ice cream technology for almost 100 years, the results of these studies can only be used as general information. The use of stabilizers and stabilization systems, sweeteners, the improvement of classical technologies and technical innovations require further study of all factors affecting the quality indicators as mixtures for the production of ice cream and finished product.

So, already in our time, Arbuckle, W. S. found that the viscosity of the mixture is a function of the composition (mainly of fats, stabilizers and sugar), the conditions of treatment (mainly pasteurization, homogenization and maturation) and the temperature of the mixture. He also believed that the effective viscosity of the mixture consists of a structural component that dissipates during the mixing process and a plastic component fluctuating in the range from 50 to 300 mPa·s. This effective viscosity at rest or at low shear rates is partly due to various phenomena (aggregation of fat globules, free water content, etc.) that increase viscosity with a decrease in the rate of displacement, including due to thixotropic properties of mixtures [10]

Moser R. etc. studied the influence of polyols and guar gum on the rheological characteristics of their aqueous solutions. The behavior of these mixtures was estimated by measuring the shear under the action of constant and oscillatory stresses, as well as after the freeze / thawing cycle of the prototype samples. An increase in the relative viscosity of guaric solutions in the case of addition of polyols and increase of their concentration is established. The exception is the system of mixtures for the ratio between 40 g/100 g of sorbitol and 1 g/100 g of guar gum, in which the viscosity decreases. Studies of systems after their freezing / defrosting showed no change in visco-elastic properties of solutions [11].

In China (Tianjin University) it has been found that for a specific molar concentration of polyol, the density and viscosity of such solutions decrease as the temperature rises. In the case of heating the solutions, the thermal energy of the molecules and the distance between them increases, and, accordingly, the density and viscosity decrease. At the same time, the density and viscosity of the mixtures, respectively, increase with increasing concentration of solutions. As the temperature rises, the viscosity of the solutions of polyhydric alcohols decreases nonlinearly, whereas the density decreases linearly. By

gradually increasing the number of carbon atoms in polyols (erythritol, xylitol, mannitol, and maltitol), their molecular weight increases accordingly, which leads to an increase in the viscosity of solutions at a specific molar concentration and temperature [12].

Siefarth etc. have proved that the addition of sucrose, polyols and fillers contributes to enhancing the perception of the aroma of aqueous solutions of relatively pure water. The relationship between taste and viscosity was not found in solutions with low viscosity [13].

The authors have previously studied the rheological characteristics of cream and aromatic ice cream with complete and partial replacement of sugar on starch molasses. It is proved that the degree of saccharification of molasses significantly affects the structural and mechanical properties of mixtures. The content of higher sugars in the low-degree of saccharification, in contrast to glucose-fructose syrup, containing the vast majority of monosubstances, contributes to a better structuring of mixtures in terms of effective viscosity. Excessive viscosity of mixtures with molasses caramel requires its combination with high-soluble molasses at a ratio of 30:70, which ensures the effective structuring of mixtures and gives the moderate sweetness of ice cream to cream and aroma, compared with control samples [14].

Consequently, it is evident that it is expedient to replace the sugar in the ice cream component with the technological-functional ingredients – polyols and starch molasses. At the same time, there is no comparative assessment of their impact on the quality of mixtures and ice cream both individually and in composition.

In the article a comparative analysis of the influence of polyols (sorbitol and erythritol) and a mixture of starch packs of different degrees of sucrose (glucose-fructose syrup and caramel molasses) on the physical parameters of cream and aromatic ice cream and mixtures for their production are given.

Materials and methods

For control of samples of creamy ice cream, a typical prescription with a mass fraction of fat was chosen – 10%, dried skim milk residue – 10%, sugar – 14% and stabilization system (Cremodan SE 709, Danisco) – 0,5%.

For the study of ice cream on the basis of sugar syrups for control sample, an aromatic mixture with a mass fraction of sugar of 28% and gelatin in the amount of 0,5% of the total mass of the mixture was chosen as the control sample.

In experimental samples, sugar was completely replaced by a mixture of glucose-fructose syrup (HFCS-42) and carotene molasses (HFCS-30) for a ratio of 30:70 and polyols of erythritol and sorbitol, based on dry matter.

Ice cream mixtures were prepared according to the classical technological scheme: they were pasteurized at 85±2 ºC for 2–3 minutes, cooled to a temperature of 4±2 ºC and, at the same temperature, matured for 12 hours. The content of sweeteners in mixtures of ice cream is shown in Table 1.

The defilement of soft ice-cream (S, %) was determined by the weight method and calculated by the formula [15]:

$$S = \frac{m_m - m}{m} \cdot 100\%$$

where m_m – the mass of a mixture of ice cream of a certain volume, g; m – weight of ice cream of the same volume, g.

Table 1

Mixes of ice cream with various sweeteners

Sample number	Mixtures type and sweetener content
1	Control 1 (ice cream) (sugar=14 %)
2	Ice cream (starchy syrups=14 %)
3	Ice cream (erytritol=14%)
4	Ice cream (erytritol=7 % + starchy syrups=7%)
5	Ice cream (sorbitol=14 %)
6	Ice cream (sorbitol=7% + starchy syrups=7%)
7	Control 2 (aromatic ice cream) (Sugar=28 %)
8	Aromatic ice cream (erytritol =28 %)
9	Aromatic ice cream (sorbitol=28 %)
10	Aromatic ice cream (starchy syrups=28%)

The viscosity characteristics of ice cream mixtures were determined on the rotating viscosimeter "REOTEST 2.1" with the cylinder cylinder measuring system by removing the curvatures of the kinetics of deformation (flow) at a temperature of 20 ºC. Measuring cylinder (rotor) S1 was selected in such a way that the gradient layer was distributed over the entire thickness of the product layer located in the annular gap of the viscometer gauge. The measurement of the shear stress was carried out in twelve values of the shear rate γ in the range from 3 to 1312.2 s^{-1} with successive incremental rates of shear rate, endurance at the highest speed and subsequent successive gradual reduction of velocities [14].

Resistance to melting was determined by the modified method by L. D. Buldenko. Ice cream samples in the form of cylinders with a diameter of 35 mm and a height of 50 mm were pre-maintained at -25 ºC for 24 hours. After that, they were warmed at a temperature of 20 ° C [16] on stainless steel grates with apertures of 2.5 mm in size. Samples were placed with a measuring cylinder. The time of occurrence of the first drop "float" and the time of leakage of 10 cm^3 "float" were fixed.

The size of the air bubbles was determined by microscopy for an increase of x = 150. A sample of ice cream was applied to the calibrated chamber Goryaev's grid, covered with a cover glass from above, and a bubble size was calculated in four to seven fields of view. The average diameter of the bubbles was calculated by the diameter of the particles in an amount not less than 400 in the five-seven fields of view [16].

Organoleptic evaluation of ice cream samples was carried out qualitatively and quantitatively (on a 10-point scale) [15].

Results and discussions

Replacing sugar with polyols and molasses due to increasing the viscosity of unpermoited water in hardened ice cream can prevent recrystallization of water and lactose due to violation of temperature regimes of storage and the emergence of consistency defects – sandy and coarse-crystalline structure. Therefore, the dynamics of changes in the effective viscosity of mixtures for the production of ice cream of different chemical composition with successive incremental increase and subsequent decrease of the shear rate γ in the range from 3 to 1312.2 s^{-1} was investigated.

The rheological characteristics of the samples under study are given in Table 2

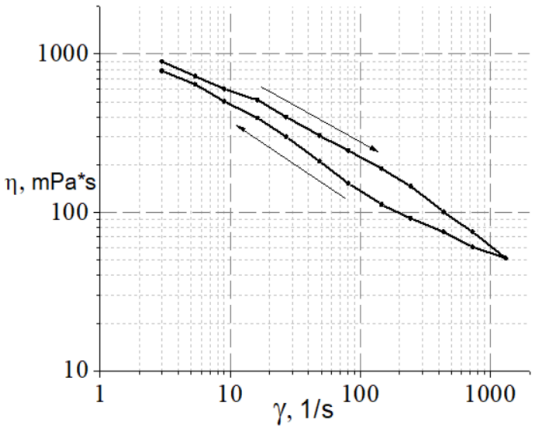
Table 2

Rheological characteristics of the studied systems

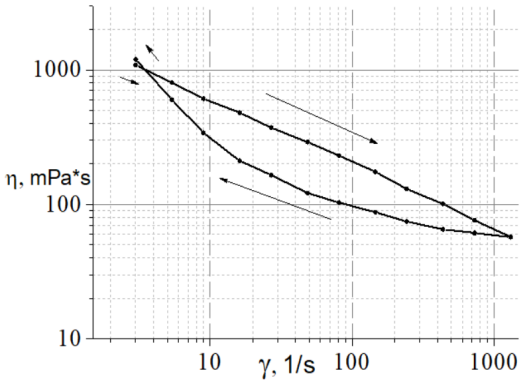
Sample number	η_1 (γ=3), mPa·s	η_2 (γ=1312,2), mPa·s	η_3 (γ=3), mPa·s	τ (γ=1312,2), s
Mixtures of ice cream				
1	896,9	51,35	782,1	336
2	1085,45	57,24	1197,2	370
3	815,4	34,93	381,5	351
4	982,65	39,20	804,31	354
5	616,8	39,88	344,5	404
6	864,41	38,81	752,32	392
Mixtures of aromatic ice cream				
7	252,3	6,2	193,5	152
8	198,52	3,48	83,6	163
9	177,32	5,91	83,74	185
10	291,6	7,8	327,9	185

The nature of the destruction of the structure of the studied food systems in the process of measuring the effective viscosity, for example, of mixtures of cream and aromatic with complete replacement of sugar on the syrup of starch and on polyols is shown on Figure 1, Figure 1.1, Figure 2.1 and on Figure 2 .

Sample No. 1



Sample No.2



Sample No.3

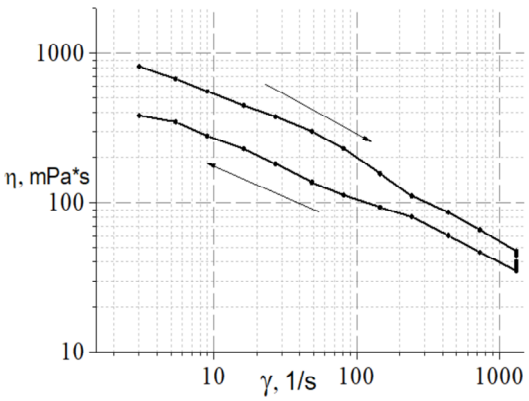
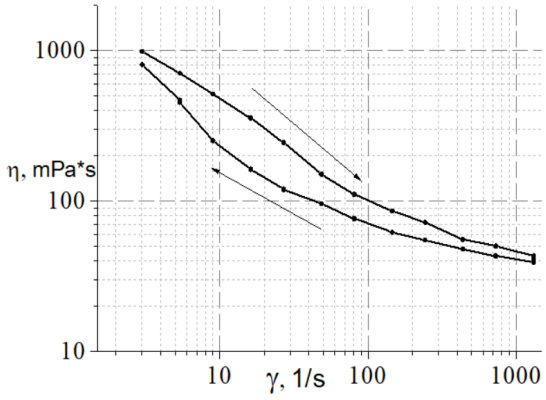
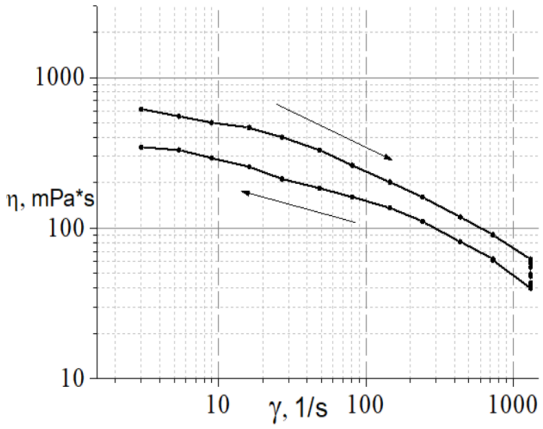


Figure 1. Dynamics of the change of effective viscosity of mixtures for the production of cream ice cream with various sweeteners

Sample No.4



Sample No.5



Sample No.6

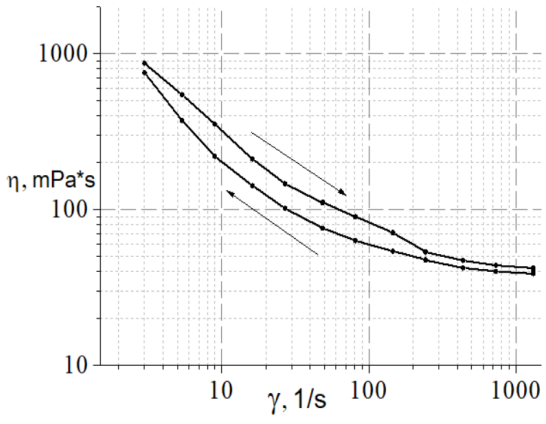
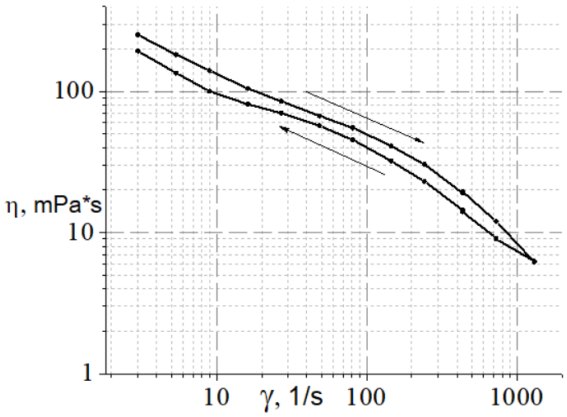
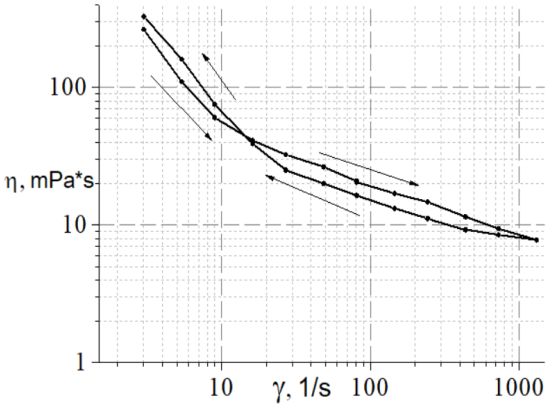


Figure 1.1. Dynamics of the change of effective viscosity of mixtures for the production of cream ice cream with various sweeteners

Sample No. 7



Sample No. 8



Sample No. 9

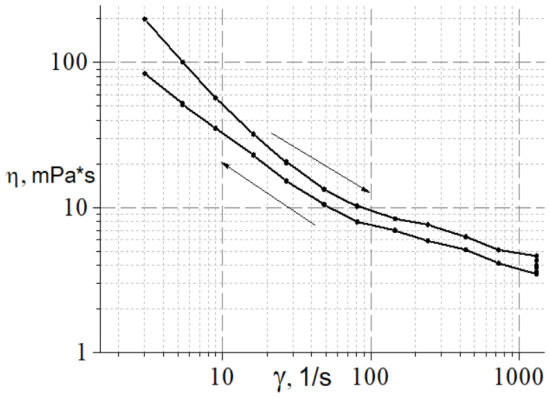


Figure 2. Dynamics of the change of effective viscosity of mixtures for the production of aromatic ice cream with various sweeteners

Sample No. 10

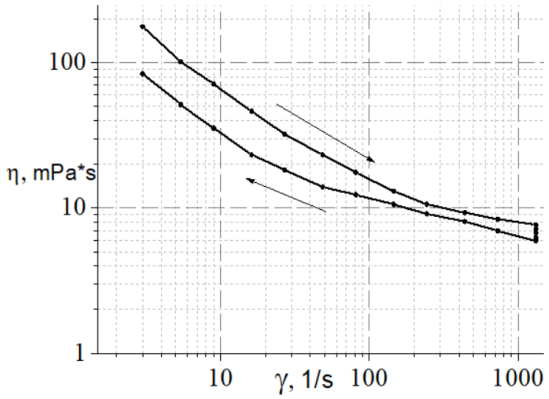


Figure 2.1. Dynamics of the change of effective viscosity of mixtures for the production of aromatic ice cream with various sweeteners

According to the results of the study, thixotropic properties revealed samples of control cream and aromatic mixtures and mixtures with molasses and polyols. For these samples, in the process of rheological research, the gradual destruction of the structure and the corresponding reduction of the effective viscosity (η_3) in comparison with the initial values (η) with the subsequent partial restoration of the structure is characteristic. The complete replacement of the traditional sweetener with polyols, in turn, contributes to reducing the viscosity of the mixture and the ability to restore its structure. Thus, for ice cream, the cream's ability to restore the structure of the control sample is 87.2%, and for creamy ice cream with a complete replacement of sugar for erythritol and sorbitol – only 46.8 and 55.9% respectively.

At the same time, the food systems containing a mixture of strains, can not only almost completely restore the structure but also reveal weak reopectic properties. The latter are manifested in increasing the effective viscosity in the shear rate reduction mode (η_3) by 10.3% for creamy ice cream and 12.4% for aromatic ice cream for complete replacement of sugar compared to the initial values (η).

In the case of the simultaneous use of a mixture of polyethylene tubes (samples number 4 and number 6), the process of structuring becomes more pronounced. Thus, the initial viscosity of the mixtures is 982.65 mPa·s for ice cream with molasses and erythritol and 864.41 mPa·s for ice cream with molasses and sorbitol in equal proportions. The reproducibility of the structure of these samples is quite high and reaches 81.9 and 87.0%, respectively. That is, the structure of mixtures with complexes of sugar substitutes of different origin allows to partially or completely restore the structure of the formed portions of soft ice-cream before quenching, which significantly increases the quality of its quality [5].

For mixtures of ice cream of classical species (milk ice cream, creamy ice cream, sundae) at a temperature of 20 ºC and a shear rate $\gamma = 3\ s^{-1}$, the relative viscosity of the mixtures should be about 200, 600 and 1200 mPa·s with respectively. For mixtures, the aromatic effective viscosity is much lower and can reach only 250 mPa·s [1]. The viscosity of all the specimens examined was within the recommended values, except for cream and aromatic mixtures with starch molars whose viscosity exceeded the norm. But the latter can

be used effectively to regulate the structural characteristics of ice cream eskimo, which should be more dense and form-resistant.

Physical parameters of ice cream made from samples of mixtures (see Table 1) are shown in the table. 3

Table 3

Physical indicators of ice cream with various sweeteners (P≥ 0.95; n = 3)

Indicator	Sample number									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Overrun, %	77,2 ±2,0	76,0 ±2,3	82,1 ±1,9	79,0 ±1,3	80,1 ±1,9	79,5 ±1,8	73,5 ±1,8	78,3 ±1,1	77,5 ±0,9	72,1 ±1,9
Resistance to melting, s	48,2 ±1,4	54,1 ±0,7	44,1 ±1,0	46,3 ±1,1	45,2 ±0,9	46,4 ±0,9	28,0 ±0,6	22,3 ±0,5	23,4 ±0,7	29,0 ±0,6
Average diameter of the bubbles, μm	45,7 ±1,0	50,2 ±1,1	22,1 ±0,6	32,8 ±0,7	25,2 ±0,6	34,2 ±0,6	51,1 ±0,7	27,8 ±0,9	28,1 ±0,8	30,2 ±0,9
The temperature of the soft ice cream,ºC	-3,5 ±0,1	-4,0 ±0,1	-7,5 ±0,2	-5,5 ±0,2	-6,0 ±0,2	-4,2 ±0,1	-5,0 ±0,2	-7,5 ±0,2	-7,1 ±0,2	-6,5 ±0,1

The highest deficiency was found in control samples with sugar (No. 1, No. 7) and samples with polyols (No. 3–6 and No. 8–9). At the same time, ice cream with erythritol and sorbitol at high bruise shows an unsatisfactory resistance to dying.

In turn, a certain decrease in the losses was recorded for samples No. 2 and No. 10 with a mixture of starch packs while improving the uniformity of the ice cream. As a result of the comparative analysis of the distribution of air bubbles by size in soft ice-cream, an increase in the dispersion of the air phase in specimens with polyols was found. This effect is probably due to a decrease in the viscosity of the mixtures, which leads to their more efficient chopping and distribution of the air phase. According to studies by Adapa and al. the more viscous system contributes to less foam formation, but the higher stability of the structure [17], which explains the detected effect.

It should also be noted that the cooling of mixtures with polyols in the process of freezing should be noted. However, the surface of ice cream on the exit from the freezer was shiny and watery due to low resistance to dessert. Ice cream with molasses is more structured, with a dry surface due to the presence of higher sugars in the molasses PC (up to 70% of the total dry matter content). All samples of ice cream on the exit from the freezer had a temperature not exceeding the recommended -3.5 ºC [16].

Regarding organoleptic characteristics, the lack of sweetness and low ability to make ice cream with a complete replacement of sugar on erythritol and sorbitol, moderate sweetness and high structural capacity for samples with starch molasses should be noted. Therefore, the highest scores were obtained from cream ice cream no. 4 and no. 6 and a sample of aromatic ice cream №10. Balance assessment of organoleptic parameters of the studied ice cream samples is shown in Figure 3.

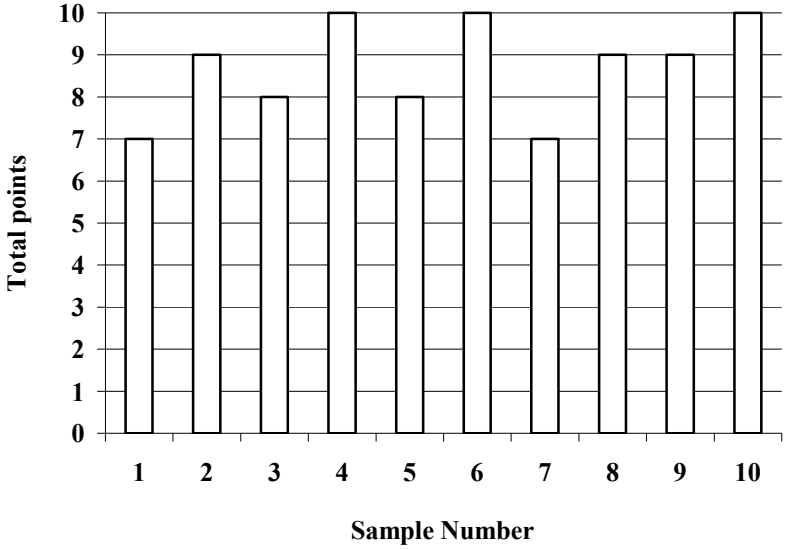


Figure 3. Organoleptic evaluation of ice cream samples on a 10-point scale

According to Figure 3, the use of polyols and patch compositions makes it possible to adjust the degree of sweetness of the finished product and to form the physical characteristics of mixtures and ice cream close to those for classical sugars.

Consequently, polyols as sugar substitutes are better used to produce ice-cream soft or packaged in rigid consumer containers before quenching. A mixture of straw is universal and can be used for different types of ice cream. But lower whip and good structuring are ideal for ice cream Eskimo.

Replacing sugar with a mixture of polyethylene tubes to a sufficient degree ensures its structuring. Using exclusively polyols does not provide ice cream with the required degree of sweetness and reduces dandruff resistance. Therefore, for the formation of a structure characteristic for a soft ice-cream, it is advisable to use a mixture of low-and high-soluble patches together with polyols.

Conclusions

1. Replacing sugar on the composition of starch hoods HFCS-42 and HFCS-30 for a ratio of 30:70 significantly increases the effective viscosity of mixtures for the production of cream and aromatic ice cream. Replacing sugar with polyols leads to the reverse effect. At the same time, the replacement of sugar on a complex of sweeteners of various origins (polyols + molasses) provides an effective viscosity of mixtures in the recommended range of values.
2. Replacement of sugar into sorbitol and erythritol leads to a decrease in the sweetness of the ice cream, an increase in its loss and worsens resistance to dying. Replacing sugar with a mixture of straw also reduces the sweetness, but reduces stiffness and improves resistance to dandruff.

3. The expediency of the complex use of polyols and a mixture of strawberries in creamy and aromatic ice cream has been proved, which makes it possible to achieve the maximum technological effect.

References

1. Goff H.D., Hartel W.R (2012), *Ice Cream*, Springer US, New York.
2. Muse M., Hartel R. (2004), Ice Cream Structural Elements that Affect Melting Rate and Hardness, *Journal of dairy science,* 87(1), pp.1–10.
3. Livesey G. (2003), Health Potential of Polyols as Sugar Replacers, with Emphasis on Low Glycaemic Properties, *Nutrition Research Reviews*, 2, pp. 163–191
4. Bordi P., Cranage D., Stokols J., Palchak T., Powell L. (2005), Effect of polyols versus sugar on the acceptability of ice cream among a student and adult population, *Foodservice Research International*, 15(1), pp. 41–50
5. Mitchell H. (2006) *Sweeteners and sugar alternatives in food technology*, Blackwell publishing ltd, Blackwell.
6. Portman M. O., Kilcast D. (1996), Psychophysical characterization of new sweeteners of commercial importance for the EC foodindustry, *Foodchemistry*, 56, pp. 291–302.
7. Breus N. M., Bass O. O., Manokha L. Yu., Polishchuk H. Ye. (2016), Optymizatsiia skladu morozyva na molochnii osnovi z tsukrystymy rechovynamy, *Naukovi pratsi Natsionalnoho universytetu kharchovykh tekhnolohii*, 1(22), pp. 166–171.
8. Sherwood F. F., Smallfield H. L. (1926), Factors Influencing the Viscosity of Cream and Ice Cream, *Journal of Dairy Science*, 1(9), pp. 68–77.
9. Cottrell J. T. L., Pass G., Phillips G. O. (1980), The Effect of Stabilisers on the Viscosity of an Ice Cream Mix, *Sci. Food Agric,* 31, pp. 1066–1070.
10. Arbuckle W. S., Marshall R. T. (2012), *Ice Cream*, Aspen Publishers, Inc, Gaithersburg.
11. Moser P., Lopes M., Vania C., Nicoletti Telis R. (2013), Influence of the concentration of polyols on the rheological and spectral characteristics of guargum, *Food Science and Technology*, 53(1), pp. 29–36.
12. Zhu C., Ma Y., Zhou C. (2010), Densities and Viscosities of Sugar Alcohol Aqueous Solutions, *J. Chem. Eng.*, 55, pp. 3882–3885.
13. Siefarth C., Tyapkova O., Beauchamp J., Schweiggert U., Buettner A., Bader S. (2011), Influence of polyol and oil concentration in cosmetic products on skin moisturization and skin surface roughness, *Food Chemistry,* 4(129), pp. 1462–1468.
14. Bass O, Polischuk G, Goncharuk E. (2017), Investigation of viscou scharacteristics of ice cream mixtures with starch syrup, Ukrainian Food Journal, 5(2), pp. 272–280.
15. Krus G. N., Shalygina A. M. (2002), *Metody issledovaniia moloka i molochnykh produktov,* Kolos, Moskva.
16. Bartkovskyi I. I., Polishchuk H. Ye., Sharakhmatova T. Ye. (2010), *Tekhnolohiia morozyva,* Feniks, Kyiv.
17. Adapa S., Dingeldein H., Schmidt K.A,. Herald T.J. (2000), Rheological properties of ice cream mixes and frozen ice creams containing fat and fat replacers, *Journal of Dairy Science*, 83, pp. 2224–2229.

Evaluation of rosemary extract effectiveness in the technology of meat-containing sausages with duck meat

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Keywords:

Antioxidant
Extract
Rosemary
Sausages
Duck

Article history:

Received 02.02.2018
Received in revised form 19.02.2018
Accepted 29.03.2018

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DOI:
10.24263/2304-974X-2018-7-1-6

Abstract

Introduction. The objective of this research was to evaluate the effectiveness of using rosemary extract in the technology of meat-containing sausages with duck meat, which is characterized by high content of polyunsaturated fatty acids.

Materials and methods. The formula of meat-containing sausages with duck meat (*Cairina moschata*), which also included first-grade beef, pork fat, soya protein, milk powder, pork skins protein, soluble fiber FV Fiber, was used as the model for studying rosemary extract effectiveness. The acid value (AV), peroxide value (PV), thiobarbitur acid reactive species (TBARS) were determined during the storage of meat- containing sausages.

Results and discussion. The results of the research indicated that incorporated antioxidant retarded the lipids degradation due to the high concentration of extract flavonoids. The rosemary extract inhibited acylglycerides hydrolytic decomposition most effectively at the concentration of 0.05%. The addition of the rosemary extract helped to slow down the oxidative processes. Among the experimental sausages samples, the peroxide value increased more intensively in the sample without the additive. The addition of the extract at the concentration of 0.05% had the greatest stabilizing effect. The peroxide value in this sample was 0,015±0,001%J_2 at the end of the storage, while in control this figure was 0,026±0,002% J_2, which is 57,69% higher.

The antioxidant action of additives is also demonstrated by the accumulation of mono- and dialdehydes reacting with 2-thiobarbituric acid. The investigation of the secondary oxidation products content allowed us to estimate the depth of the oxidative processes occurring in the samples of the sausages stored for 6 days at + 4°C. The concentration of the secondary oxidation products was the highest in the control sample, while in the experimental samples TBARS was reduced proportionally to the concentration of the added anti-oxidant additive. At the end of the storage period, TBARS in the control sample was 0.269±0.04 mg MA/kg of the finished product, while in the experimental samples this index ranged from 0.231±0.03 to 0.184±0.04 mg MA/kg. The largest effect was obtained with the additive concentration of 0.05%, which made it possible to reduce the oxidative fat deterioration by almost two times.

Conclusions. The studies confirmed the high antioxidant activity of the rosemary extract and the effective inhibition of the lipid oxidation process in meat-containing sausages with duck meat.

Introduction

Meat products are an important source of complete protein that contains essential amino-acids. They are also good sources of many essential substances such as unsaturated fatty acids, vitamins, minerals in human diet. The oxidative stability of meat depends on the balance and interaction of anti- and prooxidant substances, as well as on the content of the substrates susceptible to oxidation, including polyunsaturated fatty acids, cholesterol and others. [1].

However, cellular systems of antioxidant activity are destroyed during the technological processes of meat processing, including the mechanical destruction of muscle tissue during the mincing process in the production of emulsified meat products, such as boiled sausages.

Sausages of the boiled group are emulsified meat products, the structure of which may contain air cavities, which accelerate the oxidation inside the product under the action of the air oxygen. Oxidizing processes affect the quality of the finished product, contribute to the loss of colour, taste, smell and reduce the shelf life.

During the oxidation of fats, various products of degradation are formed: free acids, in particular their trans isomers, oxygen-containing derivatives, aldehydes, ketones, peroxides, many of which are toxic substances. The most common way of solving the problem of the oxidative damage of meat products is the use of the variety of antioxidant food additives that allow the purposeful regulation of the oxidizing processes of the lipid fraction of meat systems [2, 3, 4].

The use of synthetic antioxidants in the meat industry is more widespread than the use of natural ones, raising many questions concerning their safety. For this reason, the preparations of natural antioxidants, namely extracts of herbs and spices, berries, fruits, etc attract interest. There is certain experience of their use in manufacturing meat and poultry products [5–7].

The antioxidant efficiency of plant extracts is explained by the features of the chemical composition and concentration of biologically active substances, namely, the high total content of phenolic compounds, tannins and free organic acids [8, 9]. One of the perspective antioxidant preparations for the meat industry can be rosemary extract.

The effectiveness of the rosemary extract was found when it was used in the technology of various types of meat products, including natural and minced semi-finished products from pork, beef, sausage made from pork, natural semi-finished products from poultry [10-16].

On the other hand, there is a prospect for using waterfowl meat in the meat processing industry in Ukraine, which, unfortunately, has not spread enough in this country. However, this type of meat could be used by the meat processors as the perspective raw material due to the complex of physical, chemical, functional and technological indicators, nutritional and biological values.

Meat of the Muscovy ducks (*Cairina moschata*), has a high protein content – 17,2 g/100 g, a relatively low fat content – 17.4 g/100 g, the concentration of mineral elements is 1.3 g/100 g. Studies have shown that meat of Cairina moschata exceeds the ideal protein both in the sum and the content of most essential amino acids. By the sum of essential amino acids protein of duck meat exceeds the ideal protein by 14.7 %. Amino acids score of lysine, tryptophan and methionine + cysteine is 126.2%, 122.0%, 94.2%) respectively [17, 18].

One of the features and important biological value indicators of duck meat is fatty acid composition of lipids. Unsaturated fatty acids have the highest proportion in total content

(68.91 %). Oleic acid share comprises 37.1% among the monounsaturated fatty acids. Among the polyunsaturated fatty acids, linoleic acid predominates (18,10 %). The content of saturated fatty acids is 30,6%, with the largest proportion of palmitic acid (20.80 %) [19–21].

Waterfowl meat can be used to improve and develop the technology of meat-containing products of boiled group but it needs scientific justification. The existing classification of animal products has no justified standards for storage of meat-containing products with the high proportion of meat, which is non-traditional for the production of boiled sausages.

The high content of unsaturated fatty acids in waterfowl meat creates a certain risk of lipid oxidation in the finished products with duck meat during storage, hence, requires additional technological techniques to prevent negative effects. Therefore, the investigation as for justification of meat product quality and safety indicators are the topical issues.

The aim of this study was to evaluate the effect of using the extract of rosemary in the technology of meat-containing sausages with duck meat.

Materials and Methods

Experimental design

To carry out the investigation, in the laboratory of Milk and Meat Technologies Department of the Faculty of Food Technologies (SNAU) the recipe for meat-containing sausages with duck meat *(Cairina moschata)*, first-grade beef, pork fat, soya protein, milk powder, pork skins protein, soluble fiber FV Fiber was developed.

The rosemary extract (Food Ingredients Mega Trade, USA) was added to the minced meat. The extract was added to the forcemeat samples according to the following scheme: № 1 – RE 0,03 %; № 2 – RE 0,04 %; № 3 – RE 0,05 % to the raw material mass, the forcemeat sample without antioxidants was the control one.

The recommended concentration of antioxidants applied in meat products technology varies from 0,01 to 0,1 % [22–24]. For this reason, the corresponding concentration of rosemary extract was selected with regard for the content of different groups of substances with an antioxidant property and synergetic effect of their combined use.

All the ingredients were mixed for 20 min, and then the mixture was stuffed into the natural casing. The samples were heat processed until they reached the internal temperature of 72^0C. The sausages samples were then rinsed with cooled water and stored at 4^0C for 6 days.

Acid and peroxide values (AV and PV), thiobarbituric acid reactive species (TBARS) were the control indicators. The generally accepted methods were used for the definition of these indicators [25, 26].

Production of sausages

Meat-containing sausages were made according to the recipe containing meat of duck (Cairina moschata), first-grade beef, pork fat, soya protein, milk powder, pork skins protein, soluble fiber FV Fiber, salt and spices in the ratios given in Table 1.

The recipe-analogue of boiled sausage “Duck” was taken as a basis [27].

Table 1

Created recipes of sausages with duck meat

Raw materials	Analogue	Recipe 1	Recipe 2	Recipe 3
Raw unsalted, kg per 100 kg				
Duck Pecking	40	-	-	-
Duck (*Cairina moschata*)	-	40	45	50
Pork fat	10	10	10	10
Soya protein	-	10	10	10
First-class beef	47	10	10	10
Milk powder	-	3	3	3
FV Fiber	-	2	2	2
Pork skins protein	-	25	20	15
Potato starch	3	-	-	-
Total	100	100	100	100
Spices and materials, g per 100 kg of unsalted raw materials				
Salt	2,5	2,5	2,5	2,5
$NaNO_2$	0,005	0,005	0,005	0,005
Sugar	0,1	0,1	0,1	0,1
Pepper black	0,1	0,1	0,1	0,1
Coriander	0,05	0,05	0,05	0,05
Garlic fresh	0,2	0,2	0,2	0,2

The production of samples was carried out in accordance with the technology of minced meat with the addition of hydrated soybean isolate and 20% water [27].

Duck meat and beef are crumbled, cleaned of tendons and comminuted on the gyroscope with the grating orifices diameter 2–3 mm. Soy isolate is preliminarily hydrated in the ratio of the preparation:water – 1:5. The pork skins protein is prepared according to the following scheme: cleansing of the skins, cutting into small pieces, cooking in the presence of water in the amount of 50% at a temperature of 90–95 °C for 30–40 minutes, chopping hot with the meat mincer with the grille hole diameter of 2–3 mm. At the same time, auxiliary materials are being prepared.

All ingredients are mixed for 20 min, and the mixture then is stuffed into the natural casing. Samples are heat processed until they reached the internal temperature of 72 °C. The sausages samples are then rinsed with cooled water and stored at 4 °C for 6 days.

Lipid oxidation measurements (acid value, peroxide number, thiobarbituric acid reactive species)

The acid value was determined by the batch titration with sodium hydroxide in the concentration in the presence of fenolftalein alcohol solution [25, 26]. 3–5 g of the investigated forcemeat was weighted in the conic retort with the volume of 150–200 cm^3 with the error of no more than 0,001 g. The batch was heated on the water bath and after the addition of 50 cm^3 of neutralized ether-alcohol mixture shaken. Then 3–5 drops of fenolftalein alcohol solution with the mass share of 1 % were added. The received solution while shaking was titrated fast with potassium hydroxide solution with the molar

concentration 0,1 mol/dm^3 till the distinct rose coloration appeared and kept for 1 min. The acid number was calculated by the formula:

$$X=(V\times K\times 5,61)/m, \quad (1)$$

where V – volume of potassium hydroxide solution, with the molar concentration 0,1 mol/dm^3, used for titration; K – correction to alkali solution for recalculation on the distinct (0,1 mol/dm^3) one; 5,61 – number of milligrams of potassium hydroxide, contained in 1 cm^3 (0,1 mol/dm^3) of solution; m – forcemeat batch mass, g.

The method of PV determination is based on the batch extraction by the mixture of chloroform and icy acetic acid and further titration by the sodium hyposulfite solution with the previously added starch solution [25, 26]. 0,8–1 g of a batch, weighted with accuracy of no more than 0,0002 g were placed in the conic retort with the stopper, melt on the water bath and 10 cm^3 of chloroform and 10 cm^3 *of* icy acetic acid were gently poured on the retort sides. 0,5 cm^3 of saturated, freshly prepared potassium iodine solution was quickly added. The retort was closed with the stopper, the content was mixed by turning movements and put into the dark place for 3 minutes. Then 100 cm^3 of distilled water with the previously added 1 cm^3 of starch solution with the mass share of 1 % was gently poured into the retort. After that it was titrated with sodium hyposulfite solution with the molar concentration of 0,01 mol/dm^3 until the blue coloration disappeared.

To verify the clearness of reagents the control determination without a batch was realized. The peroxide number was calculated by the formula:

$$X=[(V-V1)\times K\times 0,00127\times 100/m, \quad (2)$$

where V – volume of sodium hyposulfite solution with the molar concentration 0,01 mol/dm^3, used for titration in the main experiment with the forcemeat batch, cm^3; V1 – volume of sodium hyposulfite solution (0,01 mol/dm^3), used for titration in the control experiment without a forcemeat batch, cm^3; K – coefficient of correction to sodium hyposulfite for recalculation on the distinct (0,01 mol/dm^3) solution; 0,00127 – number of grams of iodine, equivalent to 1 cm^3 (0,01 mol/dm^3) of sodium hyposulfite; m – mass of the studied forcemeat batch, g.

TBARS was determined by measuring the coloration intensity of the mixture of the studied sample distillate and thiobarbituric acid solution (1:1) after 35 minutes on the water bath on the spectrophotocolorimeter "Spекol-11" (Germany) at the wave length 535 nm [28].

50 g of forcemeat batch were put into the porcelain mortar, 50 cm^3 of distilled water were measured by the glass cylinder, added to the mortar and ground with the pestle into the uniform mixture. The prepared sample was quantitatively transferred into Kjeldahl retort, remains were washed away from the mortar with 47,5 cm^3 of distilled water and then 2,5 cm^3 of hydrochloric acid were added. The distillation was carried out in Kjeldahl apparatus, collecting 50 cm^3 of distillate in the volumetric flask. 5 cm^3 of distillate were taken, poured into the retort with the fitted stopper. After the addition of 5 cm^3 of thiobarbituric acid, the retort was closed with the fitted stopper and heated on the boiling water bath for 35 min.

Simultaneously the control experiment was held, using 5 cm^3 of distilled water instead of the distillate. Then the solutions were cooled in the cold running water for 10 min, and the optic density at the wave length of 535±10 nm as to the control solution was measured.

The thiobarbituric acid reactive species, mg of MA (malonic aldehyde) / kg of the product, was calculated by the formula:

$$X=D\times 7,8, \quad (3)$$

where D – optic density of the solution; 7,8 – coefficient of proportional dependency of MA density on its concentration in the solution. This coefficient is a permanent value.

Statistical analysis

The absolute error of measurements was determined by Student criterion, the reliable interval P=0,95, the number of repeatitions in calculations – 3−4, the number of parallel tests of studied samples – 3.

Results and discussion

To characterize the effect of RE on the course of hydrolytic processes in the lipid fraction of the meat-containing sausages, the AV was determined, as shown in Fig. 1.

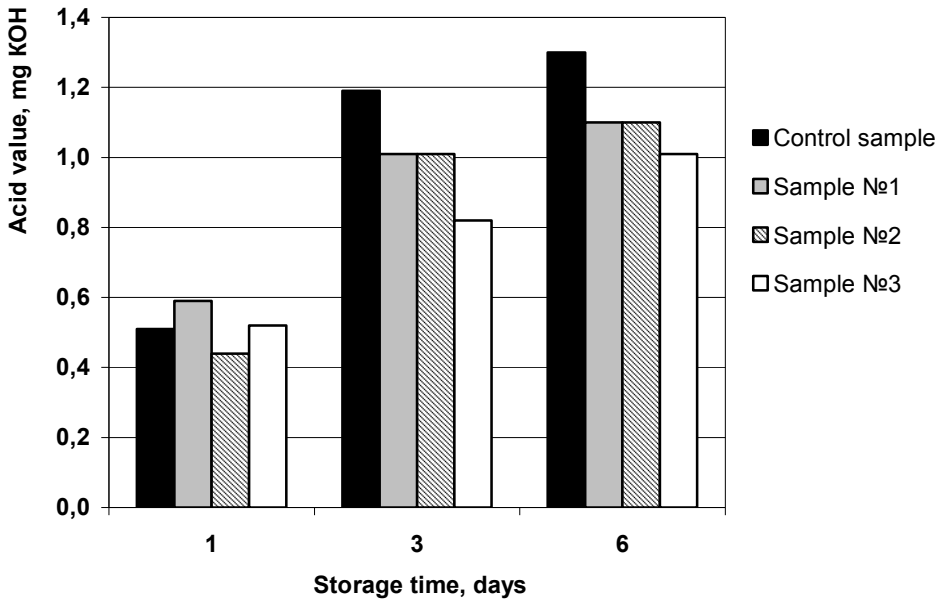

Figure 1. The dependence of the acid value on the concentration of the added rosemary extract, mg KOH

Among the experimental samples, the smallest amount of free fatty acids was observed with rosemary extract concentration of 0.05%. At the end of the storage period, after 6 days, the AV in the sample number 1 reached 1,095 ± 0,007 mg of KOH, in the sample number 2 – 1,105 ± 0,007, and in the third sample – 1,01 ± 0,13, which is 15-21% lower than in the control sample.

The obtained results indicate that the introduced antioxidant inhibits fat hydrolysis due to the high concentration of flavonoids in the extract. Sample 3 had the highest effectiveness.

The dynamics of the PV shift in the meat-containing sausages with duck meat is shown in Figure 2.

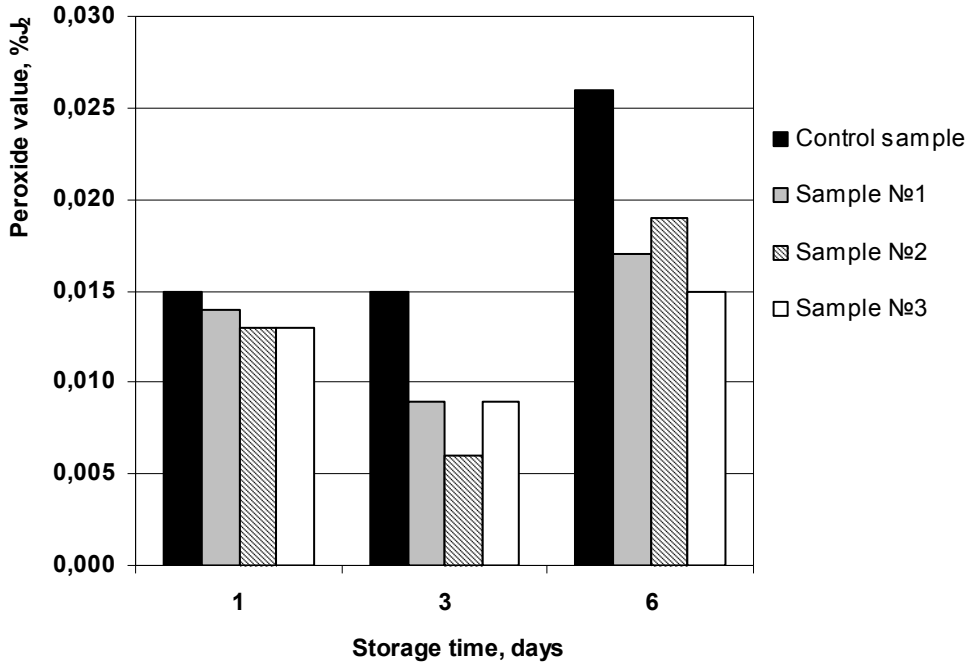

Figure 2. The dependence of the peroxide value on the concentration of the added rosemary extract, % J_2

The addition of rosemary extract helps slow down oxidative processes, as evidenced by the results of the research. Among the experimental samples, the PV increased more intensively in the sample without an additive. The largest stabilizing effect was produced by the concentration preparation used in sample 3. The PV in this sample on the expiration date was 0.015 ± 0.001% J_2, whereas in the control sample, this value was 0,026 ± 0,002% J_2, which is 57,69% higher.

The study of the dynamics of the peroxide value in the samples indicates that the rosemary extract contains the optimal ratio of biologically active compounds that actively contribute to the inhibition of lipid peroxide oxidation. The depression of deep lipid oxidation is due to the high content in the rosemary extract of carnosine and rosemary acids, the activity of which is twice as high as the activity of synthetic antioxidants [29].

The antioxidant action of the additives is also manifested in the accumulation of mono and di-aldehydes that react with 2-thiobarbituric acid. To determine the volume of secondary oxidation products accumulation on the last day of the fat samples storage, the thiobarbituric acid (TBARS) value of the fat was studied, and the TBARS results are presented in Fig. 3.

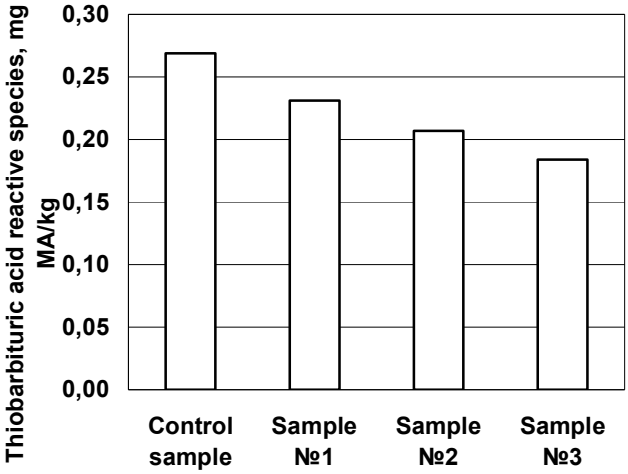

Figure 3. The influence of bioflavonoids of the rosemary extract on the accumulation of secondary products of oxidizing the lipids of the meat-containing sausages, mg MA/kg

Secondary oxidation products, namely, peroxides and hydroperoxides, are the carriers of unpleasant taste and odor of oxidized fats. The addition of RE helps slow down the accumulation of secondary oxidation products. At the end of the storage period, the amount of secondary oxidation products in the control sample was 0,269±0,04 mg MA/kg of the finished product, whereas in the experimental samples it reached the following values: 0,231±0,03 mg MA/kg in sample 1, 0,207±0,03 mg MA/kg in sample 2, and 0,184±0,04 mg MA/kg in sample 3.

The rosemary extract had the highest effectiveness at the concentration of 0.05% in sample 3, where the amount of malonic aldehyde in the sausage at the end of its shelf life was the lowest; 31,6% lower than in the control sample.

The research of the secondary oxidation products content allowed us to estimate the depth of the oxidative processes occurring in the specimens of the sausages while stored for 6 days at + 4 ° C. The concentration of the secondary oxidation products was the highest in the control sample, and in the experimental ones, the concentration of the added antioxidant additive reduced proportionally. It is known that the carnosic acid and carnosol of the rosemary extract are the active oxygen absorbers, preventing the formation of hydroperoxides and propanal [24, 29, 30].

The components of the rosemary extract make the joining of oxygen and glycerides impossible, thereby inhibiting the oxidative processes in minced meat. Carnosic acid and

carnosol block peroxide radicals particularly effective in the systems based on the high content of lipid components.

The effectiveness of the antioxidant additive depended on the concentration, but in all experimental samples of meat-containing sausages, the concentration of malonic aldehyde was lower compared to the control product.

Conclusions

1.The conducted research has confirmed the high antioxidant activity of rosemary extract and the effective inhibition of the oxidation process of duck meat lipids.
2.The addition of the RE in the amount of 0,03–0,04 % helps slow down the hydrolytic oxidation of the minced duck meat lipids by 15–21 %.
3.The addition of rosemary extract in the concentrations of 0,03–0,05% to the forcemeat mass contributes to the slowing of lipid peroxide oxidation in meat-containing sausages with duck meat. Peroxide value decreases by 26,92–57,69% depending on the concentration of the RE.
4.Stabilization of lipid peroxide oxidation in meat-containing sausages with duck meat as a consequence inhibits the formation of secondary oxidation products, which is confirmed by the results. The number of secondary oxidation products that react with tiobarbituric acid was the smallest at the end of the storage period of meat-containing sausages with musk duck meat with an RE concentration of 0.05% and amounted to 0.184 ± 0.04 mg MA/kg, which is lower than in the control sample, by 31.6%.
5.The largest effect was obtained with the rosemary extract concentration of 0.05%, which reduces the oxidative deterioration of fat almost by two times.

References

1. Bertelsen G., Jakobsen M., Juncher D., Moller J., Kroger-Ohlsen M., Weber C., & Skibsted L.H. (2000), Oxidation, shelf-life and stability of meat and meat products, *Proceedings of the 46th international congress of meat science and technology*, 4.II-L2, pp. 516–524.
2. Pasichnyj V.M., Zheludenko Ju.V. (2014), Perspektyva natural'nyh antyoksydantiv dlja vykorystannja v m'jasopererobnij galuzi, *Zbirnyk naukovyh prac' HDUHT*, 2(20), pp. 264-276.
3. Shahidi F. (1997), *Natural Antioxidants. Chemistry, Health Effects and Applications*, Champaign, Illinois, AOCS Press.
4. Ukrainets A., Pasichniy V., Zheludenko Yu., (2016), Plant extracts antioxidant properties for meat processing industry, *Biotechnologia Acta*, 2, pp. 19–27.
5. Nunez de Gonzalez M., Boleman R., Miller R., Keeton J., Rhee K. (2008), Antioxidant properties of dried plum ingredients in raw and precooked pork sausage, *Journal of Food Science*, 73, pp. 63–71.
6. Naveena, B., Sen, A., Vaithiyanathan, S., Babji, Y., & Kondaiah, N. (2008), Comparative efficacy of pomegranate juice, pomegranate rind powder extract and BHT as antioxidants in cooked chicken patties, *Meat Science*, 89, pp. 304–308.
7. Lee C., Reed J., Richards M. (2006), Ability of various polyphenolic classes from cranberry to inhibit lipid oxidation in mechanically separated turkey and cooked ground pork, *Journal of Muscle Foods*, 17, pp. 248–266.

8. Kandaswami C., Middleton E. (1994). Free radical scavenging and antioxidant activity of plant flavonoids, *Adv. Exp. Med. Biol.*, 366, pp. 351–361.
9. Velasco V., Williams P. (2011), Improving meat quality through natural antioxidants, *Chilean Journal of Agricultural Research*, 71, pp. 313-322.
10. Fernandez-Lopez J., Zhi N., Aleson-Carbonell L., Perez-Alvarez J. A., Kuri V. (2005), Antioxidant and antibacterial activities of natural extracts: application in beef meatballs, *Meat Science*, 69, pp. 371–380.
11. Bozhko N., Tishhenko V., Pasichnij V. (2017), Ekstrakt zhuravlini v texnologiiy varenih kovbas z myasom vodoplavnoyi ptyci, *Naukovij visnyk LNUVMBT imeni S.Z. Gzhyczkogo*, 75, pp. 106–109.
12. Lara M.S., Gutierrez J.I., Tim´on M., Andr´es A.I. (2011). Evaluation of two natural extracts (*Rosmarinus officinalis L.* and *Melissa officinalis L.*) as antioxidants in cooked pork patties packed in MAP, *Meat Science*, 88, pp. 481–488.
13. Trindade R.A., Lima A., Andrade-Wartha E.R., Oliveira e Silva A.M., Mancini-Filho J, Villavicencio A.LC.H. (2009), Consumer's evaluation of the effects of gamma irradiation and natural antioxidants on general acceptance of frozen beef burger, *Radiat Phys Chem,* 78, pp. 293–300.
14. Sebranekab J.G, H.Sewalt V.J., Robbins K.L., Housera T.A. (2005), Comparison of a natural rosemary extract and BHA/BHT for relative antioxidant effectiveness in pork sausage, *Meat Science,* 69, pp. 289–296.
15. Rižnar K., Čelan Š., Knez Ž., ŠKerget M., Bauman D. , Glaser R. (2006), Antioxidant and Antimicrobial Activity of Rosemary Extract in Chicken Frankfurters*, Journal of Food Science*, 71(7), pp**.** 425–429.
16. Mc.Bride N., Hogan S., Kerry J.P. (2007), Comparative addition of rosemary extract and additives on sensory and antioxidant properties of retail packaged beef, *Internat. J.Food Science and Technology*, 42, pp. 1201–1207.
17. Hernandez-Hernandez E., Ponce-Alquieira E, Jaramillo-Flores M., Guerrero-Legaretta I. (2009). Antioxidant effect rosemary and oregano extracts on TBARS and colour model raw pork batters. *Meat Science*, 81 (2), pp. 410–417.
18. Mitrofanov N.S., Makoveev I.I. (2006), Miaso ptitsy osnova dlia rasshireniia assortimenta miasnykh produktov, Miasnaia industriia, 4, pp. 26–29.
19. Makhonina V.N. (2016), Izuchenie morfologicheskogo i khimicheskogo sostava miasa potroshennykh tushek utok dlia opredeleniia ego sortnosti, *Ptitsa i ptitseprodukty*, 1, pp. 61–64.
20. Zalialieva D.R., Krishtafovich D.V., Krishtafovich V.I. (2011), Kachestvo miasa muskusnykh utok, *Miasnaia industriia*, 9, pp. 29–35.
21. Krishtafovich V.I., Zalialieva D.R. (2011), Issledovanie potrebitelskikh svoistv i pishchevoi tsennosti miasa muskusnykh utok, *Tovaroved prodovolstvennykh tovarov*, 6, pp. 23-27.
22. Kumar Y., Yadav D., Ahmad T., Narsaiah K. (2015), Recent Trends in the Use of Natural Antioxidants for Meat and Meat Products, *Comprehensive Reviews in Food Science and Food Safety*, 14, pp. 796–812.
23. Gupta A. D., Bansal V. K., Babu V., Maithil N. (2013), Chemistry, antioxidant and antimicrobial potential of nutmeg (Myristica fragrans Houtt), *J. Genet. Engin. Biotechnol*, 11, pp. 25–31.
24. Sisse Jongberg, Mari Ann Torngren, Annemarie Gunvig, Leif H. Skibsted, Marianne N. Lund (2013), Effect of green tea or rosemary extract on protein peroxidation in Bologna type sausages prepared from oxidatively stressed pork, *Meat Science*, 93, pp. 538–546.

25. Bozhko N., Tischenko V., Pasichnyi V., Marynin A., Polumbryk M. (2017), Analysis of the influence of rosemary and grape seed extracts on oxidation the lipids of Peking duck meat, *Eastern-European Journal of Enterprise Technologies*, 4/11(88), pp. 4–9.
26. Zhuravskaia N.K., Gutnik B.E., Zhuravskaia N.A. (2001), *Tekhnokhymycheskyi kontrol proyzvodstva miasa s miasoproduktov*, Kolos, Moscow.
27. Nikitin B.I., Nikitina N.B. (1983), *Pererabotka pticy, krolikov i proizvodstvo pticeproduktov,* Moscow.
28. Bozhko N. Tischenko V., Pasichnyi V., Marynin A., Polumbryk M. (2017), Study of oxidation processes in duck meat with application of rosemary and grape seed extracts, *EUREKA: Life Sciences*, 4, pp. 10–15.
29. Brewer M. S. (2011), Natural antioxidants: Sources, compounds, mechanisms of action, and potential applications, *Comprehens. Rev. Food Science and Food Safety*, 10, pp. 221–247.
30. Brewer S. (2008), Preserving beef quality with natural antioxidants, *Research knowledge management*, 12, pp.1–14.

Beer enrichment with biologically active hop compounds

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Keywords:

Hop
Beer
Xanthohumol
Beta-acids
Polyphenols

Article history:

Received 17.01.2018
Received in revised form 14.03.2018
Accepted 29.03.2018

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DOI:
10.24263/2304-974X-2018-7-1-7

Abstract

Introduction. The research was aimed at studying the influence of biologically active compounds of the Ukrainian hop varieties on beer quality indicators and peculiarities of their use in brewing.

Materials and methods. The research was focused on the aroma Slavyanka hop variety with a high beta-acid content and on the special Ruslan and Xantha hop varieties with an increased xanthohumol content, as well as on the beer made of them. To identify the amount and composition of bitter substances and xanthohumol in the hop plant, as well as the products of their transfer during brewing, the liquid chromatography (HPLC) was employed, while bitterness of the hopped wort and the final beer was controlled by the spectrophotometric methods.

Results and discussions. In beer enrichment with biologically active hop compounds, an optimal ratio of the fine aroma hops to the bitter ones, which ensures high beer quality, is as follows: 40% of the rated bitterness derived from alpha-acids were added with the special Ruslan and Xantha hop varieties, and 60% were obtained through addition of fine aroma hop varieties with a high beta-fraction content. The suggested method of combined dosing of fine aroma hops and special hop varieties makes it possible to obtain up to 13.0–20.0 mg/dm^3 of iso-alpha-acids in beer with further achievement of a 160.0–200.0 mg/dm^3 content of polyphenolic compounds. This ensures higher colloid stability of the beer and a 15–20% increase in the extent of applying bitter substances. In wort hopping, the use of the fine Slavyanka aroma hop variety, having a great amount of beta-acids and the best ratio of beta- to alpha-acids of 1.3:1.8 as a raw material contributes to producing compounds with pleasant, soft bitterness. Whereas the use of the Slavyanka hops with a low cohumulone content of alpha-acids (21.4%) provides a reduced, up to 5.0–7.0 mg/dm^3, isocohumulone content of beer, which improves the quality of bitterness. Meanwhile, the use of the special Ukrainian hop varieties, Ruslan and Xantha, with a content of xanthohumol up to 1.2% makes for the isoxanthohumol formation in beer in the range of 2.0–5.0 mg/dm^3.

Conclusion. Combined use of the Slavyanka hop variety and the Ruslan and Xantha hops in the suggested ratio enriches the drink with biologically active hop compounds, thus improving its functionality.

Introduction

The use of the hop plants in brewing is due to the presence of numerous substances, biologically active compounds, which impart biological stability to beer, contribute to its conservation and create the foam and a unique bouquet of taste and aroma properties. It is different hop varieties that are responsible for the peculiar characteristic aroma and taste of the beer [1–3]. Besides brewing, the hop plant is used in breadmaking, pharmacology, official and folk medicine. The major substances responsible for the hop cone biological activity are bitter and phenolic compounds, as well as the essential oil [4, 5]. Bitter substances are the most beneficial and specific constituents of the hop cones, which in this form are not available in other plants [2, 6]. The most profound effect on the specific properties of beer is exerted by isomers of the starting bitter hop substances, which exist in minor amounts in its cones, but are formed on wort boiling with hop.

Alpha- and especially beta-acids inhibit the development of gram-positive and gram-negative bacteria, as well as acid-forming microorganisms [2], but have no effect on yeast development and vital activity. This is of great importance for the brewing technology since an optimal bitter substance content increases microbiological stability of the beer. Humulone, besides its antibiotic properties toward the bacterial microflora, hampers the growth of some harmful fungi.

The Japanese scientists have proven that β-acids inhibit the growth of the bacterium (Helicobacter pylori), which has invaded almost half of the population of the planet and causes onset of gastritis, as well as gastric and duodenal ulcer. The association between the presence of this bacterium and onset of gastric cancer has been proven [7].

Colupulone, the constituent of β-acids, is known to hamper the development of various microorganisms, including the pathogens, such as Staphylococcus aurers, Mycobacterium tuberculosis and Mycobacterium phei. As long ago as 1949, it was found out that α- and β-acids bring under adequate control the growth of tubercle bacilli [8]. Along with the antiseptic action, they also exert the sedative effect [9].

There is no doubt that taste and aroma of the beer made of various hop varieties also depends on different content of polyphenolic compounds. The polyphenolic hop compounds are the antioxidants, increasing the beer's recovering capacity and effecting taste stability. On boiling, they make for protein precipitation and formation of composite protein-polyphenolic complexes, the precipitation of which favors wort lightening, and thus prevents oxidation and losses of bitter hop substances. However, on prolonged boiling, high-molecular polyphenols cause unpleasant beer mouthfeel. So, the polyphenolic hop substances influence the beer taste and quality not on their own, but in a complex with bitter hop substances, proteins and amino acids.

Salach et al., when analyzing the hop quality dependency on the polyphenol content, noted that in the Czeck varieties, the latter is much higher than in the hop varieties of other countries. Thus, the polyphenol content of the Czeck Zhatetsky hop variety, noteworthy for the highest quality, comprises 5.2–5.9 %, whereas that of the American one is no more than 26 %. They considered a high polyphenol content of the Zhatetsky hop as its advantage over the other varieties. Contemporary scientists also claim that the best quality has the beer made of hop with about 5% of polyphenol [10, 11].

Among hop phenols, the unique compounds are available, such as prenylated flavonoids of the halcone and flavanone types. Previously, the prenylated flavonoids were treated somewhat meagerly in terms of either hop growing or their subsequent use in brewing. Only at the end of the last century [12, 13], the scientists became deeply involved in studying these substances due to their high biological activity. At present [14, 15], more

than two tens of compounds belonging to the group of prenylated flavonoids have been revealed in the hop plant. The prenylated hop flavonoids exhibit an extremely wide spectrum of biological activity. They exhibit anticancer, phytoestrogenic, antioxidant and antiviral properties. In particular, xanthohumol is being studied now as a potential anticancer agent. Rather wide spectrum of antiviral activity of the prenylated hop flavonoids has been presented [16–22]. In the cell culture, the isoxanthohumol-enriched hop extracts moderately inhibit reproduction of the bovine viral diarrhea, which serves as a surrogated model of the human HCV, 2 HSV–2 and rhinovirus [23].

There has also been established an antioxidant activity of the prenylated flavonoids, which neutralize active radicals of oxygen and inhibit the processes of free radical oxygenation behind the development of cardiovascular diseases [24, 25]. Among halcones, the most important is xanthohumol. The xanthohumol content of different hop varieties immediately after harvesting ranges 0.2–1.1% of the weight [7, 9, 24, 25]. As wort is boiled with hop, about 70% of xanthohumol undergo isomerization to form isoxanthohumol [26]. Of this amount, about 30% end up in beer. Isoxanthohumol also has a high anticancer potential.

Xanthohumol and isoxanthohumol, as expected, are the main compounds responsible for the positive human health consequences of beer in case of its moderate consumption [5, 17, 27]. In this context, the currently pressing problem in the world brewing practice is an increase of prenylated chalcone content of beer, as well as the development of brewing technologies for beer and hop extracts enriched with xanthohumol [17, 27].

Materials and methods

The research employed modern international physical and chemical methods to analyze bitter substances and xanthohumol of hops and hop extracts, as well as the products of their transfer in the process of brewing, namely: high-performance liquid chromatography (HPLC), spectrophotometry and methods of control harmonized with the procedures of European Brewing Convention [28, 29].

Methods of studying quality indicators of hops

The fine aroma Slavyanka hop variety with a high content of beta-acids, as well as the bitter Xantha and Ruslan hops with increased xanthohumol content were studied. The weight of the average sample used for identification and biochemical investigations was no less than 0.5 kg of the hop dry weight. The alpha-acids in the hop were identified by conductometry according to the EBC procedure 7.4 [28]. Bitter hop substances were extracted with using an organic solvent – methanol. The weight ratio of the hop cone to the extractant was 1:10. The HPLC was employed to measure the amount of α- and β-acids, as well as the cohumulone content of alpha-acids and the colupulone content of beta-acids, and also the content of isoxanthohumol. The chromatography was performed on the Ultimate 3000 chromatographer with the UV detector at the temperature of 35 °C. The 100 x 2.1 mm column filled with the Pinacle DB C18, 3 μm was used. As a mobile phase, the solution of methanol, water and acetonitrile was used in the 38:24:38 ratio. The quantitative analysis of the bitter substance components was carried out by the international ICF-3 standard.

Method of beer sampling at the mini-brewery

The experimental brewing with using the hop samples under study was carried out at the laboratory and at the mini-brewery of the Agricultural Polissya Institute of the National Academy of Agrarian Sciences of Ukraine, with a capacity of 100L of beer per cycle, which is rather an adequate prototype of an actual brewing conditions. In the brewing experiments, grain mash was prepared, saccharified and filtered according to the procedure accepted at this brewhouse. The wort was prepared of 100% barley malt. After wort had reached the full volume, it was boiled for 15 minutes, which led to coagulation of protein compounds. The hop products were added in three stages. The overall wort boiling with hop lasted 75 minutes.

Methods of studying quality indicators of beer and wort

Bitterness obtained during wort boiling with hops, as a result of extraction and isomerization of bitter hop substances, was measured on the spectrophotometer as per EBC 8.8 [28]. The method is based on determing optic density of the isooctane resulted from the extraction of bitter substances of the acidulated hopped wort or beer with isooctane (2,2,4-trimethyl penthane), the wavelength being 275 nm. The bitterness value expressed in the International Bitterness Units as per EBC, was estimated based on the optic density index.

The polyphenolic compound content of wort and beer was measured on the spectrophotometer as per EBC 8.11 and EBC 9.11 [28].

Results and discussion

To study the effect of biologically active hop compounds, in particular, beta-acids, polyphenols and xanthohumol, on quality indicators of wort and beer, a series of experiments was performed with using the Ukrainian hop varieties having an increased content of the above substances. The suggested method of wort preparation provides combined use of the fine aroma Slavyanka hop variety with a high content of beta-acids and hops of special Ruslan and Xantha varieties with an increased content of xanthohumol, as summarized in Table 1.

An alpha-acids content of the Slavyanka hop variety comprises 4.5–7.5 %, while that of beta-acids – 6.0–10.0%. This variety contains a great amount of bitter substances and the best ratio of beta- to alpha-acids of 1.3:1.8. This pattern is the varietal attribute. One of the major features of beta-acids is their high antiseptic action, which is important for increasing beer stability on storage. A high farnesene content of the essential oil is responsible for soft and gentle aroma of wort and beer. The ratio of beta- to alpha-acids, as well as the amount and composition of the essential oil, combined with other components, make the fine aroma Slavyanka hop variety particularly valuable for brewery. The beer made of the Slavyanka hop variety exhibits high taste properties. It is characterized with soft and gentle bitterness.

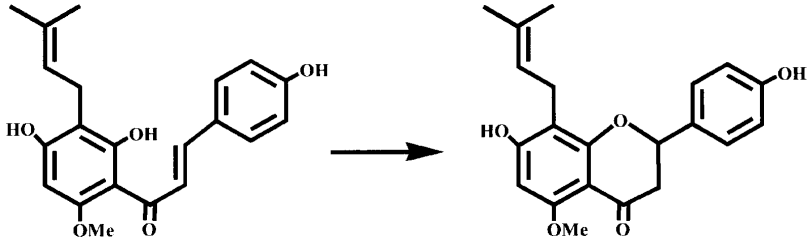
Table 1

Quality indicators of the Slavyanka, Ruslan and Xantha hop varieties

Quality indicators	Hop variety		
	Slavyanka	**Ruslan**	**Xantha**
Bitter substances, %	24.0–28.8	27.0–32.6	25.0–27.5
α-acid mass concentration, %	4.5–7.5	8.6–10.8	8.2–11.1
β-acid mass concentration, %	6.0–10.0	4.8–6.8	5.1–6.0
Cohumulone within α-acids, %	20–26	30–35	29–33
Colupulone within β-acids, %	38–46	48–56	49–57
Beta- to alpha-acids ratio	1.3–1.8	0.7–0.9	0.7–1.0
Essential oil, mL/100 g of the hop dry weight, including	1.0–2.0	1.6–2.6	0.7–1.2
myrcene,%	20–50	40–50	35–42
caryophyllene,%	7–8	5–8	10–12
humulene,%	14–16	15–20	20–30
farnesene,%	12–18	< 1.0	< 1.0
selinene, %	< 1,0	6.2–10.0	< 1.0
Total polyphenols, %	4.5–7.0	4.0–6.5	4.0–6.0
Xanthohumol, %	0.4–0.5	0.9–1.2	0.8–1.1
Brewer's assessment	Excellent, soft, gentle bitterness and sweet aroma	Excellent, noble bitterness and aroma	Excellent, evident and balanced bitterness and aroma

In composition of bitter substances and essential oil, the Ruslan and Xantha hop varieties should be assigned to the bitter hop type. Increased cohumulone content of alpha-acids (30–35%) and the absence of farnesene in the essential oil would give beer harsh bitterness. Nevertheless, due to the high beta-acid content and ratio of beta- to alpha-acids (0.7–0.9) typical of the aroma hop varieties, the beer made of these varieties has excellent quality and evident, yet pleasant bitterness. Beta-acids improve the quality of bitterness, soften and smoothen it, thus balancing the overall bitterness of the beer. There is one more parameter which distinguishes advantageously these varieties among others. This is an increased content of biologically active compounds, namely: prenylated flavonoids, and first of all, xanthohumol. The content of this compound in the Ruslan and Xantha varieties is about 1 %.

In brewing technology, like in the process of alpha-acid isomerization to iso-alpha-acids, wort hopping results in isomerization of 70% of xanthohumol to isoxanthohumol, which also exhibits anticancer properties (Figure 1). In this context, an increase in the isoxanthohumol content of beer and the development of brewing technologies for beer enrichment with xanthohumol are the urgent tasks of the world brewing.



Hop xanthohumol Hop isoxanthohumol

Figure 1. Structural formulas of hop xanthohumol and beer isoxanthohumol

In-process testing of experimental brewing with the combined use of the fine aroma Slavyanka hop variety having a high beta-acid content and the special Ruslan and Xantha hop varieties having an increased xanthohumol content was carried out at the mini-brewery at the Agricultural Polissya Institute of NAAS of Ukraine. The brewing procedure was as follows. Grain mash was prepared, saccharified and filtered according to the procedure accepted at this brewhouse. After wort had reached the full volume, it was boiled for 15 minutes, which led to coagulation of the protein structure. The wort was boiled with hop for 75 minutes. The starting materials for wort hopping were the hop cones of the fine aroma Slavyanka variety and the bitter Ruslan and Xantha varieties with an increased xanthohumol content, as summarized in Table 2.

Table 2

Quality indicators of hop samples

№	Hop quality indicators	Test version (variety name)		
		Slavyanka	**Ruslan**	**Xantha**
1	α-acid content,% dry substances	4.1	9.5	8.9
2	Cohumulone within α-acids %	21.4	33.2	30.4
3	ß-acid content,% dry substances	5.8	6.9	7.2
4	Colupulone within α-acids, %	42.8	54.3	53.8
5	ß/α-acids ratio	1.41	0.73	0.81
6	Isoxanthohumol content,% dry substances	0.40	1.08	0.96
7	Total polyphenol content,% dry substances	5.6	4.3	5.1

Experimental brewing was performed with these hop samples. Hop dosage adjusting in all wort samples was performed at 80 mg of bitter substances per 1 dm^3 of wort. The amount of added alpha- and beta-acids, and xanthohumol, as well as the total amount of hop polyphenols, were determined by calculation, as presented in Table 3.

Table 3

Amount of bitter substances, xanthohumol and polyphenolic compounds added to wort with the Slavyanka, Puslan and Xantha hop varieties

№	Test version (variety name)	Added with hop to 1 dm^3 of wort, mg/dm^3			
		α-acids	ß-acids	Xanthohumol	Total polyphenols
1	Slavyanka	80.0	113.2	6.8	110.0
2	Ruslan	80.0	58.2	9.1	36.2
3	Xantha	80.0	64.8	8.6	45.9

As evident from the Table, on dosing hops of the varieties under study, the same amount of alpha-acids (about 80 mg/dm^3) is added to 1 dm^3 of the wort, since the adjustment is based on their content. At the same time, when using the Slavyanka hop variety, twice as much alpha-acids and 2,4-3 times more polyphenolic compounds are added, as compared to the Ruslan and Xantha varieties. However, in case of the Ruslan and Xantha varieties, much more xanthohumol is added. Having analyzed different options of wort hopping, in using either a single fine and bitter hop variety or varietal blends, we have established an optimal ratio of the fine aroma to bitter hops, which ensures high quality of the beer, namely: 40% of the rated bitterness derived from alpha-acids were added with bitter hops, and the rest 60% – with hop pellets of the fine aroma Slavyanka variety. The rate of hopping can be changed with the formulation chosen and hopping conditions at a certain enterprise. Meanwhile, there are undoubted prerequisites for the adjustment of beer taste and aroma properties, beer enrichment with biologically active hop compounds, improvement of its quality and widening its assortment.

The technological solution of the suggested procedure is illustrated by the experiments presented.

Experiment 1

The starting raw materials for wort hopping were hop cones of the fine aroma Slavyanka and bitter Ruslan variety, containing an increased xanthohumol content. The hop products were added in three stages.

Wort hopping was performed at 80 mg of bitter substances in 1 dm^3 of the wort, which constitutes 0.8 g/daL. Hop dosage adjusting during the experiments was performed according to the alpha-acid content as follows:

$$H_x = \frac{R_c \times 10^4}{AK \times (100 - W)}, .$$

here H_x is the hop rate g/daL;

R_c – rate of bitter substances of the hop wort for this beer variety, g/daL;

AK – mass concentration of hop alpha-acids,% dry substances;

W – mass concentration of hop humidity, %.

An example of calculation of the amount of the Ruslan hop variety added to the wort is as follows:

$$H_x = \frac{0.8 \times 10^4 \times 0.4}{9.5 \times (100 - 10)} = 3.74\, g / daL\ .$$

In example of calculation of the amount of the Slavyanka hop variety added to the wort is as follows:

$$H_x = \frac{0.8 \times 10^4 \times 0.6}{4.1 \times (100 - 10)} = 13.01\ g / daL.$$

The first portion of hops, i.e. all the bitter Ruslan hops (40% of rated bitterness in terms of the alpha-acid content), were added 15 minutes after the start of wort boil. The rest 60% of bitterness were added with hop pellets of the fine aroma Slavyanka variety in two steps: 90% of the weight of the fine aroma Slavyanka hop variety were added 15 minutes after the addition of the first portion and 10% – 10 minutes before the hopping completion. The overall wort boiling with hop lasted 75 minutes. The beer made from a single fine aroma Slavyanka hop variety was used as a control.

The value of beer bitterness and the content of bitter substances measured by the HPLC method and spectrophotometry is given in Table 4.

Table 4

Composition of bitter substances of the beer samples

№	Beer quality indicators	Test version	
		Slavyanka 100 %	Slavyanka 60% + Ruslan 40%
1	Beer bitterness, for EMS	23.9	22.2
2	Iso-alpha-acid content, mg/dm^3	16.8	14.2
3	Isocohumulone within alpha-acids, mg/dm^3	5.3	7.0
4	Isohumulone + isoadhumulone within alpha-acids, mg/dm^3	11.5	7.2
5	Alpha-acid content, mg/dm^3	0.62	0.97
6	Isoxanthohumol content, mg/dm^3	3.71	4.51
7	Total polyphenol content, mg/dm^3	199.8	160.6

As evident from Table 4, the beer samples differ in the amount and composition of bitter substances, isoxanthohumol and polyphenolic compounds. This is due to different content of all hop components and their ratio, and not just to alpha-acids. At the same time, of great importance is involvement of some hop compounds into creation of taste and aroma features of beer, as well as efficiency of their extraction and isomerisation in the wort hopping process. It should be noted that one adds much more xanthohumol to the second beer sample with the Ruslan hop variety. In the hopping process, xanthohumol undergoes

isomerization to isoxanthohumol, contained in the given sample in abundance, thus enriching beer with xanthohumol and isoxanthohumol, and imparting some functionality to it.

The organoleptic quality assessment of the experimental beer samples (in scores) showed them to differ in taste and bitterness (Table 5). According to degustation, the beer samples had the clear hop aroma, however in the first sample it was softer. This sample also had the full balanced taste and gentle, smooth, and soft bitterness.

Table 5

Mean score assessment of beer

Test version	Quality indicators							
					Flavor			
	Clarity	Color	Foam formation	Aroma	Fullness	Bitterness	Overall score	Grade
Slavyanka,100 %	3	3	5	4.0	4.8	4.8	24.6	Excellent
Slavyanka 60% + Ruslan 40 %	3	3	5	3.9	4.7	4.7	24.3	Excellent

The second sample differed from the first one in taste. Since alpha-acids of the Ruslan hop variety contained more cohumulone (Table 1 and 2), the beer made through adding this hop also had a higher isocohumulone content of iso-alpha-acids (Table 4). In the beer bitterness formation, a negative role is assigned to this fraction. However, beta-acids, introduced into the wort with the Slavyanka hop variety, improved the quality of bitterness, having softened and smoothened it, and thus made the whole bitterness balanced. Therefore, bitterness of the second sample was more evident and, at the same time, noble and pleasant. At the same time, the polyphenol content of beer comprises 160.6–199.8 mg/dm^3, which ensures not only high biological but also colloid stability of beer. An increased isoxanthohumol content of the second sample, in case of combined use of the Slavyanka and Ruslan hop varieties at the suggested ratio, enriches the drink with biologically active hop compounds, thus improving its functional properties.

Experiment 2

The procedure of wort preparation differs from the previous experiment in using the Xantha hop variety as a raw material, which also has an increased xanthohumol content. The hop was added in three stages.

Wort hopping was performed at 80 mg of bitter substances in 1 dm^3 of wort, that is 0.8 g/daL. Hop rating during experiments required for wort hopping, was performed by the alpha-acid content, as follows

$$H_x = \frac{R_c \times 10^4}{AK \times (100 - W)},$$

here H_x is the hop rate g/daL;

R_c – rate of bitter substances of the hop wort for this beer variety, g/daL;
AK – mass concentration of hop alpha-acids,% dry substances;
W – mass concentration of hop humidity %.

An example of calculation of the amount of the Xantha hop variety added was as follows:

$$H_x = \frac{0.8 \times 10^4 \times 0.4}{8.9 \times (100 - 10)} = 4.00 \ \text{g / daL.}$$

An example of calculation of the amount of the Slavyanka hop variety added to the wort is as follows:

$$H_x = \frac{0.8 \times 10^4 \times 0.6}{4.1 \times (100 - 10)} = 13.01 \ \text{g / daL.}$$

The first portion of hops, i.e. all the bitter Ruslan hops (40% of rated bitterness in terms of the alpha-acids content), were added 15 minutes after the start of wort boil. The rest 60% of bitterness were added with the hop pellets of the fine aroma Slavyanka variety in two steps: 90% of the weight of the fine aroma Slavyanka hop variety were added 15 minutes after the addition of the first portion and 10% – 10 minutes before the hopping completion. The total period was 75 minutes. The beer made from a single fine aroma Slavyanka hop variety was used as a control.

The value of beer bitterness and the content of bitter substances measured by the HPLC method and spectrophotometry is given in Table 6. As seen from Table 6, the samples differ in the amount and composition of bitter substances, isoxanthohumol and polyphenolic acids. This is due to the different content of all hop components in different hop varieties and their ratio and not just alpha-acids.

Table 6

Bitter substance content of the beer samples

No.	Beer quality parameters	Test version	
		Slavyanka 100 %	**Slavyanka 60% + Ruslan 40 %**
1	Beer bitterness, units of EBC	23.9	22.8
2	Iso-alpha-acid content, mg/dm^3	16.8	14.0
3	Iso-cohumulone within alpha-acids, mg/dm^3	5.3	6.1
4	Iso-humulone + iso-adhumulone within alpha-acids, mg/dm^3	11.5	7.9
5	Alpha-acid content, mg/dm^3	0.62	1.03
6	Iso-xanthohumol content, mg/dm^3	3.71	4.67
7	Total polyphenol content, mg/dm^3	199.8	163.1

It should be noted that one adds much more xanthohumol to the second sample with the Xantha hop variety. In the hopping process xanthohumol undergoes isomerisation to isoxanthohumol, contained in the given sample is abundance, thus enriching beer with xanthohumol and imparting some functionality to it. The score beer assessment is given in Table 7.

Table 7

Mean score degustation assessment of beer

Test version	Quality parameters							
					Flavor			
	Clarity	Color	Foam formation	Aroma	Fullness	Bitterness	Overall score	Grade
Slavyanka 100 %	3	3	5	4.0	4.8	4.8	24.6	Excellent
Slavyanka 60% + Xantha 40 %	3	3	5	3.8	4.8	4.8	24.4	Excellent

Both beer samples had the clear hop aroma, but in the first sample it was softer due to farnesene, contained in the essential oil of the Slavyanka. This sample also had the full balanced taste and soft, gentle and smooth bitterness. The beer of the second sample had full harmonic taste and pleasant balanced and evident bitterness. At the same time, the polyphenol content of beer is 163.1 mg/dm^3, which ensures not only high biological but also colloid stability of beer.

An increased isoxanthohumol content of the second beer sample, in case of the combined use of the Slavyanka and Xantha hop varieties as a raw material in the suggested ratio, enriches the drink with biologically active hop compounds, thus increasing its functionality.

For comparison, the physico-chemical parameters of the beer samples under study were determined. As seen from Table 8, the combined use of the Slavyanka and special Ruslan and Xantha hop pellets did not change physico-chemical parameters of the beer but enriched the beer with biologically active hop compounds, thus increasing its functionality.

Table 8

Physical and chemical parameters of the beer samples under study

Beer quality parameters	Test version (beer variety)		
	Slavyanka (control)	Slavyanka+ Ruslan	Slavyanka + Xantha
Alcohol mass concentration, %	3.59	3.63	3.58
Mass concentration of dry substances in the starting wort, %	11.47	11.40	11.49
Acidity, cm^3 1 mole/dm^3 solution of sodium hydroxide per 100 cm^3 of beer	1.8	1.7	1.7
Color, cm^3 0.1 mole/dm^3 of the iodine solution per 100 cm^3 of water	0.8	0.8	0.8

Having analyzed different versions of wort hopping, when using either a single fine aroma and bitter hop variety or the varietal blend, the suggested optimal ratio of aroma to bitter hops, ensuring high quality of beer, was confirmed namely: 40% of rated bitterness derived from alpha-acids were added with bitter hops, and the rest 60% – with the fine aroma Slavyanka hop variety. The hopping rate can be changed with the formulation chosen and the hopping conditions at a certain enterprise.

The above research resulted in the developed of a beer model with an optimal content of bitter substances, polyphenols, isomers of alpha-acids, xanthohumol and isoxanthohumol.

Application of the suggested brewing procedure enables the following technical result:

–wort hopping with using the Slavyanka hop variety, having a great amount of beta-acids and the best ratio of beta- to alpha-acids of 1.3:1.8 as a raw material results in the formation of the compounds with pleasant soft bitterness;

–due to beta-acids, high antiseptic action is ensured, which exhibits a beneficial effect upon beer stability on storage;

–soft gentle aroma is imparted to the beer due to farnesene within the essential oil of the Slavyanka hop;

–the Slavyanka hop polyphenols, along with their bitter substances, in contrast to the polyphenols of malt and barley, are particularly responsible for fullness and clearness of the drink taste, and also act directly on the stability of foam and beer on storage, when interacting with high molecular wort proteins and forming composite complexes, which, when precipitate, improve the lightening of wort and beer;

–low isocohumulone content of beer is ensured due to the low cohumulone content of alpha-acids (21.4 %) of the Slavyanka hop variety;

–the presence of biologically active compounds – prenylated flavonoids, exhibiting an extremely wide spectrum of biological activity and revealing anticancer, antimicrobial, anti-inflammatory and antiviral properties, being also natural antioxidants, due to the use of the Ruslan and Xantha hop varieties on beer hopping;

–the presence of isoxanthohumol, also exhibiting the anticancer properties in beer, is due to mainly the Ruslan and Xantha varieties.

An increased isoxanthohumol content of beer, in case of combined use of the Slavyanka hop varieties with those of Ruslan and Xantha in the ratio suggested enriches the drink with biologically active hop compounds, thus improving its functionality.

The suggested dosing procedure favors adjustment of optimal varietal hop blending, as well as the products of its processing with ensuring the best values of bitterness and its quality at minimal hop consumption.

Conclusions

Combined dosage adjustment of fine aroma hops and those of special varieties according to the procedure suggested makes it possible to obtain up to 13.0–20.0 mg/dm^3 iso-alpha-acids in beer, including isocohumulone up to 5.0–7.0 mg/dm^3, with further achievement of polyphenolic compound contemt of beer in the range of 160.0–200.0 mg/dm^3 and isoxanthohumol within 2.0–5.0 mg/dm^3. At the same time, the conditions are formed for beer enrichment with biologically active hop compounds due to the use of special Ukrainian varieties with an increased content of beta-acids, polyphenolic compounds and xanthohumol.

References

1. Narziß L. (2005), *Abriß der Bierbrauerei*. 7th ed., Wiley-VCH, Weinheim, pp. 163–170.
2. Lyashenko N.I. (2002), *Hops and hop products ɞiochemistry*, Polissia, Zhytomyr.
3. Biendl M., Pinzl C. (2007), *Arzneipflanze Hopfen. Deutsches Hopfenmuseum Wolnzach*, Wolnzach.
4. Danila A.O., Gatea F. and Radu G.L. (2011), Polyphenol composition and antioxidant activity of selected medicinal herbs, *Chemistry of Natural Compounds*, 47(1), pp. 22–26.
5. Żołnierczyk AK, Mączka WK, Grabarczyk M, Wińska K, Woźniak E, Anioł M (2015), Isoxanthohumol - biologically active hop flavonoid, *Fitoterapia*, 103(71), p. 82.
6. Hanke S. (2010), *Untersuchungen zum Einfluss der Hopfungstechnologie auf die Geschmacksstabilität und Harmonie untergäriger Biere*, Technische Universität München, Freising.
7. Lyashenko N.I., Mykhajlov M.G. (2010), Curative potential of hop and beer, *Agropromyslove vyrobnytstvo Polissja*: *Zbirnyk naukovykh prats'*, 3, pp. 50−54.
8. Stevens J.F., Taylor A.W., Clawson J.E. (1999), Fate of xanthohumol and related prenylfiavonoids from hops to beer, *Journal Agricultural Food Chemistry*, 47, pp. 2421−2428.
9. Fukao T., Sawada H., Ohta Y. (2000), Combined effect of hop resins and sodium hexametaphosphate against certain strains of Escherichia coli, *J. Food Prot.*, 63(6), pp. 735–740.
10. Pavlovič V., Pavlovič M., Čerenak A., Košir I.J., Čeh B., Rozman Č., Turk J., Pazek K., Krofta K., Gregorič G. (2012), Environment and weather influence on quality and market value of hops, *Plant Soil Environ,* 58, pp. 155–160.
11. Srečec S., Zechner-Krpan V., Marag S., Špoljarić I., Mršić G. (2011), Morphogenesis, volume and number of hop (Humulus lupulus L.), glandular trichomes and their influence on alpha-acids accumulationin fresh bracts of hop cones, *Acta Bot. Croat*, 70, pp. 1–8.
12. Stevens J.F., Miranda C.L., Buhler D.R. (1998), Chemistry and biology of hop flavonoids, *Am. Soc. Brew. Chem*, 56(4), pp. 136–145.
13. Miranda C. L., Stevens J.F. [et al.] (2000), Antioxidant and prooxidant action of prenylated and nonprenylated chalcones and flavanones in vitro, *Agric. Food Chem*., 48, p. 3876.
14. Magalhães PJ, Carvalho DO, Cruz JM, Guido LF, Barros AA (2009), Fundamentals and health benefits of xanthohumol, a natural product derived from hops and beer, *Nat. Prod. Commun.*, 4(5), pp. 591–610.
15. Protsenko Lidiya, Litvynchuk Svitlana (2017), Features of using hops and CO_2-extract in brewing, *Ukrainian food journal*, 6(1), pp. 77–84., DOI: 10.24263/2304-974X-2017-6-1-9
16. Strathmann J., Klimo K., Sauer S.W., Okun J.G., Prehn J.H.M. and Gerhäuser C. (2010), Xanthohumol-induced transient superoxide anion radical formation triggers cancer cells into apoptosis via a mitochondria-mediated mechanism, *FASEB Journal*, 24(8), pp. 2938–2950.
17. Ferk F., Huber W.W., Filipič M. et al. (2010), Xanthohumol, a prenylated flavonoid contained in beer, prevents the induction of preneoplastic lesions and DNA damage in liver and colon induced by the heterocyclic aromatic amine amino-3-methyl-

imidazo[4,5-f]quinoline (IQ), *Mutation Research – Fundamental and Molecular Mechanisms of Mutagenesis*, 691, 1–2, pp. 17–22.
18. Monteiro R., Calhau C., Silva A.O.E. et al. (2008), Xanthohumol inhibits inflammatory factor production and angiogenesis in breast cancer xenografts, *Journal of Cellular Biochemistry*, 104(5), pp. 1699–1707.
19. Xiu-Li Zhang, Yong-Dong Zhang, Tao Wang, Hong-Yun Guo, Qi-Ming Liu and Hai-Xiang Su (2014), Evaluation on Antioxidant Effect of Xanthohumol by Different Antioxidant Capacity Analytical Methods, *Journal of Chemistry,* Article ID 249485, DOI: 10.1155/2014/249485.
20. Zamzow D.R., Elias V., Legette L.C., Choi J., Stevens J.F., Magnusson K.R. (2014), Xanthohumol improved cognitive flexibility in young mice. *Behav. Brain Res.*, 275(1), p. 10.
21. Warnakulasuriya S.N. Ziaullah, Vasantha Rupasinghe H.P. (2014), Long chain fatty acid acylated derivatives of quercetin-3-*O*-glukoside as antioxidants to prevent lipid oxidation, *Biomolecules,* 4, pp. 980–993.
22. Żołnierczyk Anna K. , Baczyńska Dagmara , Potaniec Bartłomiej, Kozłowska Joanna , Grabarczyk Małgorzata , Woźniak Edyta , Anioł Mirosław (2017), Antiproliferative and antioxidant activity of xanthohumol acyl derivatives, *Medicinal Chemistry Research*, 26(8), pp. 1764–1771.
23. Yang M., Li N., Li F., Zhu Q., Liu X., Han Q., Wang Y., Chen Y., Zeng X., Yi L., Zhang P., Yang C., Liu Z. (2013), Xanthohumol, a main prenylated chalcone from hops, reduces liver damage and modulates oxidative reaction and apoptosis in hepatitis C virus infected Tupaia belangeri, *Int Immunopharmacol*, 16, pp. 466–474.
24. Stevens J.F., Page J.E. (2004), Xanthohumol and related prenylflavonoids from hops and beer: to your good health!, *Phytochemistry*, 65(1317), p. 1330.
25. Protsenko Lidiya, Litvynchuk Svitlana (2015), Competitiveness of Ukrainian pellet hops production, *Ukrainian Journal of Food Science*, 3(1), pp. 51–59.
26. Protsenko Lidiya, Grynuk Tetiana, Litvynchuk Svitlana (2014), Influence of the constituent alpha acids of Ukrainian varieties of hops and hop preparations on quality indicators of mash and beer, *Ukrainian food journal*, 3(3), pp. 389–396.
27. McCullough M.P., Volpe R. (2017), *Beer and the U.S. Dietary Guidelines: What is Healthful Consumption? Choices. Quarter 3,* Available at: http://www.choicesmagazine.org/choices-magazine/theme-articles/beer-policy-and-a-changing-global-market/can-beer-consumption-be-part-of-a-healthy-diet.
28. Ahalitika – EBC (1987), *European Brebery Convention*, *Fourth edition.*
29. Jaskula B., Goiris K., De Rouck G., Aerts G. and De Cooman, L. (2007), Enhanced quantitative extraction and HPLC determination of hop and beer bitter acids, *J. Inst.Brew.*, 113(4), pp. 381–390.

Technological features of biological protection of grain stocks against complex of phytophages of Lepidoptera (Pyralidae, Tineidae, Gelechiidae)

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Keywords:

Granary
Storage
Phytophages
Entomophage
Entomopathogen
Protection
Organics

Article history:

Received 12.01.2018
Received in revised form 23.03.2018
Accepted 29.03.2018

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DOI:
10.24263/2304-974X-2018-7-1-8

Abstract

Introduction. The receptions of biological protection with use of entomophages and entomopathogens in conditions of granaries in relation to complex of dominant populations of phytophages of Lepidoptera of grain stocks were scientifically grounded.

Materials and methods. During 2010–2017 years of researches were investigated stocks of cereals, legumes and industrial crops for food, fodder and seminal appointments, complex of arthropods – insects and mites, which related trophic and environmentally with them, and laboratory cultures of entomophages and entomopathogens. For researches were used receptions of visual (analysis of average samples) and instrumental (food and pheromone traps) monitoring, microbiological, population and statistical methods.

Results and discussion. As result of long-term researches was shown principled possibility of effective biological protection, as well control of strength of dominant complex of phytophages of Lepidoptera of grain stocks. Technological parameters and expediency of using laboratory cultures of entomophages combined with microbiological preparations have been optimized. It is important that whole arsenal of biological protection was used during critical periods of ontogenesis of insect-phytophages. This process was accompanied not only by fighter effect of operational character, but also by regulatory influence with subsequent transition of populations in long depressive state. The specific biocenotic regularity was established. It is because population of entomophages and active substances of biological preparations were characterized by pronounced aftereffect, which manifests in physiological anomalies, in particular, violation of rhythm of oogenesis with subsequent decreasing real fecundity of females and trophic activity of caterpillars. Constituent parts of original technology showed pronounced efficiency in relation to phytophages. In particular, laboratory cultures of entomophages parasitized corresponding stages of phytophages at level of 64.2 %. Effect and aftereffect of microbiological preparations as part of the technology were also effective. Mortality of phytophages was 70.4 %. As result, the biological strategy of protection of grain stocks provided total efficiency at level of 82.7 % against 93.1 % in chemical standard. Approbation of biological receptions has shown their manufacturability and adoption by practice of plant protection under such specific conditions.

Conclusions. The realization of technology ensures preservation of 96.6 % of gross stock of grain from phytophages of Lepidoptera.

Introduction

Relevance of topic in the world

It is generally accepted that among other indicators economic well-being of the state determine by its food stock. Particularly relevant is issue of protecting plant products in connection with latest global environmental, economic and political problems. In most cases, these problems are solved by comparatively long-term storage of harvest stocks of current year, according to existing traditions for each individual state, its size, character and consumer ability of population.

It is known that row of stress factors of biotic and abiotic origin accompany process of storage of grain and products of its processing, including in modern high-tech elevators. Often negative consequences of their manifestation acquire catastrophic character, accompanied by losses not only of gross part of harvest, but also decrease indicators of its quality. We also emphasize that over 80 % of all negative factors concern to harmful activity of phytophages – insects and mites. Their species composition in granaries is more than 400 species. It should be noted that class of insects characterize by exceptional viability, reproductive activity, survival and property to withstand any stress anomalies. To these representatives of the animal world are over 400 million years old with corresponding physiological and ecological parameters of sustainability.

Many countries of the world use wide variety of receptions, means and technologies for solving problem of protection of strategic biological raw materials against expansion of arthropod–phytophages. In their composition are rather low-effective receptions of preventive character, with considerable expenditure of manual labor and other efforts, and modern technologies of total destruction of complex of arthropods, using all existing assortment of chemical preparations.

Existing assortment of preparations is characterized by rather significant level of toxicity, in relation to not only target objects, but also exhibit poisoning effect to animals and human. However, it is necessary to search real alternative technologies for protection of grain stocks and products of its processing, which involve partial or radical decrease of pesticide press in this branch, taking into account level of newest developments in the field of population ecology, genetics, toxicology and medical hygiene.

Literature review

There are technologies providing receptions from partial decrease of pesticide load to most radical approaches in the system of organic plant growing. Objective critical analysis of latest scientific and technical developments in this system was showed principal possibility of realization to known technologies, based on use of natural populations of entomophages, as means, partially restraining to expansion of phytophages in conditions of closed rooms (Drozda, Bondarenko, patent of Ukraine № 119532. Way of protection of grain and grain products against phytophages during long-term storage in the system of organic plant growing).

Among pathogens of insects are viruses, bacteria, protozoa and fungi (Moore et al., 2000). There are data about absence of side action of entomopathogens of bacterial and fungal etiology to parasites. Insects able to be as sources of accumulation and vectors of spread of entomopathogens.

Using spores of white muscardine was most common among entomopathogenic fungi (Lord, 2005). The expediency of using various microbiological preparations on basis strains

of entomopathogenic microorganisms, which really existing in nature, mainly bacterial and fungal etiology was established experimentally (Flinn, Scholler, 2012). However, at this stage fungal entomopathogenic preparations for practical use were not registered to control of strength of the population of phytophages of grain stocks (Lord, 2005).

Most researches are aimed at studying features of mass laboratory production of cultures of entomophages – species of the genus Trichogramma sp. and Habrobracon sp. in branches of integrated protection of grain stocks and organic plant growing (Chen et al., 2013; Chimire, Phillips, 2014; Shah Alamet al., 2016). Specific predictors that allow assessing suitability of host for laboratory rearing of Trichogramma and Habrobracon, namely level of parasitizing, quantity of laid eggs by female, lifetime of entomophage, sex ratio in received posterity were developed (Drozda, 2005; Chimire, Phillips, 2014; Gavriliţa, 2015). The problems of role of nutrient media to development of phytophages and their entomophages, and action of hydrothermal conditions by them are investigated (Eslampour, Aramideh, 2016; Golizadeh et al., 2017). The exploring biology, physiology and ecology of entomophages and their hosts for increasing their reproductive potential and lifetime occupies important part of experimental researches (Drozda, 2003, 2011; Pezzini et al, 2017).

There are fragmentary researches to introduction of biological technologies with use of entomophages – parasites, predators and entomopathogens, as elements of integrated protection of plant products during long-term storage (Grieshop et al., 2006; Casada et al., 2008; Hagstrum, Subramanyam, 2009; Adarkwah et al., 2010; Scholler, 2010; Upadhyay, Ahmad, 2011; Flinn, Scholler, 2012; Drozda, Bondarenko, 2017).

Nowadays, the world mass production of useful insects for branch of grain protection is limited by three European countries – Germany, Netherlands and Switzerland. The use of entomophages in protection of grain stocks has become commercial character in Central Europe. There are several biological laboratories for mass rearing of cultures of entomophages in order to using them as element of integrated protection of grain and products of its processing in period of long-term storage against arthropod-phytophages (Scholler, 2010). At this stage, realization of technologies of biological protection of grain has not acquired scale of industrial storage. Seven species of parasites and predators are commercially available for protection of grain stocks against arthropod-phytophages in the United States of America (White, Johnson, 2010). Expert analysis was showed that the realization of technologies of biological protection in system of organic plant growing characterized by pronounced economic efficiency with certain perspectives. It is also stressed that guaranteed efficiency ensured by joint use of entomophages (Grieshop et al., 2006; Niedermayer, Steidle, 2010; Scholler, 2010).

In the countries of central and eastern Europe, the distribution has received mass production of laboratory cultures of Trichogramma in order to protecting agricultural crops, mainly in agrocenoses (Drozda, 2000; Reiliants, 2008; Gavrilitsa, 2010; Molchanova et al., 2015). Elements of biological control in protection of grain stocks are represented only fragmentarily by partial use of current spectrum of commercial microbiological preparations, predominantly bacterial etiology in mixtures with insecticides (Bondarenko, 2015).

At the same time, there are no fundamental works based on thorough exploring biology, ecology and physiology of dominant phytophages of grain stocks, trophic activity of entomophages and entomopathogens, connectivity of their life cycles. In fact, at this stage were obtained contradictory, unsustainable effects by indicators of positive result with clear trend of perspective of this direction.

Proceeding from the above, it is obvious that qualitatively new approaches to solution of such important state problem as ensuring protection of grain stocks are needed. The authors assume that these approaches should be based on detailed exploring features of physiology and ecology of phytophages, their entomophages and entomopathogens, taking into account their life strategies, level of adaptability and ecological heterogeneity.

Purpose of researches

The main purpose of researches was assessment of level of viability of phytophages and their entomophages with original elements of their physiological monitoring, ecological valence and adaptability. On such peculiar scientific foundation were determined most important technological parameters, based on real production characteristics of level of technical equipment of granaries, periods of beginning expansion of phytophages, character of mastering ecological niches and initial manifestation of phenomenon of phytophagy. The task was set to propose of separate receptions as part of completed technologies of biological and integrated protection of grain stocks against complex of phytophages of Lepidoptera for production.

The clear technological parameters, concerning prediction of level of risk and appropriateness of use of biological receptions as part of holistic technology according to results of these researches are formulated. An important component of experimental work was determining sequence and compatibility of individual elements as part of original technology of grain protection. During researches was set task of justification not only level of protection and preservation of harvest, but also ecological aspect, namely problem of using organic product as raw material for food industry.

Materials and methods

Investigational materials

Long-term experimental researches (2010–2017 years) in warehouses of granaries for floor storage of grain and modern technically equipped modules of elevators, mainly in regions of the Forest-Steppe and Polissya of Ukraine were carried out. The main biological substrate is cereal grains with predominance of winter wheat, leguminous and industrial crops.

As means of biological control were used laboratory cultures of egg parasite of phytophages of Lepidoptera – *Trichogramma evanescens* Westw. (Hymenoptera, Trichogrammatidae). This parasite is reared massively in numerous bio-laboratories of Ukraine, using standard culture of Angoumois grain moth – *Sitotroga cerealella* Oliv. (Lepidoptera, Gelechiidae) (Drozda, parent of Ukraine № 22701. Way of mass rearing Trichogramma). As part of arsenal of biological control of phytophages was ectoparasite of caterpillars – *Habrobracon hebetor* Say. (Hymenoptera, Braconidae) with using known technologies of his laboratory production in our modification (Drozda, patent of Ukraine № 49250. Way of rearing laboratory populations of ectoparasite – *Habrobracon hebetor* Say.).

Order of conducting researches

The receptions of visual and instrumental phytosanitary monitoring of granaries and elevators were integral part of technology of grain storage and its protection. Instrumental

monitoring has assumed use of various technical adaptations for catching individual stages of insects. In addition, we used pheromone traps with set of modern assortment of targeted dispensers.

The obtained results of phytosanitary monitoring served as basis for choice of means and receptions of control of strength of phytophages of Lepidoptera, taking into account such universal indicator as threshold level of harmfulness. At the same time, level of domination of individual phytophages, density of their populations, relative prevalence, potential and real harmfulness were established.

In course of industrial tests were conducted receptions of manual resettlement of entomophages, taking into account fragmentarity and hearths of initial expansion of various grain substrates by phytophages. Starting populations of entomophages were reared by original author's technology, aimed at induction of such characteristics as motor activity of adult females and their search ability. This is essential methodological feature of proposed technology.

Trichogramma and Habrobracon – entomophages of first class of quality, previously adapted to conditions of closed rooms, was exhibited in special containers. The norm of resettlement of Trichogramma was 10,000 individuals per 1 m^2. The reception of resettlement of adults of Habrobracon at period of beginning emergence of caterpillars of phytophages of Lepidoptera of third age was carried out in norm of 15–20 individuals per 1 m^2 of area of grain substrate.

In addition, character of oogenesis of females of entomophages, functioning in pro- and synovigenic regimes was taken into account. As rule, the starting populations of entomophages only first class of quality were used. Evaluation predictors are based to level of viability, motor activity of females of entomophages in process of searching certain stages of development of phytophages.

We accounted pronounced species-specific reaction of caterpillars to acting substances of biological preparations. It's biological and ecological basis for using fungal entomopathogens in form of preparations. This allowed entering two microbiological preparations as part of technology – Boverin and Petsilomin, created on basis of entomopathogenic fungi of white muscardine (*Beauveria bassiana* (Bals.) Vuill.) and pink muscardine (*Paecilomyces farinosus* (Holmsk.) A.H.S. Br. & G. Sm.) (Deuteromycetes, Fungi Imperfecti).

Usually entomopathogenic preparations were used sequentially after resettlement of entomophages in event of existence of threat of increasing strength of populations of phytophages of Lepidoptera. It should be noted that their acting substances do not have pronounced entomocidal activity in relation to entomophages. The interval between these receptions was from 10 to 14 days. The hearths of spreading target phytophages were treated by working suspensions of entomopathogenic preparations. As rule, large quantity of initial material in laboratory and production experiments was involved, which allow making objective conclusions about efficiency of conducted receptions.

Description of methods, installations

Special engineering constructions are aimed at protection of biomaterial against mechanical damage and influence of other stress factors. In addition, these modules capable of supporting optimal regimes for daughter populations, nutrition in form of specific carbohydrate-protein diet, mating and unhindered resettlement in thickness of grain in places of concentration of corresponding stages of phytophages. In most cases, natural honey and hemolymph of caterpillars of senior ages of owlet moths as diet were used.

Developed devices are specific plastic containers with corresponding blocks of multifunctional use. Modules with biomaterial are designed for its resettlement on surface of grain. Their construction is protected by patents of Ukraine.

Processing research results

The obtained digital material was processed statistically. The statistical processing results of phytosanitary monitoring on infestation of grain by phytophages with use of program Excel was involved. Levels of dominance and density of populations of phytophages were established. The level of dominance was determined by the formula:

$$D = 100 \text{ x} \frac{k}{K},$$

where D – the degree of dominance of phytophages; k – quantity individuals of certain species; K – total quantity of all collected species.

The density of populations of phytophages of grain stocks was determined by the formula:

$$V = \frac{k}{n}$$

where V – density of populations of phytophages in samples; k – the sum of all individuals of species in samples; n – quantity of investigated samples.

For determining indicators of linear correlation ($Y = a + b \cdot X$) of obtained experimental data was used computer program of «Statgraphics plus».

Results and discussion

Researches of species composition of arthropods-phytophages of grain stocks. As results of long-term researches have shown, the total fund of phytophages of grain stocks was over 80 species of arthropod, which belong to 3 classes (Arachnida, Entognatha, Insecta), 9 orders (Psocoptera, Pseudoscorpionida, Thysanura, Sarcoptiformes, Trombidiformes, Acarina, Mesostigmata, Coleoptera, Lepidoptera), 29 families (Psocidae, Atropidae, Cheliferidae, Lepismatidae, Acaridae, Glycyphagidae, Cheyletidae, Tydeidae, Pediculoididae, Parasitidae, Lealaptidae, Curculionidae, Tenebrionidae, Cucujidae, Dermestidae, Cryptophagidae, Bostrychidae, Anobiidae, Ostomatidae, Nitidulidae, Ptinidae, Bruchidae, Lathridiidae, Notoxidae, Cleridae, Tineidae, Gelechiidae, Pyralidae, Noctuidae). During phytosanitary monitoring of granaries and elevators, it was established that percentage of species of Lepidoptera was about 30 % from general structure of phytophages. Among phytophages of grain stocks from order of Lepidoptera were observed such species as *Plodia interpunctella* Hb., *Ephestia ellutela* Hb., *E. kuehniella* Zell., *Pyralis farinalis* L. (Pyralidae), *Sitotroga cerealella* Oliv. (Gelechiidae), *Nemapogon granella* L., *Tineola bisselliella* Humm., *Tinea translucens* Meyr., *Haplotinea ditella* P. et Diak., *Niditinea fuscipunctella* Hw. (Tineidae). Detailed exploring their biology, physiology, and ecology (*Table 1*) showed that all of them develop in polyvoltinic regime.

Table 1

Characteristic of population structure of dominant phytophages of Lepidoptera of grain stocks

Species of dominant phytophages of Lepidoptera of grain stocks	Quantity of generations in conditions of closed rooms	Reproductive potential	Reaction to biogenic stress factors	Manifestation of trophic competition	Character of formation of ecological niches
Indianmeal moth (*Plodia interpunctella* Hb.)	1–6 generations during year	The total fecundity of female is 70–160 eggs; scattered oviposition alternates with group of 30 eggs per day on surface of plant products	The spread of snout moth is limited to temperature indicators; insect is sensitive to action of low temperatures, however, shows resistance in relation to high	Indianmeal moth prefers cereal, technical and oil crops as trophic substrate; it is observed broad polyphagia, partially keratophagy, characterized elements of predation; trophic substrate of caterpillars is grain embryo	It is observed characteristic expansion of grain substrate with penetration to depth of embankment of about 10 cm, migration increases to 1.5–2.0 meters at low temperatures
Mediterranean flour moth (*Ephestia kuehniella* Zell.)	during year is changed 2–6 generations	The total fund of egg production is 50–200 eggs; scattered or group oviposition with emphasis on various unevenness's in buildings, significant part of eggs is concentrated on grain substrate	Process of oviposition of females and development of caterpillars are limited by conditions of temperature regime and quality of trophic substrate; Mediterranean flour moth are characterized by pronounced adaptation to low temperatures, insect is resistant to high temperatures	Caterpillars are broad polyphages, mainly feed on products of grain processing, trophic specialization is phytophagia and keratophagia; snout moth is adapted to feeding by solid varieties of agricultural crops	Characteristic feature of expansion of substrate is superficial uniform distribution followed by intensive migration in embankment on depth up to 15 cm

Table 1 (Continue)

Characteristic of population structure of dominant phytophages of Lepidoptera of grain stocks

Species of dominant phytophages of Lepidoptera of grain stocks	Quantity of generations in conditions of closed rooms	Reproductive potential	Reaction to biogenic stress factors	Manifestation of trophic competition	Character of formation of ecological niches
Cacao moth (*Ephestia ellutela* Hb.)	For this species is characteristic 2–3 generations	Genetically determined reproductive function ensures the deposition of highly viable eggs in the range from 60 to 130	The process of oviposition and duration of development of caterpillars are determined temperature regime, genus and quality of trophism; insect is adapted to various synoptic anomalies	Trophic specialization is broad polyphagia, insect prefers cereals, oilseeds and products of its processing, feed on germ of grain that ensures high level of viability of daughter generations	This species is adapted to expansion predominantly surface portion of grain
Angoumois grain moth (*Sitotroga cerealella* Oliv.)	High level of strength and constant presence at warehouses are explained by existence of 3–4 generations and insignificant mortality of preimaginal stages	Females are characterized by mixed strategy of egg placement in time and space; the competitiveness of moth is ensured by oviposition on ears of grain in field and shell or longitudinal groove in granaries; fecundity is in range from 80 to 150 eggs	The spread of this species is determined largely temperature regime; the development of caterpillars is limited strongly by level of relative moisture of environment and trophic substrate	Moth is characterized broad polyphagia, caterpillars prefer mainly cereals, less often legumes and corn as trophic resource, in this case use endosperm	Characteristic feature of this species is that adults create colonies exclusively on surface of grain, where they lay eggs, subsequently population occupies depth of no more than 10 cm

Table 1 (Continue)

Characteristic of population structure of dominant phytophages of Lepidoptera of grain stocks

Species of dominant phytophages of Lepidoptera of grain stocks	Quantity of generations in conditions of closed rooms	Reproductive potential	Reaction to biogenic stress factors	Manifestation of trophic competition	Character of formation of ecological niches
European grain moth (*Nemapogon granella* L.)	Not pronounced competitiveness among Lepidoptera is determined limited quantity of generations (1–2)	Real fecundity of females is from 50 to 70 eggs; scattered oviposition is concentrated on surface of grain substrate	Pronounced sensitivity to synoptic anomalies, the activity of this moth is limited moisture content of grain substrate	Caterpillar feeds by endosperm within grain, preferring to threshed grain of wheat, rye, barley, oats as trophic substrate	Insect belongs to group of phytophages that occupy upper part of embankment of grain
Drab clothes moth (*Haplotinea ditella* P. et Diak.)	Significant quantity of generations (up to 4) provides permanent presence and pronounced harmfulness of this species in warehouses	As rule female lays insignificant quantity of eggs, within limits of 40–100, but newly born caterpillars are characterized pronounced trophic activity	The dependence of development of this moth from level of moisture content of trophic substrate and ambient temperature is traced	Insect specializes on nutrition by grain and products of its processing; prefers products of plant origin, especially affected by mold fungi and putrefactive bacteria	Uniqueness of ecological niches is explained by preference of excessive moisture and presence of fungal and bacterial microflora

Table 1 (Continue)

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Angoumois grain moth (*Sitotroga cerealella* Oliv.)	High level of strength and constant presence at warehouses are explained by existence of 3–4 generations and insignificant mortality of preimaginal stages	Females are characterized by mixed strategy of egg placement in time and space; the competitiveness of moth is ensured by oviposition on ears of grain in field and shell or longitudinal groove in granaries; fecundity is in range from 80 to 150 eggs	The spread of this species is determined largely temperature regime; the development of caterpillars is limited strongly by level of relative moisture of environment and trophic substrate	Moth is characterized broad polyphagia, caterpillars prefer mainly cereals, less often legumes and corn as trophic resource, in this case use endosperm	Characteristic feature of this species is that adults create colonies exclusively on surface of grain, where they lay eggs, subsequently population occupies depth of no more than 10 cm

Their development are limited not so much trophic factor, so much hydrothermal parameters. It is also established that the lower limit for development of populations of most species of phytophages of Lepidoptera of grain stocks is from 10 to 15 degrees. It means that period of active nutrition and harmfulness is limited by the summer-autumn season. Two expressed peaks of trophic and flight activity, intensive increase of strength of Lepidoptera in June and September were observed.

Experimental researches of the author's technology of biological protection of grain against phytophages of Lepidoptera

These materials were served as basis for optimization of receptions of biological protection of grain against phytophages (*Table 2*). In fact, the first three years of researches against background of high level of strength of phytophages of Lepidoptera were conducted. It was observed domination of such species as Indian meal moth (*Plodia interpunctella* Hb.), cacao moth (*Ephestia ellutela* Hb.), Mediterranean flour moth (*E. kuehniella* Zell.) (Pyralidae) and Angoumois grain moth (*Sitotroga cerealella* Oliv., Gelechiidae). It is over 85 % of the total fund of Lepidoptera. The technology with sequential using *Trichogramma evanescens* Westw. (Trichogrammatidae), entomopathogenic fungal preparations and *Habrobracon hebetor* Say. (Braconidae) is realized for transition of populations of these phytophages to prolonged depressive state. It is this sequence was maximized biological fighter activity of different stages.

Special meaning was attached to resettlement of Trichogramma that is important reception, taking into account prevention of spreading caterpillars of phytophages in range from 35 to 65 %. This reception is one of the most effective, ecologically safe and characterize by pronounced economic importance. As rule, it is enough to hold two receptions of resettlement of Trichogramma in period of beginning process of mass oviposition at indicators from one to three threshold levels, based on materials of pheromone and visual monitoring. This period lasts from 10 to 12 days. Obviously, reception is prevented potential harmfulness of phytophages of Lepidoptera.

As result, Trichogramma parasitized from 43.4 to 68.7 % eggs, mainly ineffective part of populations of phytophages of Lepidoptera. The most viable females of Trichogramma parasitized from 16.8 to 34.6 % of effective part of populations of snout moths and moths. This is most significant part of researches that indirectly characterizes heterogeneity of the starting populations of phytophages, trophic and ecological specialization of Trichogramma. It also should be noted that significant part of ovipositions of effective population of phytophages died as result of act of nutrition of females of Trichogramma by their hemolymph. It is from 13.4 to 18.6 % of the total stock of eggs. Trichogramma does not lay eggs in such eggs of phytophages. As result, phytophages are eliminated.

However, remainder part of populations of Lepidoptera represents real threat of increasing harmfulness, given high initial level of strength of phytophages. Therefore, one reception of local treatment of grain substrate with aqueous solution of entomopathogenic fungal preparation – Boverin was carried out. This reception was conducted only in initial period of mass emergence of caterpillars of Lepidoptera. The titer of viable spores of fungus of white muscardine was 6.3 billion in 1 g. Shelf life of preparation did not exceed 2 months. The efficiency of this reception ranged from 48.4 to 68.5 %.

Table 2

Efficiency of technologies of protection of grain stocks against phytophages of Lepidoptera (Industrial testing, 2010–2017 years)

Technologies of protection of grain stocks	Initial strength of phytophages of Lepidoptera, ind. / kg	Level of dominance, %		Factors of mortality of phytophages, %		Harmfulness, %	Efficiency of grain protection, %
		Snout moths	Moth	Entomophages	Entomopathogens		
Original author's technology of biological protection	29,6	76,4	23,6	64,2	70,4	3,4	82,7
Chemical standard	33,7	80,2	19,8	2,1	4,3	1,2	93,1
Control	45,8	77,9	22,1	5,7	5,2	24,6	–
SSD_{05}	–	–	–	1,2	1,6	1,3	5,7

As our researches have shown, the period of emergence of caterpillars from eggs lasts from 23 to 32 days. The viable part of caterpillars after realization of these two receptions represented also immediate threat, primarily as factor of growth populations of phytophages. In this case, the application of laboratory culture of Habrobracon, exclusively of first class of quality was justified. Adults of Habrobracon function during long period, namely from 17 to 24 days, in contrast to Trichogramma. It is essential that process of oogenesis of females also characterized by high activity and duration. It was provided parasitization of caterpillars of phytophages of Lepidoptera at level from 63.2 to 74.8 %, given high motor and search ability of Habrobracon. The tactic of their operational control are timed strictly to this period due to specific rhythmics of ontogeny of these phytophages, in particular their trophic binary activity.

The status of phytophages for Angoumois grain moth (*Sitotroga cerealella* Oliv., Gelechiidae) and European grain moth (*Nemapogon granella* L., Tineidae) in second period of activity of Lepidoptera actually was lost. Only single individuals were noted. The results of phytosanitary monitoring indicated about trend of increase of strength of dominant species of snout moths, which is observed in beginning September. It created certain threat of hearth spread. These materials were basis for application of reception of single-entry resettlement of Trichogramma as restraining and regulatory factor, followed by continuous treatment of grain substrate by entomopathogenic fungal preparation – Petsilomin. Acting substance of preparation is spores of pink muscardine with titer of 5.5 billion in 1 g. The choice of this preparation was due to much higher level of adaptability to low temperatures and pronounced entomocidal activity, in comparison with Boverin. The terms of treatment were analogical to first receptions. The level of mortality of different stages of Lepidoptera was within of 56.9–82.3 %.

Discussion of research results

The proposed strategy provides acceptable efficiency of sharp decline of starting populations of phytophages of Lepidoptera with use entomophages and entomopathogens. The expediency of introducing further fighter technologies with use biological receptions depends on quality phytosanitary monitoring for determine occupancy and infestation of grain stocks by phytophages. Trichogramma is mandatory reception in all cases regarding practical realization of technologies of biological protection of grain at moderate indicators of strength of phytophages of Lepidoptera. It is explained by comparative simplicity of obtaining unlimited quantity of biomaterial, its cheapness, and small size of adults.

By results of researches, important biocenological aspect was established. This aspect is manifested in fact that the deceased populations acted as source of accumulation, passive and active spread by inoculum of fungi in grain substrate. Beetle-phytophages (Coleoptera), accompanying insects and adults of Habrobracon were as vectors. The phenomenon of partial process of self-regulation of this particular ecological niche by rather pronounced activity of daughter generations of entomophages, and circulation of spores and vegetative bodies of entomopathogenic fungi was noted.

The absence of phenomenon of formation of resistant populations of target phytophages was established. According to the results of long-term researches, this fact is important point in using entomopathogenic fungi. The evolutionary saprophytic genetic life strategy of these entomopathogens in conditions of closed rooms is practically not realized. It is due to total absence of relevant trophic substrate. Consequently, adaptation and directed selection form only entomocidal activity of preparations. In the authors' opinion, proposed technology is main integral part of organic plant growing, taking into account

sanitary-hygienic characteristic of these preparations with absence of negative action to warm-blooded, human and entomophages. Important role is played by the fact that these preparations and authoring receptions of using entomophages are intellect-product of domestic technologies.

Conclusions

The strategy of scientific search to original technical solutions was formulated on the grounds of expert analysis of condition of branch of grain protection during its long-term storage. They are aimed at solving important state problem, related to radical ecologization of existing technologies of protection of grain stocks, predominantly pesticide receptions.

The conducted experiments showed principal possibility of adaptation of laboratory cultures of species of the genus Trichogramma and Habrobracon for specific conditions of closed rooms. The phenomenon of trophic interaction of these entomophages with target species of phytophages (moths and snout moths) was established. The norms, terms and multiplicities of application of entomophages during storage of grain based on worked parameters were established. Various technical improvements, aimed at preserving biomaterial and their long-term contact with phytophages for optimization parameters of realization of biotic potential of entomophages were suggested.

Experimentally were established feasibility and efficiency of using entomopathogenic fungal preparations – Boverin and Petsilomin for destabilize structure of populations of phytophages. The operational sequence of application of entomophages and biopreparations was shown. For the first time have been studied in detail features of biology, physiology and ethology of dominant species of phytophages, established critical periods in their ontogeny. This made it possible to effectively influence on processes of reproduction and spread of phytophages. A range of problems was defined that must be studied for increasing efficiency of technologies of biological protection with simultaneous search of promising species of entomophages and entomopathogens for needs of production.

Acknowledgements
The authors would like to thank management and engineering staff of agricultural enterprises for opportunity to conducting experimental researches (Hhutianskyi elevator; Poltava Grain Receiving Enterprise; Poltava State Agricultural Experimental Station of Institute of Swine Breeding and Agro-Industrial Production named after M. I. Vavylov). The authors also express their gratitude to Bondariev Yevgenii – engineer of the 2nd category of «Radionix» for designing and development of modules-containers for resettlement of entomophages in warehouses.

References

1. Adarkwah Charles, Buttner Carmen, Reichmuth Cristoph, Scholler Matthias (2010), Ability of the larval ectoparasitoid *Habrobracon hebetor* (Say., 1936) (Hymenoptera: Braconidae) to locate the rice moth *Corcyra cephalonica* (Stainton, 1965)

(Lepidoptera: Pyralidae) in bagged and bulk stored rice, *Journal of Plant Diseases and Protection*, 117 (2), pp. 67–70.
2. Bondarenko I.V. (2014), Chlenistonogie vrediteli zapasov zerna v zernokhranilishchakh Poltavskoi oblasti, *Zashchita rastenii, In-t IZR, Belarus,* 38, pp. 183–195.
3. Bondarenko I.V. (2014), Khimicheskii i biologicheskii kontrol chislennosti vreditelei khlebnykh zapasov, *Visnyk Poltavs'koyi derzhavnoyi ahrarnoyi akademiyi*, 2, pp. 161–164.
4. Bondarenko I.V., Sekun M. P., Vlasova O. H. (2016), Shkidnyky zerna kolosovykh kul'tur v period zberihannya, *Zakhyst i karantyn roslyn*, 62, pp. 64–71.
5. Bondarenko I.V. (2015), Sravnitelnaia toksichnost insektitsidov i biopreparatov dlia osnovnykh vreditelei zerna v period khraneniia v Ukraine, *Vestnik Prikaspiia*, 2 (9), pp. 33–37.
6. Bondarenko I.V. (2015), Vydove riznomanittya chlenystonohykh-shkidnykiv zerna kolosovykh kul'tur v period zberihannya, *Zbirnyk naukovykh prats' Natsional'noho naukovoho tsentru «Instytut zemlerobstva NAAN»*, 3, pp. 69–76.
7. Bondarenko I. V. (2015), Zaselenist' ta zarazhenist' zapasiv zerna shkidlyvymy chlenystonohymy, *Selektsiya i nasinnytstvo*, 108, pp. 83–91.
8. Casada M. E., Ram M. S., Flinn P. W. (2008), Thermal design of shipping containers for beneficial insects, *Appl. Eng. Agric*, 24, pp. 63–70.
9. Chen Haoliang, Zhang Hongyu, Kun Yan Zhu, Throne James (2013), Performance of diapausing parasitoid wasps, *Habrobracon hebetor*, after cold storage, *Biological control*, 64(3), pp. 186–194.
10. Chimire M. N., Philips T. W. (2014), Oviposition and reproductive performance of *Habrobracon hebetor* (Hymenoptera: Braconidae) on six different Pyralid host species, *Ann. Entomol. Sok. Am*., 107(4), pp. 809–817.
11. Drozda V., Bondarenko I., Zagaiko O. (2017), Regulatory and modifying role of natural populations of entomophages in biocenoses of the exclution zone of the Chernobyl nuclear power plant, *Agrobiodiversity for improving nutrition, health and life quality*, 1, pp. 102–107.
12. Drozda V.F., Bondarenko I.V. (2017), Zhiznennaia strategiia dominiruiushchikh fitofagov zapasov zerna, *Zemledelie i zashchita rastenii, In-t IZR, Belarus*, 3 (112), s. 16–20.
13. Drozda V.F. (2003), Dodatkove zhyvlennya imaho yizdtsiv. Osoblyvosti rozmnozhennya, formuvannya statevoyi produktsiyi, poshyrennya, teoretychni ta praktychni aspekty problemy, *Zakhyst roslyn*, 10, pp. 9–11.
14. Drozda V.F., Kocherha M.O. (2011), Ekolohichni ta biotekhnolohichni problemy vyroshchuvannya ta vykorystannya vydiv rodu Trichogramma, *Ukrayins'kyy entomolohichnyy zhurnal*, pp. 25–27.
15. Drozda V.F. (2000), Kontseptual'ni problemy biolohichnoho zakhystu roslyn, *Visnyk ahroekolohichnoyi akademiyi Ukrayiny*, pp. 314–316.
16. Drozda V.F. (2005), Operatsiyna tekhnolohiya rozvedennya ta vykorystannya synovihennykh entomofahiv – skladovoyi chastyny intehrovanykh system zakhystu roslyn, *Mizhnarodnyy naukovo-praktychnyy forum «Osnovy molekulyarno-henetychnoho ozdorovlennya lyudyny i dovkillya»*, Kyyiv, pp. 50–52.
17. Eslampour Leila, Aramideh Shahram (2016), Adult longevity, fertility and sex ratio of *Habrobracon hebetor* (Say) (Hymenoptera: Braconidae) parasitizing *Ephestia*

kuehniella (Zeller) (Lepidoptera: Pyralidae): effect of host artificial diets, *Journal of Entomology and Zoology Studies*, 4 (1), pp. 189–192.
18. Flinn P.W., Scholler M. (2012), Biological control: Insect pathogens, parasitoids, and predators, In: Hagstrum D. W., Phillips T. W., Cuperus G., editors, *Stored Product Protection*, S156, Manhattan, KS: Kansas State University, pp. 203–212.
19. Fursov V.N. (2001), Biologicheskii metod zashchity rastenii: mezhdunarodnye issledovaniia i prioritetnoe znachenie taksonomii, *Vestnik zoologii*, 35 (3), pp. 97–101.
20. Gavriliţa Lidia (2015), Biological protection of stored grain products against the moth's complex, *Muzeul Olteniei Craiova, Oltenia. Studii şi comunicări, Stiinţele Naturii*, 31, 2, pp. 129–134.
21. Gavrilitsa L.F. (2010), Vliianie sposoba razvedeniia na effektivnost trikhogrammy, *Zashchita i karantin rastenii*, 2, pp. 35–36.
22. Golizadeh A., Alikhani M., Hassanpour M., Enkegaard A., Rafiee-Dastjerdi H., Razmjou J. (2017), Comparative biology and life table of *Habrobracon hebetor* (Hymenoptera: Braconidae) on *Anagasta kuehniella* (Lepidoptera: Pyralidae) at five constant temperatures, *International Journal of Pest Management*, 63 (4), pp. 364–370.
23. Grieshop M. J., Flinn P. W., Nechols J. R. (2006), Biological control of Indianmeal moth (Lepidoptera: Pyralidae) on finished stored products using egg and larval parasitoids, *I. Econ. Entomol*., 99, pp. 1080–1084.
24. Hagstrum D.W., Subramanyam Bh. (2009), *Stored product insect resource*, AACC International, St. Paul, Minnesota.
25. Lord J.C. (2005), Low humidity, moderate temperature, and desiccant dust favor efficacy of *Beauveria bassiana* (Hyphomycetes: Moniliales) for the lesser grain borer, *Rhyzopertha dominica* (Coleoptera: Bruchidae), *Biological control*, 34, pp. 180–186.
26. Molchanova E. D., Sheikina E. B., Gorodetskii S. A. (2015), Optimizatsiia korma dlia vyrashchivaniia melnichnoi ognevki, *Nauchno-prakticheskii tsentr NAN Belorussii po zemledeliiu, Sbornik nauchnykh trudov «Zashchita rastenii»*, 39, pp. 191–196.
27. Moore D., Lord J.C., Smith S.M. (2000), Pathogens, In: Subramanyam B. and Hagstrum D. W. (eds.), *Alternatives to pesticides in stored-product entomology*, Kluwer, Boston, pp. 191–227.
28. Niedermayer S., Steidle J.L. M. (2010), Some like it hot – some not: Differences in temperature preference of two parasitic wasp species, *International European Symposium on Stored Product Protection «Stress on chemical products»*, 429, pp. 31–33.
29. Pezzini C., Jahnke S.M., Köhler A. (2017), Morphological characterization of immature stages of *Habrobracon hebetor* (Hymenoptera: Braconidae) ectoparasitoid of *Ephestia kuehniella* (Lepidoptera: Pyralidae), *Journal of Hymenoptera Research*, 60, pp. 157–171.
30. Reiliants N.V. (2008), Biologicheskoe obosnovanie primeneniia *Trichogramma evanescens* Westw. dlia reguliatsii chislennosti *Helicoverpa armigera* Hb. na tomatakh i sakharnoi kukuruze, Dissertatsiia na soiskanie uchenoi stepeni doktora biologicheskikh nauk, IZR i ekologicheskogo zemledeliia, Keshineu.
31. Scholler Matthias (2010), Prospects for biological control of stored-product pests, *International European Symposium on Stored Product Protection «Stress on chemical products»*, 429, pp. 25–31.
32. Selitskaia O.G., Mitina G.V., Shchenikova A.V., Choglokova A.A., Levchenko M.V. (2016), Vliianie letuchikh soedinenii entomopatogennykh gribov na povedencheskie reaktsii vreditelei zapasov, *Vestnik zashchity prirody*, 3 (89), pp. 150–152.

33. Shah Alam, Zintul Alam, Syed Nurul Alam, Ramiz Uddin Miah et al. (2016), Host suitability of *Bracon hebetor* Say. on different lepidopterous host larvae, *Academic Journal of Entomology*, 9 (3), pp. 41–50.
34. Upadhyay R.K., Ahmad S. (2011), Management strategies for control of stored grain insect pests if farmer stores and public warehouses, *World Journal of Agricultural Sciences*, 7 (5), pp. 527–549.
35. White J., Johnson D. (2010), *Vendors of beneficial organisms in North America*, University of Kentucky Cooperative Extension Service, Entfact.

Peculiarities of microbial exopolysaccharide ethapolan synthesis on mixed waste oils

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Keywords:

Acinetobacter sp.
IMV b-7005
Exopolysaccharide
Waste oils
Cultivation
Emulsification

Article history:

Received 18.12.2017
Received in revised form 21.03.2018
Accepted 29.03.2018

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DOI: 10.24263/2304-974X-2018-7-1-9

Abstract

Introduction. Possibility of the microbial exopolysaccharide (EPS) ethapolan (the producer − *Acinetobacter* sp. IMB B-7005) synthesis intensification on the mixture of waste oils of various types and quality, as well as the emulsifying properties of that EPS, synthesized in such conditions, were studied.

Materials and methods. Cultivation of *Acinetobacter* sp. IMV B-7005 strain was performed in liquid medium, containing as a carbon source waste oils (sunflower, corn, olive) at concentration 5%, v/v. EPS concentration was determined gravimetrically after precipitation with isopropanol, EPS-synthesizing ability − as a ratio of EPS concentration to biomass concentration, wich was expressed as g EPS / g biomass.

Results and discussions. Regardless of the oil type in the inoculum obtaining medium (olive or sunflower), the ethapolan synthesis indexes on the mixture of waste sunflower and olive oils (in the ratio of 1:4; 4:1; 1:1) were slightly lower than in conditions of the producer growth on refined sunflower oil, but at the same time increasing of the EPS-synthesizing ability on 14−41% was observed. Using mixed after frying meat, potatoes, onions and cheese sunflower oil as a substrate for the ethapolan production accompanied by the synthesis of the same polysaccharide concentration, as well as on refined oil. Reduction of the initial quantity of mixed sunflower oil to 1.25−2% with followed fractional adding in portions of 1.25−1.5% in the cultivation process to the final amount of 5% was accompanied by increase of ethapolan concentration on 15−20% compared to a one-time addition of 5% substrate. Solutions of the synthesized under such conditions polysaccharide at concentration of 0.05% emulsified hexadecane, gasoline, diesel fuel (emulsification index 48−52%), and the formed emulsion was stable for 20 days.

Conclusion. The results demonstrate the possibility of universal technology creating for microbial exopolysaccharide ethapolan production on mixed waste sunflower oil, regardless of the substrate type and supplier.

Introduction

Microbial exopolysaccharides (EPS) are important class of natural polymers with different properties: the ability to change the rheological properties of aqueous systems. These biopolymers have several advantages over synthetic and plant polysaccharides: they are non-toxic and biodegradable, resistant to mechanical and oxidative degradation, temperature and low pH values. They are widely used in various spheres of human activity, including agriculture, textile, chemical (household chemicals) and in the food industries. As mainly EPS are characterized by low toxicity, they are also used in the pharmaceutical industry: as bases for ointments, liniments or as thickeners for syrups [1, 2].

The analyzed foreign and domestic literature shows that despite the long study of microbial EPS (more than 50 years) and widespread use in various fields – expensive carbohydrates (glucose, sucrose, starch) remain the main substrate for their production [3], and there are only some reports about EPS synthesis on industrial waste.

In 2017, in accessible literature, the work about xanthan synthesis (6.46 g/l) by the strain *Xanthomonas campestris* LRELP-1 on a medium containing 50 ml of food residues hydrolyzate (500 g of waste was mixed with 1 liter of 1.5% H_2SO_4 and filtered out) from the Shanghai University dining room appeared [4]. In the work [5], using of rice straw hydrolyzate, previously treated with NaOH at 100 °C, as an alternative source of carbon for the xanthan synthesis by *X. campestris* PTCC 1473 was studied. Under using such substrate, the yield of the product was 8.6–9.36 g EPS / 100 g substrate, and its properties were practically the same compared with the xanthan of Sigma-Aldrich firm, the USA. Drakou et al investigated the synthesis of EPS by the *Pseudomonas aeruginosa* LVD-10 and *Enterobacter* sp. SW strains on non-carbohydrate substrates [6]. Under *Pseudomonas aeruginosa* LVD-10 and *Enterobacter* sp. SW cultivation on technical glycerin (4.5%, v/v), the amount of synthesized polysaccharide was 3.2 and 2.5 g/l, respectively, under undiluted sewage using in quantity of 100 ml, LVD-10 strain synthesized 1.3 g/l, where as SW only – 0.7 g/l [6].

In our previous studies [7] the possibility of the microbial polysaccharide ehtapolan synthesis under its producer *Acinetobacter* sp. IMV B-7005 cultivation on medium with 5% of waste after frying meat or potatoes sunflower oil was shown. Later, in order to expand the raw material base for this EPS synthesis, as a substrate, waste corn, olive and rapeseed oils were used [8]. However, on factories that process plant raw materials or in catering establishments, oils of different types and after frying various products are mixed together without separation.

Proceeding from the foregoing, the purpose of this work is to investigate the ability of *Acinetobacter* sp. IMV B-7005 to synthesize ethapolan on a mixture of different types of waste oils.

Materials and methods

Object of research

The EPS-synthesized strain of bacteria *Acinetobacter* sp. 12S, which is deposited in the Depository of Institute of Microbiology and Virology, National Academy of Sciences of Ukraine by the number of IMV B-7005 was used as the object of research.

Cultivation conditions

Cultivation of *Acinetobacter* sp. IMV B-7005 was carried out in a liquid mineral medium of such composition (g/l): KH_2PO_4 − 6.8; KOH − 0.9; $MgSO_4 \times 7H_2O$ – 0.4; $CaCl_2 \times 2H_2O$ – 0.1; NH_4NO_3 – 0.6; $FeSO_4 \times 7H_2O$ – 0.001.

The following types of oils were used as a source of carbon and energy, in the quantity of 5% (v/v):

- Refined: sunflower (TM "Oleina", Ukraine), olive of cold press (TM «Salvadori», Italy), corn (LLC «Kama» Ukraine);
- Waste: sunflower after frying meat (from the McDonald's network, Kyiv, Ukraine), corn after frying meat, olive after frying potatoes or meat (obtained at home after three-times frying for 20 minutes), mixed sunflower oil after frying meat, potatoes, onions, cheese (obtained from fast-food restaurants "RockerPub" Kyiv, Ukraine).

The content of poly- and monounsaturated fatty acids in used oils is presented in Table 1 [9].

Table 1

Characteristics of vegetable oils used as a substrate

Oils	Content of fatty acids (% of the total mass)	
	Polyunsaturated	Monounsaturated
Sunflower	60	33
Corn	54	27
Olive	12	87

In some variants, sunflower and olive oil were added into the medium in a ratio of 4:1; 1:4 and 1:1. In one research, the initial concentration of mixed oil was reduced to 1.25−2%, and further it was brought to a final concentration 5% in portions 1.25−1.5% in the process of cultivation.

In additionally yeast autolysate (0.5%, v/v) and multivitamin complex "Complevit" (0.00095%) were added to the medium as growth promoter and source of pantothenate, respectively.

Culture from the exponential phase, grown in the medium with 0.5% (v/v) of refined (sunflower, olive or corn oil) or waste oil (sunflower after frying meat, olive or corn after frying potatoes) was used as the inoculum. Quantity of inoculum was 10% from the volume of the medium. Cultivation of *Acinetobacter* sp. IMV B-7005 was carried out in flasks (750 ml) with 100 ml of medium in shacker (320 rpm) at 30 ºC for 120 hours.

Indicators of growth and of the target product synthesis

Biomass concentration was determined by optical density of the cell suspension with the following recalculation on the absolutely dry biomass according to the calibration curve. Quantity of synthesized ethapolan was determined gravimetrically. For this, 1.5−2 volumes of isopropanol were added to a certain amount of culture liquid (usually 10−15 ml), the precipitate of EPS was washed by clean isopropyl alcohol and dried at room

temperature for 24 h. EPS-synthesizing ability was determined as the ratio of the EPS concentration to the concentration of biomass and was expressed in g EPS/g biomass.

Emulsifying properties of ethapolan

The emulsifying properties were determined for 0.05% (for polysaccharide) culture fluid solutions and 0.05% ethapolan solutions. Ethopolan was isolated from the culture liquid by isopropanol deposition followed by washing of the EPS precipitate in a pure organic solvent and drying at room temperature for 24 hours.

Determination of the emulsifying properties (emulsification index, E_{24},%) was carried out as follows: 2 ml of 0.05% culture liquid solution or ethapolan solution were added with 2 ml of emulsifying substrate (hexadecane, gasoline, diesel fuel) and shaken for 2 minutes. Measurement of the emulsification index was carried out in 24 hours as the ratio of the emulsion layer height to the total fluid height in the test tube and expressed as a percentage.

The formed emulsions were stored for 20 days at room temperature to check its stability.

Statistical analysis

Statistical analysis of experimental data were performed according to Lakin [10]. The results of the experiment in accordance with the Student t-test were statistically significant at the 5% significance level.

Results and discussions

In previous studies [7] for the synthesis of polysaccharide ethapolan on the waste oils (sunflower, corn, olive, rapeseed), inoculum was grown on the corresponding refined substrate. However, using of waste oils for inoculum obtaining is more appropriate both from an environmental and technological points of view. Therefore, at the first stage of the study, the synthesis of ethapolan was investigated with using waste oil as a carbon source for both inoculum preparation and EPS biosynthesis. In these experiments different types of waste oils for inoculum production and EPS biosynthesis (Table 2) were used in order to develop a universal technology of ethapolan synthesis independent of the oil quality and supplier.

Experiments have shown that the replacement of sunflower, olive, corn oils with the appropriate waste one in medium for inoculum obtaining was accompanied by decrease on 7–17% of ethapolan concentration synthesized on the olive after frying potato and meat and corn after frying meat oils (see Table 2).

Considering the obtained results, the refined oil was used for inoculum preparation in the following studies.

As a rule, in catering establishments and enterprises of plant raw materials processing, oil-containing wastes are mixed before utilization. Consequently, it was advisable to investigate the synthesis of polysaccharide ethapolan on mixed oils of different types after frying certain products.

Since sunflower oil is traditionally used for frying in Ukraine and also olive oil has become more and more popular in recent years, on the next stage the synthesis of strain IMV B-7005 EPS on a mixture of these substrates was investigated (Table 3).

Table 2

Ethapolan synthesis depending on the inoculum preparation

Oil in the medium for		EPS,% from control	EPS-synthesizing ability,% from control
EPS biosynthesis	**Inoculum obtaining**		
Olive after potatoes frying	Sunflower after meat frying	81,3	66,7
	Sunflower refined	93,8	112,8
Corn after meat frying	Olive after potatoes frying	79,6	69,4
	Olive refined	65,6	63,9
Olive after meat frying	Corn after potatoes frying	80,9	72,5
	Corn refined	97,1	60,0

Note: 1. Control (100%) – indexes of the ethapolan synthesis under inoculum obtaining on the corresponding refined oil.
2. In the synthesis rates determining, the error did not exceed 5%.

Table 3

Indexes of the ethapolan synthesis on the mixture of waste oils

Oil in the medium for		EPS,% from control	EPS-synthesizing ability,% from control
inoculum obtaining	**EPS biosynthesis**		
Sunflower refined	Olive + sunflower (1:4)	80,8	136,1
	Olive + sunflower (4:1)	69,3	122,2
	Olive + sunflower (1:1)	76,9	141,7
	Mixed sunflower oil	107,7	130,6
Olive refined	Olive + sunflower (1:4)	85,1	134,3
	Olive + sunflower (4:1)	68,7	114,3
	Olive + sunflower (1:1)	62,7	128,6
	Mixed sunflower oil	95,5	91,4

Note: 1. Control (100%) – indexes of the ethapolan synthesis under strain *Acinetobacter* sp. IMV B-7005 cultivation on refined oil.
2. In the synthesis rates determining, the error did not exceed 5%.

Experiments have shown that under *Acinetobacter* sp. IMV B-7005 cultivation on a mixture of sunflower and olive oils in any ratio, reduction of ethapolan concentration was observed, but at the same time, the EPS-synthesizing ability increased in 14–41% compared with those on refined sunflower oil. Data about using mixed sunflower oil as a substrate for the EPS biosynthesis are noteworthy: regardless of the oil type used for the inoculum preparation (refined sunflower or olive), the concentration of the synthesized ethapolan was practically the same as under producer cultivation on refined oil, which makes use of such substrate promising in the development of highly efficient EPS technology.

The waste oil contains a large amount of toxic substances (acrolein, acrylamide, lipid peroxides) [11] and addes into the *Acinetobacter* sp. IMV B-7005 cultivation medium in high concentration (5%), which may be the reason of low rates of ethapolan synthesis. Therefore, in order to reduce the content of these toxic substances, the initial concentration of oil in the cultivation medium of the IMV B-7005 strain was reduced, with following fractional substrate application during cultivation to a final concentration of 5%. This approach is used in biotechnology to reduce the duration of the lag phase, as well as the intensification of microbial technologies [12].

For example, the initial concentration of glucose in the cultivation medium of *Agrobacterium* sp. ATCC 31749 (producer of EPS curdlan) was 30 g/l and NH_4Cl – 0.5 g/l. During the first 14 hours of cultivation, the sources of carbon and nitrogen were added into the medium to the final concentration 119 and 3.6 g/l, respectively. Under such conditions, the concentration of polysaccharide was 72 g/l, which in 2 times more than under one time substrate adding [13]. Hyun Mi Kim et al [14] investigated the effect of fed-batch fermentation on the synthesis of *Ganoderma resinaceum* DG-6556 EPS. The initial concentration of glucose in the medium was 10 g/l, at 6 days of cultivation 50 g/l of glucose were added additionally, which made it possible to increase the amount of synthesized polysaccharide to 4.6 g/l. In cultivation medium of *Tremella mesenterica* NRRL Y- 6158 20 g/l of glucose were added fractionally at interval of 50 h. durring 7 days. Under such conditions, the producer synthesized 9.9 g/l of polysaccharide, which in 2.2 times more than under one-time adding of the substrate [15]. The fractional adding of milk whey into the cultivation medium of *Lactobacillus kefiranofaciens* JCM 6985, producer of EPS kefiran, was accompanied by increase of the synthesized polysaccharide concentration almost in 2 times (to 2514 ± 93 mg/l), compared to the one-time substrate addition [16]. Concentration of EPS, synthesized by marine bacteria *Zunongwangia profunda* SM-A87 on milk whey with a fractional adding of this substrate into 5 L fermenter reached 17.2 g/l [17].

Our experiments have shown that reducing of initial concentration of oil in the *Acinetobacter* sp. IMV B-7005 cultivation medium to 1.25–2%, with following substrate fractional addition to the final concentration of 5%, contributed to increase of synthesized ethapolan amount to 15–20% compared to a one-time addition of 5% of the substrate.

The practical value of microbial exopolysaccharides is determined primarily by their ability in small concentrations to change the rheological properties of water systems – to increase viscosity, to form gels, to exhibit emulsifying and suspending properties in water systems. Thanks to these properties, EPS can be used as emulsifiers in the food and pharmaceutical industries, cosmetology. Increasingly, exopolysaccharides are found in solving the problems of secondary oil production due to its high viscosity, pseudoplasty, resistance to high pressure and temperature [12].

Today the following microbial EPS are the most promising in the world for using in oil extraction: xanthan (producer *Xanthomonas campestris*) and scleroglucan (producer *Sclerotium glucanicum*). It should be noted that ethapolan solutions are characterized by

unique emulsifying properties that are not inherent to most known microbial polysaccharides, including xanthan, due to its acylated polysaccharide which containes fatty acids (C_{10}–C_{18}) [12]. The lipophilic part in the ethapolan molecule provides formation of a stable emulsion of water with oil and other hydrocarbons. Nowadays, only one such polysaccharide as emulsant (producer *Acinetobacter calcoaceticus* RAG-1) in which fatty acids are attached to the carbohydrate chain via of ethereal bonds has been studied in sufficient quantity [18]. Due to the presence of fatty acids in its composition emulsan is a great emulsifier.

Taking into account the above, the emulsifying properties with hydrophobic substrates such as hexadecane, gasoline and diesel fuel of the ethapolan, synthesized on mixed waste oils, were investigated at the next stage of the work. Precipitated and dried polysaccharide was used in the studies, since such product form is the most popular on the polymer market.

However, the unique feature of the domestic polysaccharide is practically confirmed possibility of its using in the form of post-fermentation culture fluid in the technology of oil production [12]. Excluding the stages of target product precipitation and drying in industrial production of EPS ensures a significant reduction in the cost of the product, as well as the preservation of the polysaccharide properties. Using such form of ethapolan has an additional advantage, since polysaccharides are stabilized with ingredients that are the part of the culture fluid. Therefore, the emulsifying properties were investigated also for the strain IMV B-7005 culture fluid containing ethapolan.

Studies have shown that, regardless of the marketable type of the ethapolan solutions, the emulsification indexes for all substrates were practically the same (48–52%, Fig. 1).

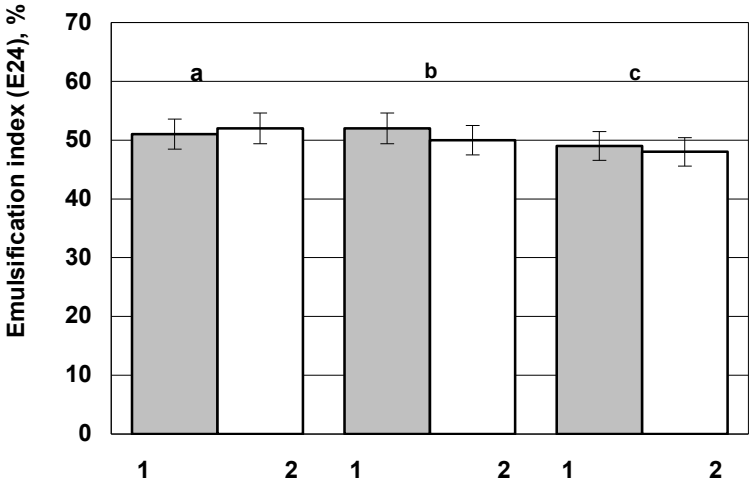

Figure 1. Emulsification index of the ethapolan solutions obtained on the mixed waste oil:
Substrate for emulsification: a – hexadecane, b – diesel fuel, c – gasoline.
Emulsifier: 1 – 0,05% solution of ethapolan, 2 – 0,05% (for polysaccharide) solution of strain IMB B-7005 culture fluid.

An important feature of polysaccharides is not only the ability to form gels, suspensions or emulsions with different substrates, but also to ensure the stability

(preservation of initial properties) of these two-phase systems for a long time of storage. The formed emulsiones of ethapolan with hexadecane, gasoline and diesel fuel were stored for 20 days, the emulsification index decrease didn't exceede 5%.

It is known from the literature, that the formed emulsion of hexadecane with emulsan (at a concentration of 1 mg/ml) was kept for 4 days within the pH range of 4–8 [19]. The EPS synthesized by *Enterobacter cloaceae* at concentration of 1 mg/ml is capable to form an emulsion with a wide range of hydrophobic substrates, with a shelf life of emulsions not more than 10 days [19]. According to the authors, the emulsifying properties of this polysaccharide are provided by the proteins included in its composition, but their low thermostability makes it impossible to use this EPS under elevated temperatures. Though, liposan produced by *Candida lipolytica* did not exhibit significant surface-active properties, it emulsified various hydrocarbons and oils at 8 mg/ml of hydrocarbon. These emulsions were stable only for 50 min. Thus, ethapolan has a great advantages over other EPS used as emulsifiers, that makes the strain IMV B-7005 polysaccharide promising for use in various technologies [19].

Conclusions

Thus, as a result of this work, the possibility of different types of waste oils using, including mixed, for the synthesis of the microbial polysaccharide ethapolan was shown for the first time. The obtained results testify the possibility of a "flexible" and versatile technology developing for obtaining this EPS with stable emulsifying and rheological properties, that does not depend on the quality of the oil (its nature and the product that was heated), the region and the supplier of raw materials.

References

1. Moscovici M. (2015), Present and future medical applications of microbial exopolysaccharides, *Frontiers in Microbiology*, 6, DOI: 10.3389/fmicb.2015.01012
2. Madhuri1 K. V., Prabhakar V. K. (2014), Microbial exopolysaccharides: Biosynthesis and potential applications, *Oriental Journal of Chemistry*, 30(3), pp. 1401–1410, http://dx.doi.org/10.13005/ojc/300362
3. Roca C., Alves V.D., Freitas F., Reis M.A. (2015), Exopolysacchrides enriched in rare sugars: bacterial sources, production, and applications, *Frontiers in Microbiology*, 6, DOI: 10.3389/fmicb.2015.00288.
4. Li P., Zeng Y., Xie Y., Li X., Kang Y., Wang Y., Xie T., Zhang Y. (2017), Effect of pretreatment on the enzymatic hydrolysis of kitchen waste for xanthan production, *Bioresource Technology*, pp. 84–90, http://dx.doi.org /10.1016/j. biortech.2016.10.035
5. Jazini M. H., Fereydounia E, Karimiab K. (2017), Microbial xanthan gum production from alkalipretreated rice straw, *Royal Science of Chemistry Advances*, 7, pp. 3507–3514, DOI: 10.1039/c6ra26185j.
6. Drakou E.M., Amorim C. L., Castro P. M. L., Panagiotou F., Vyrides I. (2017), Wastewater valorization by pure bacterial cultures to extracellular polymeric substances (EPS) with high emulsifying potential and flocculation activities, *Waste biomass valorization*, DOI: 10.1007/s12649-017-0016-9
7. Ivakhniuk M.O., Pirog T.P. (2015). Vplyv sposobu pidhotovky posivnoho materialu

na syntez polisakharydu etapolanu na oliyevmisnykh substratakh, Naukovi pratsi NUHT, 21(5), pp. 17–21
8. Ivakhniuk N.A., Voronenko A.A., Pirog T.P. (2017), Mikrobnyi sintez ekzopolisakharida etapolana na razlichnykh vidakh otrabotannykh rastitelnykh masel, *Izvestiia Natsionalnoi akademii nauk Belarusi. Seriia biologicheskikh nauk*, 2, pp. 87−93
9. Obukhova L.A., Garagulia E.B. (2016), Rastitelnye masla v pitanii. Sravnitelnyi analiz, Available at: http://www.argo-shop.com.ua/article-9182.html
10. Lakin G.F. (1990), *Biometriia*, Vysshaia shkola, Moskow.
11. Guillén M. D., Uriarte P. S. (2012), Aldehydes contained in edible oils of a very different nature after prolonged heating at frying temperature: Presence of toxic oxygenated α, β unsaturated aldehydes, *Food Chemistry*, 131, pp. 915–926, DOI:10.1016/j.foodchem.2011.09.079.
12. Pidhors'kyy V.S., Iutyns'ka H.O., Pirog T.P. (2010), *Intensyfikatsiya tekhnolohiy mikrobnoho syntezu*, Naukova dumka, Kyiv.
13. Pirog T.P., Antoniuk M.M., Skrotska O.I., Kihel N.F. (2016), *Kharchova biotekhnolohiia*, Vydavnytstvo Lira-K, Kyiv.
14. Hyun Mi Kim, Soon-Young Paik, Kyung Soo Ra, Kwang Bon Koo, Jong Won Yun, Jang Won Choi (2006), Enhanced production of Exopolysaccharides by fed-batch culture of *Ganoderma resinaceum* DG-6556, *Microbiology*, 44(2), pp. 233–242
15. Baets S. De., Laing S. Du., Francois C., Vandamme E.J. (2002), Optimization of exopolysaccharide production by *Tremella mesenterica* NRRL Y-6158 through implementation of fed-batch fermentation, *Journal of Industrial Microbiology & Biotechnology*, 29, pp. 181–184
16. Cheirsilp B., Suksawang S., Yeesang J., Boonsawang P. (2018), Co-production of functional exopolysaccharides and lactic acid by *Lactobacillus kefiranofaciens* originated from fermented milk, kefir, *Journal of Food Science and Technology*, 55(1), pp. 331−340, DOI: 10.1007/s13197-017-2943-7
17. Sun M.L., Liu S.B., Qiao L.P., Chen X.L., Pang X., Shi M., Zhang X.Y., Qin Q.L., Zhou B.C., Zhang Y.Z., Xie B.B. (2014), A novel exopolysaccharide from deep-sea bacterium *Zunongwangia profunda* SM-A87: low-cost fermentation, moisture retention, and antioxidant activities, *Applied Microbiology and Biotechnology*, 98(17), pp. 7437−7445, DOI: 10.1007/s00253-014-5839-8
18. Panilaitis B., Castro G.R., Solaiman D., Kaplan D.L. (2007), Biosynthesis of emulsan biopolymers from agro-based feedstocks, *Journal of Applied Microbiology*, 102(2), pp. 531−537, DOI: 10.1111/j.1365-2672.2006.03078.x
19. Iyer A., Mody K., Jha B. (2006), Emulsifying properties of a marine bacterial exopolysaccharide, *Enzyme and Microbial Technology*, 38, pp. 220–222.

Influence of mechanical disperator designer parameters on equality of distribution of solution

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Keywords:

Disperator
Distribution
Spraying
Fluidized bed
Dehydration

Article history:

Received 17.12.2017
Received in revised form 25.01.2018
Accepted 29.03.2018

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DOI: 10.24263/2304-974X-2018-7-1-10

Abstract

Introduction. The results of experimental studies the influence design a mechanical disperator on the uniform distribution of a fluid in the volume of the working zone are presented.

Materials and methods. The experimental plant is equipped with volume circular circuits for measuring the flow of liquid phase over the working length of the disperator. As a model liquid, water is used at a temperature of 18 ºC. From the experiment, the average costs of the liquid phase and the mass fractions of their distribution along the length of the working zone are determined by removing the liquid from the cells of the ring module. The number of weak rotations of the dispersator was measured by an electron frequency in Hz with an accuracy of ± 1 Hz. Determination of the size of droplets was carried out by means of photographic fixation.

Results and discussion. At application of mechanical Cone type disperator with 450x per cent centrifugal force over gravitational force on the outer surface of a mechanical disperator of conical shape due to the presence of surface tension forces, fluid jets are formed which move to the edge of the disperator and facilitate the local re-use of the irrigation working zone.

The use of a conical disperser with the installation of external roller rings has increased the uniformity of distribution. The proposed criterion of estimation of uniformity allows to make a comparison of any designs of mechanical disperators according to the original method. In addition, a rational way of installing the feed supply tube of the working solution has been determined. By the results of the study have been determined, the parameters at which the size of the volume of spraying is increased with sufficient uniformity with the use of a mechanical two-cone disperator with a perforated lateral surface and the presence of external deflecting rings.

Conclusions. The expediency application of the proposed criteria for assessing the quality of work of a mechanical disperator has been theoretically substantiated and experimentally proved, which allow to determine the conditions of qualitative conduction of watering and granulation of liquid systems in the fluidized bed.

Introduction

The obtaining of solid composites with given properties during dehydration of liquid heterogeneous systems is the most appropriate use of pseudo-irradiation techniques [1,2].

In particular, in the production of granulated humic-mineral fertilizers, the finished product has a spherical shape with a uniform distribution of nutrients, micronives and humic substances, the content of which does not exceed 2% in relation to dry substances [3].

The stable kinetics of the process efficiency is determined by the method of regulation of the device for introducing the liquid phase.

Analysis of scientific works

The authors [4] established the influence of the geometrical construction, the linear parameters of the working surface of the disperator and the rheological properties of the liquid phase on the size of droplets, when the number of revolutions increases, is transformed in the form of a film on the edge of the disperator. Such a mode of operation is unsuitable for the case of dehydration and granulation of liquid systems, as it leads to a local overflow and as a consequence of the formation agglomerates.

In works [4-5] various mechanisms of spray dispersion were investigated, using a high-speed chamber. In their experiments, two different glycerin/water mixtures and three different designs of disperators with external diameters of 0.090, 0.11 and 0.128 m were used. Three studies of the disintegration mechanism were observed. However, the problem of local overflow was not effective.

The influence of the mechanical disperator structures on the size of droplets was investigated in [6-7]. As a result, a comparative analysis of the distribution, depending on the size of the droplets obtained with the help of seven different design disks operating at a flow rate of 660 liters per hour, and a linear velocity of 63.5 m/s, showed that the design of the disk had a minor effect on the size distribution of drops. The investigated parameters in these experiments were the number of blades built into the rotating surface and their configuration. But such designs can not be used when placing a disperator in the middle of a layer of granular material, due to the high risk of crushing granules.

In works [8-9], rotary discs with different edge profiles such as acute edge, straight edge, tilt edge and round edge with different radius were considered. It is determined that the change of the edge profiles leads to insignificant differences in the size of the droplets and does not allow to form a liquid phase on the surface of the granule in the form of a thin film, which leads to agglomeration of the granule by the formation of "liquid bridges".

However, studies [10] concluded that clamping the edge of a cup or disk delayed the transition from the chain mode to the film mode and pok-raises the quality of spraying, but does not solve the problem above.

Previous studies have established [11] that the use of a disk disperser leads to local overflow at the expense of reducing the working area for the introduction of liquid specialty and the formation of agglomerates with subsequent impulse process. Therefore, in order to prevent these shortcomings, it is proposed to apply a new design of a mechanical disperator with increased zone dispersion.

Materials and methods

Experimental device

The research was carried out on an experimental stand designed by the auto-frame which allows measuring the irrigation density of the working zone on the outer surface Figure 1.

The speed of the disperator was measured by an electronic frequency meter in the range of 50-90 1/s with an accuracy of ± 0.5. As a model liquid, water was used. The liquid phase was measured by a volumetric method with an accuracy of ± 0,11 l.

Materials

At a given rotational frequency of the disperator and constant losses, the liquid supplied by the feed tube 6, Figure 1 in time $\Delta\tau$ = 60 s was distributed by a mechanical disperator in the annular chamber 5, in which, with an interval Δl = 6 mm, the ring partitions were installed. Each ring cell is connected to the measuring flasks 7. The height of the liquid in the flasks allows you to determine the distribution histogram, the liquid phase.

Measuring complex

Constructions of 3 types of conical disperators with a perforated surface were investigated. Distance of the edge of the cell in the ring chamber 5, Figure 1, to the edge of the disperator is ΔZ = 15 mm.

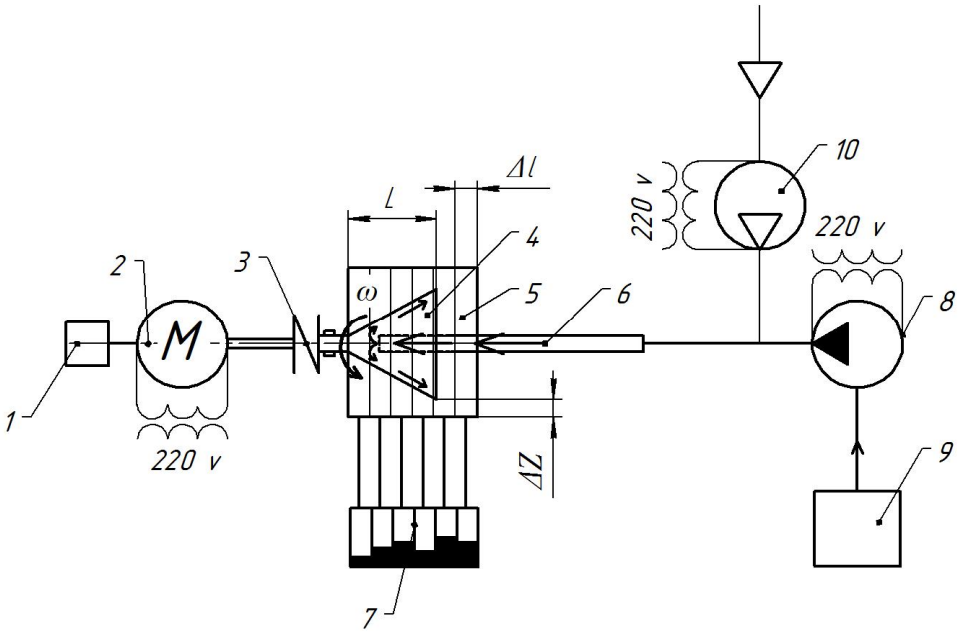


Figure 1. Test bench to evaluate the uniformity of dispersion:
1 – electronic frequency meter; 2 – engine; 3 – coupling; 4 – disperator; 5 – annular collection chamber; 6 – tube for delivery of a solution; 7 – measuring flasks; 8 – peristaltic pump; 9 – capacity of a liquid; 10 – compressor.

Results and discussion

Mechanical disperator type 1, Figure 2a, is a cut cone with a large diameter D = 80 mm, smaller D1 = 40 mm and a width L = 47 mm. In the end-ears, the plane G has 4 holes diameter 4.5 mm. The angle at the top of the cut cone 25° prevents the formation of sediment on the working surface.

On the lateral surface of the disperator type 1, Figure 2a, in the spiral trajectory of the uniformly located apertures of 4.5 mm in diameter. Relative area to the side surface of the disperator, the coefficient of the living section

$$\varphi = \frac{f_{\text{holes}}}{F_{\text{lateral}}} \cdot 100\% = 4\% \quad (1)$$

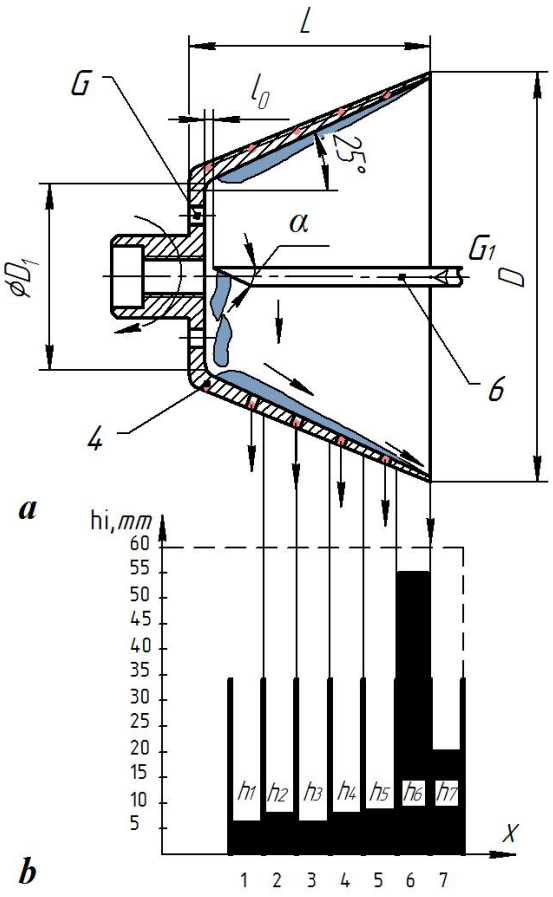


Figure 2. Mechanical disperator type 1:
4 – the disperser body; 6 – liquid supply line
a – Type 1 disperator design;
b – the histogram of the distribution of the liquid in the length G = 12,44 kg/h;
a = 0,073 kg/(m·s); n = 60 1/s; w = 9 m/s; L = 0.47 mm.

The peculiarity of introducing the liquid phase lies in the fact that the feeding tube 6, Figure 2a has a cut at an angle of 30°, which is turned down, and the end is at a l_o = 2 mm distance from the inner face of the disperator.

From previous studies [1] found that the linear velocity of the edge disperator with a diameter D = 47 mm, w_l = 9 m/s, which is achieved with a disperator wrapping frequency of n = 60 1/s.

For a comparative characterization of the mechanical disperator, a linear load is proposed for the mass flow rates of the liquid phase:

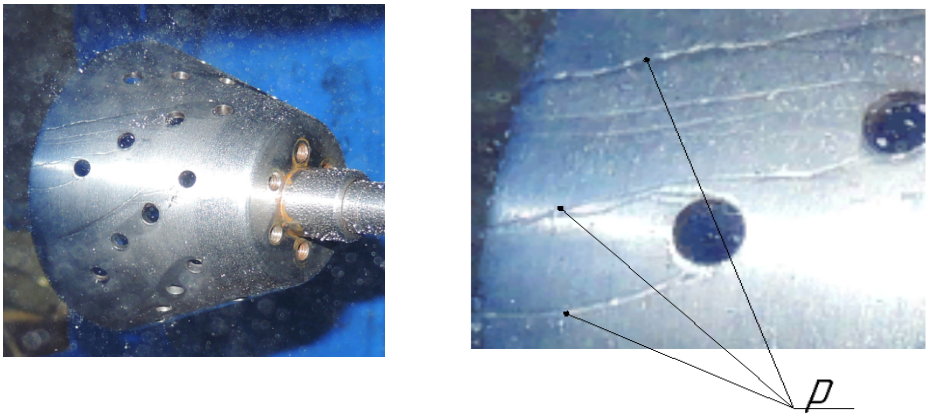
$$a = \frac{G}{L \cdot 3600} \tag{2}$$

where G – mass flow of liquid, kg/h, a – length of disperator, mm;

Experimentally, the distribution of the mass of the fluid, along the length of the working area, is expressed in terms of the ratio of heights (Figure 1):

$$h_1: h_2: h_3: h_4: h_5: h_6: h_7 = 0.9: 1.1: 0.9: 1.1: 1, 2: 11: 3$$

in dimensional flasks 7. A tenfold excess of height h_6 is due to the fact that, due to the forces of surface tension on the outer surface of the disperator, streams of rice are formed, Figure 3 a, b.



a ***b***

Figure 3. Nature of movement on the outer surface of the disperator type 1:
a – General view of outer surface;
b – Liquid flow by outer surface.

To eliminate this phenomenon, designed the disperator type 2, Figure 4a.

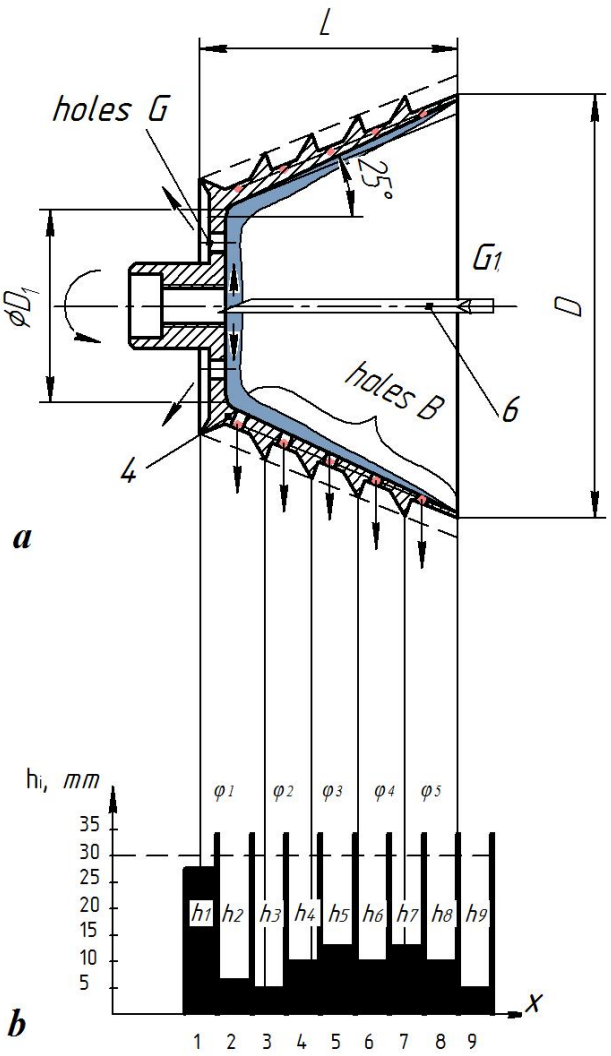


Figure 4. Mechanical disperator type 2:
a – Design of disperator type 2;
b – Flow distribution histogram;
G = 12,44; a = 0.073;
n = 60 1/s; w = 9 m/s;
L = 0.47 mm.

On the outer surface, there are setbacks in the interval between the openings with a diameter of 4.5 with the ratio of the coefficients of the living section respectively

$$\varphi 1: \varphi 2: \varphi 3: \varphi 4: \varphi 5 = 1: 1: 3: 5: 5,$$

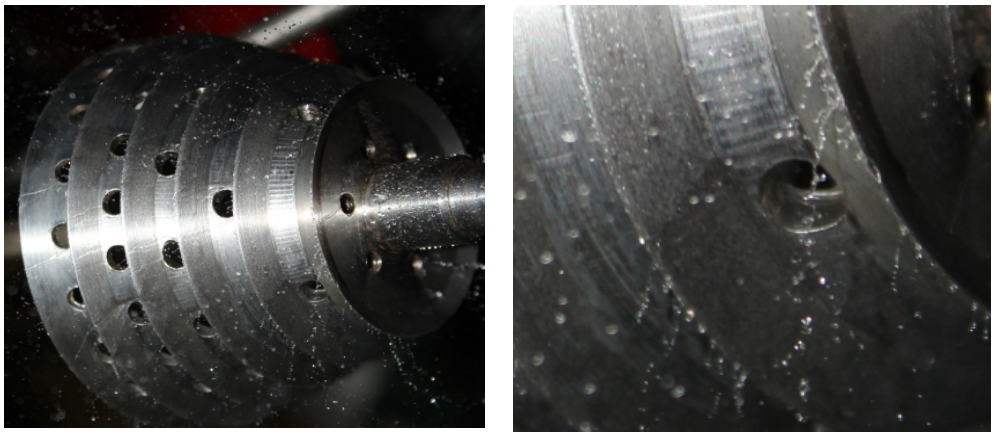
while maintaining the total coefficient of the living section f = 4%, Figure 4. Nutrient tube 6, Figure 4a, small cut edges at an angle of 30°, but turned up. The distance from the internal end surface of the disperator l_o = 0, with similar liquid phase flow rates and the number of revolutions.

This led to a change in the histogram of mass distribution of the liquid by a disperator, which was determined by the ratio of heights.

Namely

h1: h2: h3: h4: h5: h6: h7: h8 = 5.5: 1.3: 1: 2: 2.6: 2: 2.3: 1.

The analysis of photos of the outer surface of the disperator in the working condition has confirmed the effectiveness of the use of reaming rings. However, in zone 1 there was a significant increase in the parameter h1, which is due to the approximation of the edge of the power pipe 2 to the end of the disperser, Figure 5a. As a result, through the openings of G (6 pcs. ø 4,5), Figure 5b, there was a large amount of liquid.



a ***b***

Figure 5. Nature of movement on the outer surface of the disperator type 2:
a – General view outer surface;
b – Liquid flow by outer surface.

In this case, the parameter a = 0,073 kg/(s · m) for both types of disperators was identical. Therefore, the use of bulging rings on the outer surface of a conical di-sphericator has made it possible to significantly improve the distribution mass of the fluid along the length of the disperator 's working area.

To increase the length of the dispersion zone and to improve the uniform distribution of the dispersed liquid, a disperator type 3, Figure 6.

Which represents the mirror image of the disperser type 2 of the introduction of liquid into the central part, Figure 6. The working solution through the introduction tube 4 is fed into the chamber 3, in which there is a division into two streams, followed by the formation of a film that moves into a zone of greater diameter, according to the inner surface of the chamber 1, and 1a, Figure 6.

Breakers rings 2 crash the jets of fluid moving on the outer surface of the disperser and promote effective dispersion at a larger length, Figure 7 a,b, working area length L = 1.63L. The experiment was carried out with an increase in the mass flow of liquid phase from $G_{1,2}$ = 12,6 to 19,6 kg/h, but with this parameter a=0,071 $\frac{kg}{s \cdot m}$.

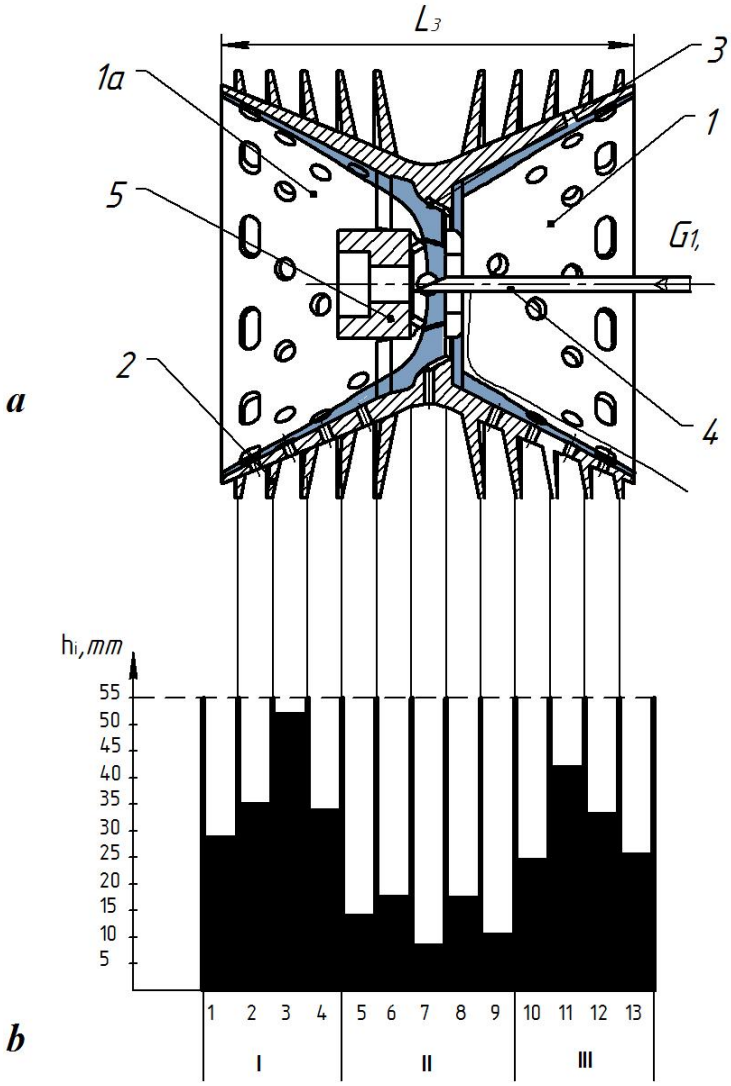


Figure 6. Mechanical disperator type 3:
1 – disperator; 2 – discontinuous rings; 3 – distribution chamber; 4 – tube for giving the working solution; 5 – element of fastening to the shaft;
a – design of type 3 disperators; Lz = 1,63, L = 77 mm;
b – histogram distribution of fluid along the length G = 19,6, a = 0,071 n = 60 1/s = w_l 9 m/s

As a result, it was possible to significantly change the histogram of the distribution along the rotor length

$h_1:h_2:h_3:h_4:h_5:h_6:h_7:h_8:h_9:h_{10}:h_{11}:h_{12}:h_{13}$ = 3,4:4,2:6,2:4:1,7:2:1:2:1,2:2,9:5:4:3.

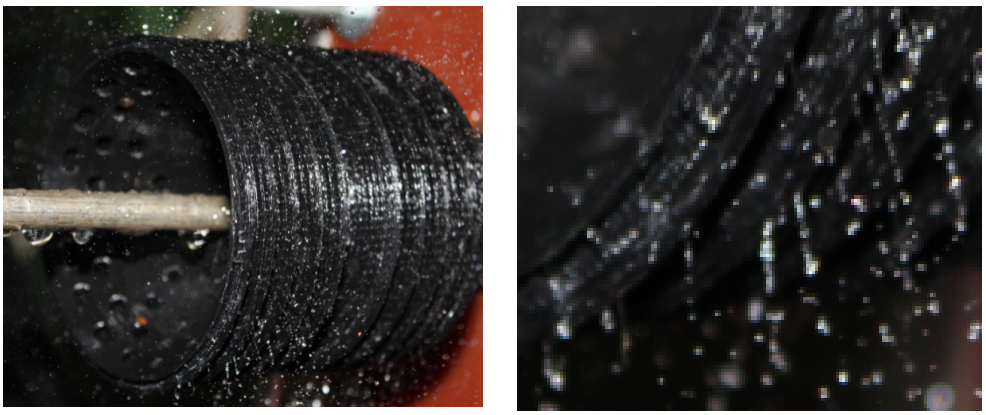
By even distribution, you can conditionally allocate to 3 zones. h_I, h_{III} irrigation zone with disperser 1 and 1a, with an average value of h_I = 37,7 mm, h_{III} = 31,3 mm. In the zone h_{II}, there is an explicit minimum of the hysterograms in comparison with the zones h_I and h_{III},

h_{II} = 13,64 mm due to the location of the distribution chamber and reduction of seams in this area w_l = 3–4 m/s.

The density of the mass distribution of the fluid along the length is determined by the formula:

$$g_i = \frac{h_i \cdot G}{\Sigma h_i \cdot 3600 \cdot L_p} \quad (3)$$

where G – mass flow rate of liquid, kg/h; h_i – height of a column of liquid in a separate cassette cell, mm; L_p – irrigation working area, mm; $\sum h_i$ – the amount of liquid column heights in all cells, mm.



a ***b***

Figure 7. Nature of movement on the outer surface of the disperator type 3:
a – general view of outer surface;
b – flow of liquid through outer surface.

The dependence g = f (L) for the three types of disperators is shown in Figure 8.

The presence of maxima for disperators of type 1 and 2, corresponding to 6 and 3 times the maximum level of the disperator, indicates an unsatisfactory volume distribution of the liquid phase over the working length of the disperator, and therefore the construction of these types of disperators will cause the formation of maximum areas of overflow.

More effective is the disperator type 3 where the ratio is much smaller.

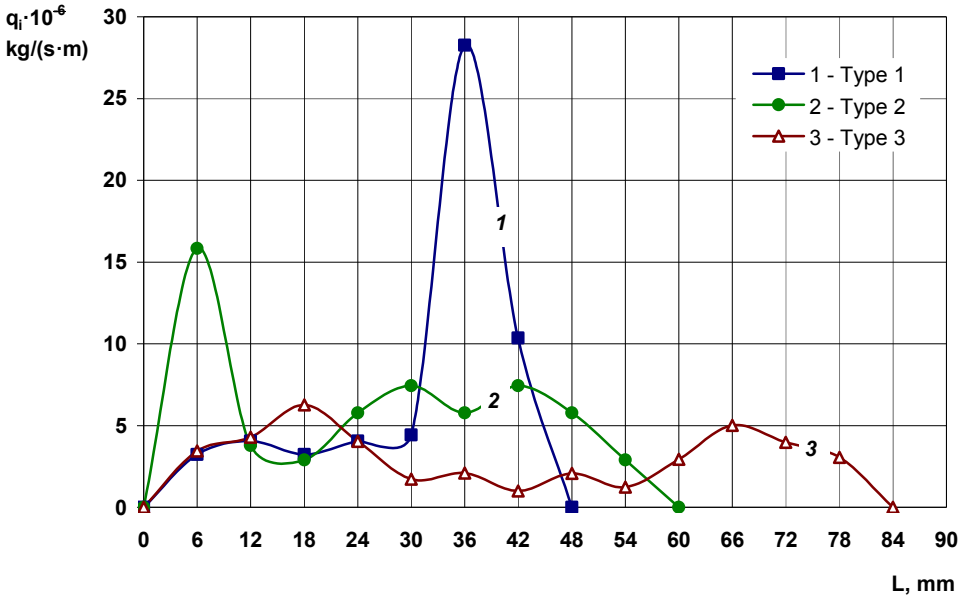


Figure 8. The density of mass distribution of the liquid along the length of the zone disperators for dispersing Type 1, Type 2, Type 3

Quality assessment conducted by the uniformity of dispersion index distribution of mass density fluid dispersion working length:

$$j_{\max} = \frac{g_{i\max}}{L_p}$$

where L_p – the width of the working spray zone, and $g_{i\max}$ – the maximum value of the density distribution of the fluid in length in a separate measuring flask.

Comparing the results of experimental studies of various types of disperators shows that the minimum value of this criterion is achieved for disperator type 3, which is 4.5 times less compared with disperator type 1 and 2.5 times disperator type 2, Figure 9.

A very important criterion for the quality of the disperator is the determination of the influence of technological parameters on the size of liquid droplets that arise when working with a disperator. Previous studies have established [12] that the implementation of the layered granule formation mechanism, the average droplet size of the liquid phase should not exceed 10% of the average grain size. According to the existing quantities to the granular product, the average size of the granules is De = 2.5 mm, so the average size of drops d_{kp} = 0.25 mm = 250 μm.

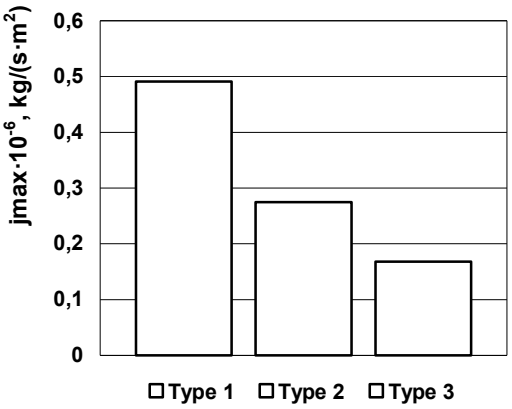


Figure 9. Jmax spray density indexes for different types of disperator

A further study on the size of droplets was performed on type 3 disperator. For the experiment, a fractional factor-type experiment was chosen

$$n = 2^{3-1} \tag{5}$$

where as parameters were chosen: x_1 – linear velocity of the edge of the disperser with a maximum internal diameter D = 47mm,

$$x_1 = \omega \cdot \frac{D}{2} = 2\pi n \frac{D}{2} \tag{6}$$

where – ω – number of revolutions of the disperser, 1/s;
x_2 – flow rate of the liquid phase supplied to the disperator, kg/h;
x_3 – the pressure of air supplied to the power supply, MPa.

The limits of measurement of these parameters are given in Table 1.

Table 1

The value of the main parameters and the limits of their variation

Parameter	Definition	Parameters value		
		Average	Deviation	Dimension
X_1	W	15,8	4,5	M/s
X_2	G_1	25,75	6,2	Kg/h
X_3	As	0,175	0,075	Mpa

Experiments were carried out on experimental installations with photophixation of droplets of the liquid phase in accordance with the experimental plan Figure 10.

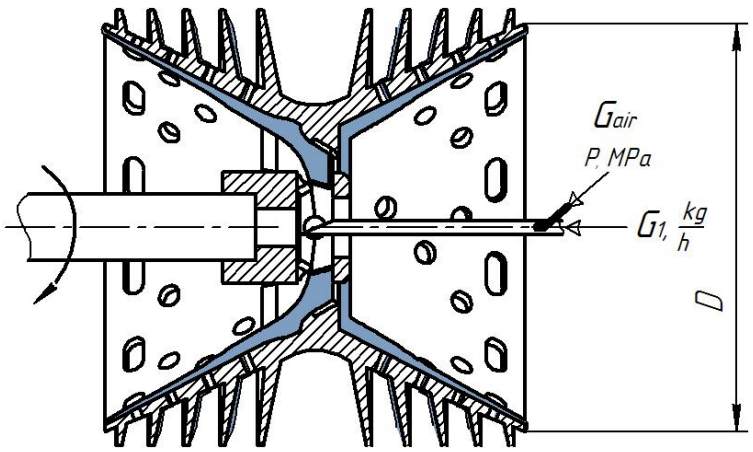


Figure 10. Diagram of determination of droplet parameters

In this case, the parameter a for the range of variation of costs indicated in the experiment plan is applied discretely within: $0,069 \le a \le 0,116$

The matrix of planning and experiment results are shown in Table 2

Table 2

The matrix of the plan and the result of the experiment

№	X_1, m/s		X_2, kg/h		X_3, MPa		D, microns		Date of the event
	Code	Medium	Code	Medium	Code	Medium	Value	Medium	
1	+	20,3	-	19,6	-	0,1	220	221,3	12.05.2017
	+		-		-		224		12.05.2017
	+		-		-		229		12.05.2017
2	-	11,3	+	32	-	0,1	410	409	14.05.2017
	-		+		-		402		14.05.2017
	-		+		-		415		14.05.2017
3	-	11,3	-	19,6	+	0,25	315	308	08.09.2017
	-		-		+		308		08.09.2017
	-		-		+		302		08.09.2017
4	-	11,3	+	32	+	0,25	355	350	16.09.2017
	-		+		+		347		16.09.2017
	-		+		+		349		16.09.2017

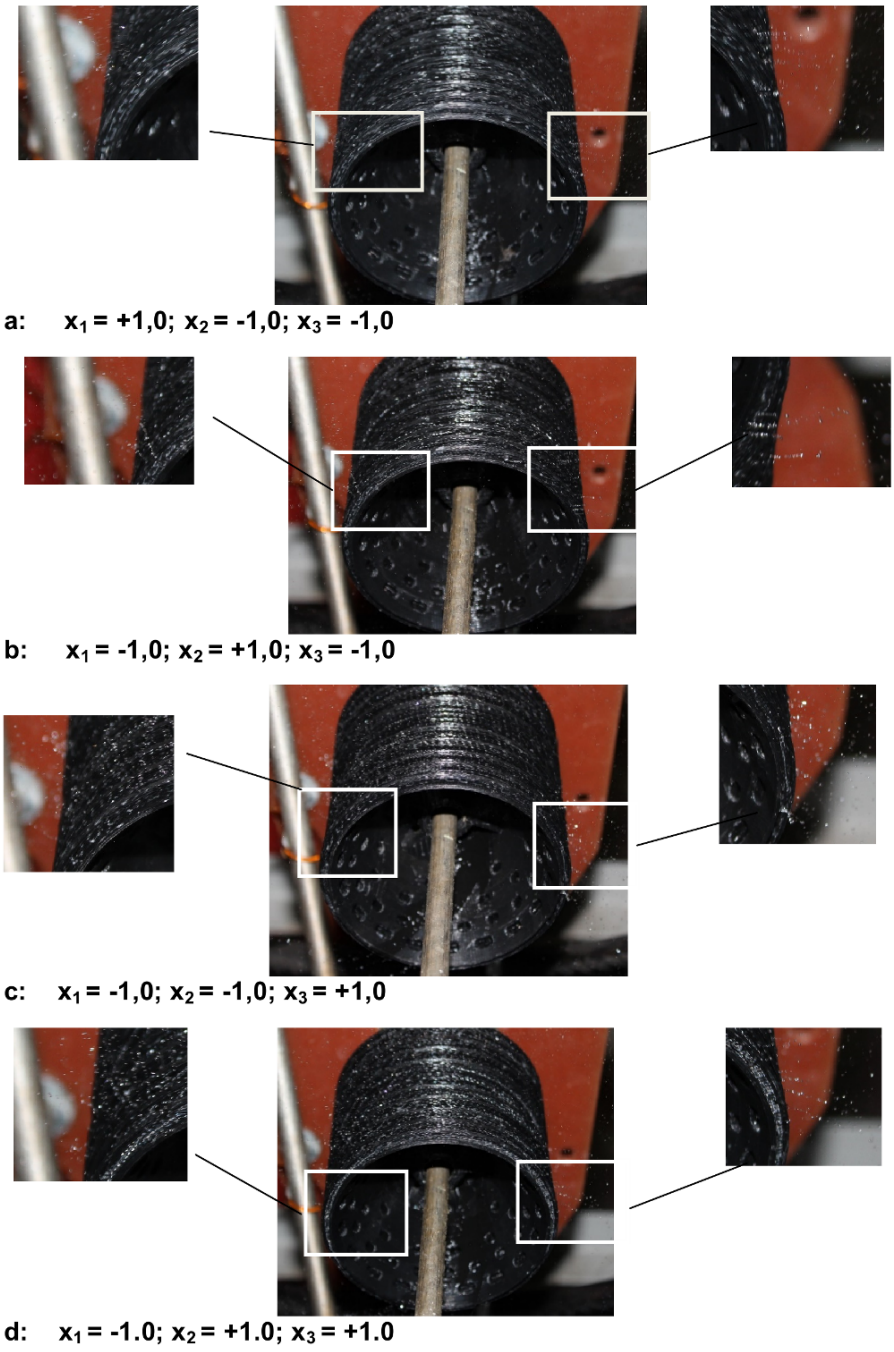


Figure 8. Photo fixation of the size of liquid drops when implementing an experiment plan

Processing the results of the experiment according to the method [13], therefore, in the equation of the form:

$$\eta = B_0 + B_1 x_1 + B_2 x_2 + B_3 x_3 \quad (8)$$

After the transformations of the values of the regression coefficients, we finally get the equation in the normalized coordinates:

$$\eta = 322 - 36,4 x_1 + 57,4 x_2 \quad (9)$$

or in real physical quantities:

$$\eta = 322 - 9,8(x_1 - 11,5) + 9,2(x_2 - 25,7) \quad (10)$$

The analysis of the equations shows that the minimum costs for dehydration dgiv = 250 microns are predicted at the upper limit of the parameter value x_1, w_l=15 m/s, and the lower paramiter x_2= 19.6 kg/h; then it is quite obvious that when increasing the size of the granule, it may be possible to increase the size of the droplets accordingly. But the linear velocity of the edge of the disperator should be at least $w_p \geq 9$ m/s. To ensure these requirements, the outer diameter of the shaft rings is practically equal to the internal diameter of the disperser.

Conclusions

The chosen quality assessment criterion, such as the density index and the size of drops, allows to provide an efficient distribution of the liquid phase. This mechanical disperator is installed inside a fluidized bed which prevents the formation of local overflow zones.

References

1. Korniyenko Y., Hayday S., Semenenko D., Martynyuk O. (2013), Hranul'ovani azotno-kal'tsiyevo-huminovi tverdi kompozyty, modyfikovani bentonitom. Protses oderzhannya, *Khimichna promyslovist' Ukrayiny*, 5, pp. 46–51.
2. Kornienko Y., Gaidai S., Martyniuk O. (2014), Improved process to obtain granular humic fertilizers, Available at: http://ela.kpi.ua/handle/123456789/11943.
3. Kornienko Y., Gaidai S., Martyniuk O. (2014), Improved process to obtain granular humic fertilizers, Available at: http://ela.kpi.ua/handle/123456789/11943.
4. Ahmed, M., Youssef, M., (2012), Characteristics of mean droplet size produced by spinning disk atomizers, *J. Fluids. Eng.-Trans*, 134(7), pp. 071103.1–071103.9 (Paper 071103).
5. Ahmed, M., Youssef, M., (2012). Characteristics of mean droplet size produced by spinning disk atomizers. J. Fluids. Eng.-Trans. 134(7), pp. 071103.1–071103.9 (Paper 071103).
6. Ahmed, M., Amighi, A., Ashgriz, N., Tran, H., (2008), Characteristics of liquid sheets formed by splash plate nozzles, *Exp. Fluids,* 44, pp. 125–136.

7. Ahmed, M., Ashgriz, N., Tran, H., (2009a), Break-up length and spreading angle of liquid sheets formed by splash plate nozzles, *J. Fluids Eng.-Trans*, 131(11), pp. 011306.1–11306.9 (Paper 011306).
8. Ahmed, M., Ashgriz, N., Tran, H., (2009b), Influence of breakup regime on the droplet sizes produced by splash-plate nozzles, *AIAA J*., 47(3), pp. 120–128.
9. Ahmed, M., Abou Al-Sood, M., Ali, A., (2011), A one dimensional model of viscous liquid jets breakup. J. Fluids Eng.-Trans, 133(11), pp. 114501.1–114501.7 (Paper 114501).
10. Ahmed, M. , Youssef, M., Abou Al-Sood, M. (2013), A two dimensional modeling of viscous liquid jets breakup, Acta Mech., 224, pp. 449–512, doi: 10.1007/s00707-012-0766-1.
11. Manastyrny M.N., Kornienko Y.N., Lyubek A.N. (2017), The evaluation efficiency of working mechanical liquid distributor, Young Scientist, 11, pp. 6–9
12. Kornienko Y., Haidai S., Liubeka A., Martynyuk O. (2016), Kinetic laws of the process of obtaining complex humic-organic-mineral fertilizers in the fluidized bed granulator, *Ukrainian Food Journal*, 5(1), pp. 144–154.
13. Krasovskii G.I., Filaretov G.F. (1982), *Planning of the experiment*, Publishing house of the Belarusian State University, Minsk.

Influence of working elements of various configurations on the process of yeast dough kneading

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Keywords:

Kneading
Yeast,
Dough
Intensity
Specific work
Porosity

Article history:

Received 17.11.2017
Received in revised form 28.12.2017
Accepted 29.03.2018

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DOI: 10.24263/2304-974X-2018-7-1-11

Abstract

Introduction. There was investigated the influence of the geometric parameters of the main working elements on the intensity and quality of the kneading of the yeast dough.

Materials and methods. There was researched the wheat yeast dough, which was mixed by a machine of continuous action using screw, cam and pin work elements. The structural and mechanical properties of the dough were determined by viscosimetry. The porosity of the finished product was determined by analyzing the look of the cut of the finished product and the ImageJ special software package.

Results and discussion. With an increase of indicators of the rate of displacement from 0 to 100 s^{-1}, a prompt jump in the bias voltage from 2000 to 6800 Pa occurs, then slowly increases to 6950 Pa in the range of the shift rate from 100 to 800 s^{-1}. As the displacement rate increases from 0 to 800 s^{-1}, the viscosity decreases with degree dependence.

Indicators of the cost of specific work during the kneading of the yeast dough by working elements of various configurations for the parameter of stabilizing grating 2,5%, reach 22-37 J/g.

The intensity of kneading the dough depends on the design of the dough kneading machine, the rotational speed of the kneading element and its configuration. Screw working elements are very intense, intensity indicators range from 0.07 to 0.12 W/g.

The porosity of the bread product after kneading by cam element is 72% and is a high indicator of the product.

Conclusions. It is confirmed the positive effect of enhanced machine processing by cam and screw working elements during the process of kneading the yeast dough. Pin working elements can be used in combination with a screw element at the beginning of the shaft. A comparative analysis confirms the expediency of using cam-shaped working elements.

Introduction

One of the effective methods for acceleration of maturation of the dough and improving the quality of the bakery products is the increased mechanical processing of the dough during the kneading process, which makes it possible to improve the structural and physico-chemical parameters [11]. To reduce the duration of the dough preparation process, there are many different solutions based on biochemical methods of intensifying the maturation of the dough by stimulating the fermentation process and its combination with physical methods of influence to the dough [5]. One such method is the use of intensive mechanical processing of the dough with high-performance working elements [1-3]. The use of new working elements in continuous-action paste machines contributes to a reduction in the length of the dough preparation process [4].

Scientists note the significant influence of the rotational speed of the turning the working elements and their configuration on the intensity of kneading and the quality of finished products in general [12]. Scientific publications indicate that during the kneading of the yeast dough, there is a critical value of the speed of the kneading element and the level of energy expended [8].

One of the effective methods of accelerating the process of kneading the dough and improving the quality of bakery products is the increased mechanical processing of the dough during kneading, which allows to influence its structural-mechanical and physico-chemical parameters [11].

Different influence on the structural and mechanical properties can be achieved by configuring the structural parameters of the working elements in a dough kneading machine of continuous action [5].

The efficiency of kneading is evaluated by a number of indicators, among which the specific work, intensity, productivity, homogeneity of the yeast dough and porosity of the finished product, with the control and observance of rational parameters of the above-mentioned indicators, the highest quality bread products are produced [14].

Thanks to many numerical studies provided by Nikolayev M., Auerman L., Goryachova A., Shcherbatenka V., B. Pareyt , K. Brijs, A. Jan it was established that an increase of the mechanical influence on the dough during the kneading affects its rheological properties [1] . The mechanical influence of the nixing element on the dough formed during the kneading, in the first period promotes swelling of proteins and the formation of a spongy gluten framework, which improves the physical properties of the dough [7].

Surveying of screw, pin and cam working elements, which are the most widespread and effective during kneading of dough in dough kneading machines of continuous action.

Materials and methods

Based on the theoretical search and analysis of existing machines, we have developed a new experimental model. The main research was carried out on a two-camer experimental installation (Figure 1) using a different configuration of working elements: cam, screw and finger work elements.

The object of the study is the process of kneading the yeast dough. The dough is considered as a complex colloidal system, consisting of several continuous and periodic phases. Solids and liquids (gluten and water) in the dough are continuous phases, starch grains and gas formed during the dough fermentation – the periodic phase. As a result, the

physical properties of the dough are characterized by parameters of solids, liquids and gases, and indicators resulting from the interaction of these phases.

During the kneading the dough, the energy required for the kneading, humidity, time, temperature and dough structure was determined. In the finished product, porosity was determined and the structure of the product examined.

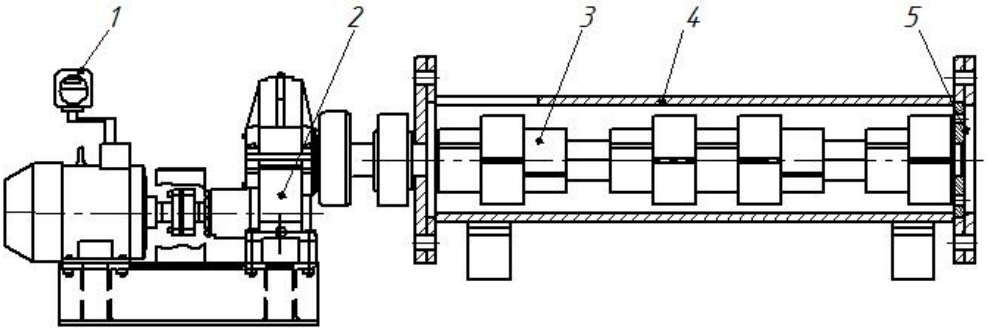

Figure 1. The scheme of an experimental installation with cam operating elements: 1 – a device for measuring electric power; 2 – drive; 3 – working element; 4 – frame; 5 – stabilizing grate.

The power consumed for kneading was determined separately for the working bodies (screw, pin, cam) with a device for measuring the electric power (wattmeter) connected to the motor of the dough kneading machine according to the corresponding scheme.

Specific work A_{sw} J/G was calculated by the formula:

$$A_{sw} = \frac{\left(N_{general} - N_{\text{no-load}}\right) \cdot \tau}{Q} \qquad (1)$$

where $N_{general}$ – the power consumed by the motor in working condition, W;

$N_{no\text{-}load}$ – the power of the idling of the corresponding working element, W;

τ – the time of kneading the dough (the time taken to pass the dough through the working chamber in continuous mode);

The research of rheological and structural-mechanical properties of the dough was carried out using professional equipment, by the method of a rotary viscometry [18,19], and a trinocular bio microscope for the scientific research of Konus Biorex-3 [20].

The structural and mechanical properties of food masses and regularities, as well as the curve of the dough mass flow, was investigated using a viscometer. A sample of the dough was placed in the Reotest viscometer on the measuring cone, a tapered-plate device, installed on the viscometer and secured with a tension ring.

The value of the torque was obtained from the measure during the 12 share rates for different duration of kneading.

The shear stress corresponding to the hydraulic resistance of the wedge-shaped gap depends on the torque M, which is converted into an electrical signal. The shear stress τ and

the shear rate γ in the wedge-shaped gap are constant. These values were calculated using the formulas given below.

Shear stress:

$$\tau = \frac{3M}{2\pi R^3}, \text{ Pa} \quad (2)$$

where M – torque, N·m;

R – is the radius of the cone, m.

Shear rate:

$$\gamma = \frac{\omega}{tg\varphi}, \text{ s}^{-1} \quad (3)$$

where ω – the angular velocity of the cone rotation, rad;

φ – the angle of the slope of the system of the cone-plate system.

Effective viscosity:

$$\eta = \frac{\tau}{\gamma}, \text{ Pa·s} \quad (4)$$

To measure the values of rheological parameters on a rotary viscometer, the following correlations are valid:

Shear stress:

$$\tau = c \cdot a, \text{ Pa} \quad (5)$$

where c – the constant value of the cone, 10^{-1} Pa/gradiatuion of the scale;

α – the value of indicators on the indicator device /gradiatuion of the scale/.

Different types of machines are used to mix the yeast dough, which, depending on the prescription composition and assortment, have different effects on the dough and its maturation. The quality of the dough kneading machines is determined by the quality of the finished product, among which the main indicator is the porosity of the finished product.

To analyze the porosity of the finished products, the tow was cut, photographed and, using the program ImageJ, found the porosity of the finished product and calculated the number of pores. ImageJ is an image processing program where you can calculate the area and level of detail of an image, statistics of user-defined selections, measure distances and angles, create density histograms and profile sections of the plot.

The solving the problem of intensifying the process of kneading under continuous tasting can be solved by applying cam, screw and pin working elements [17].

The cam (Figure 3), screw (Figure 4), pin working element (Figure 5) and their influence during the kneading on the quality of the semi-finished product and the finished product were studied. The step of the working element, was being changed and the plane of the living section was being adjusted at the outlet of the yeast dough after kneading.

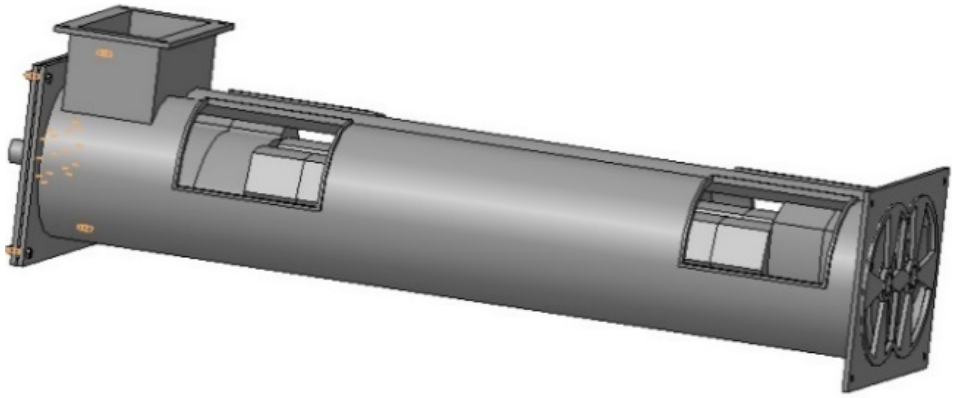

Figure 2. 3D Model of experimental installation with cam working elements inside

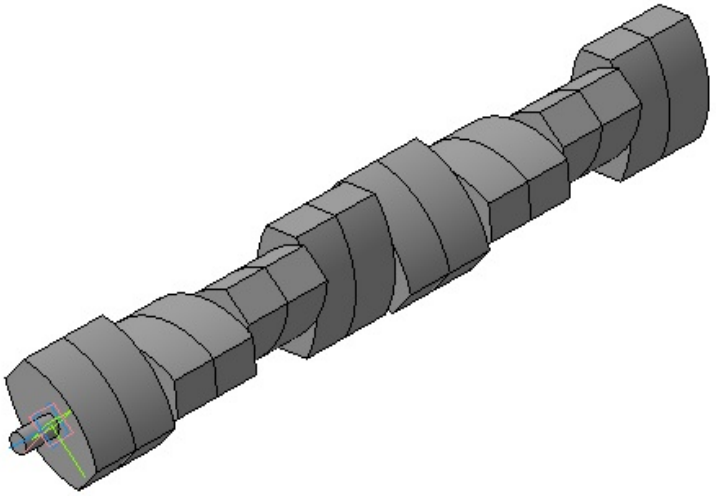

Figure 3. Cam working element

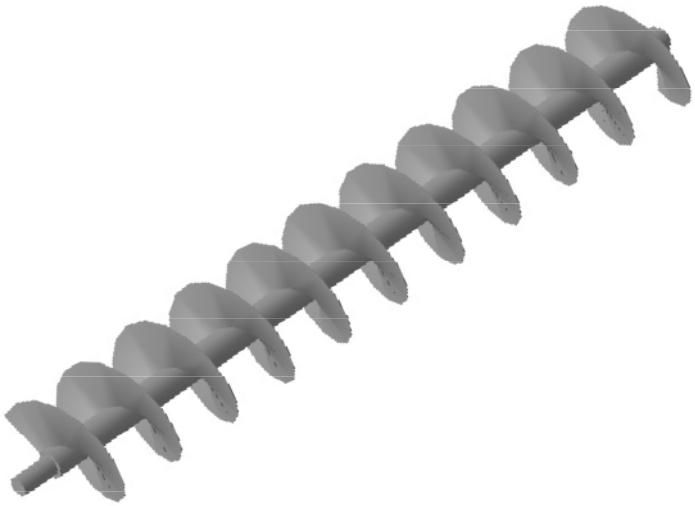

Figure 4. Screw working element

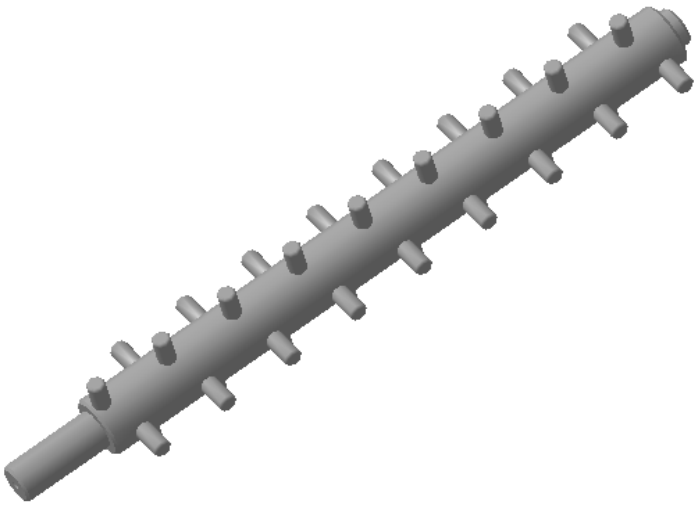

Figure 5. Pin working element

The choice of the construction of technological equipment and optimal modes of processing food products depends on the structural and mechanical properties of raw materials, which are determined by the chemical and biochemical composition and the internal structure of the material.

During the kneading the formation of the dough occurs as a result of a number of processes, of which the most important are: physical-mechanical, colloidal and biochemical processes. All these processes take place at the same time, mutually affect each other and depend on the duration of kneading, the temperature and the quantity and quality of the raw material used during kneading the dough.

Physical-mechanical processes take place during a kneading under the influence of a kneading element which mixes particles of flour, water, yeast suspension and solutions of raw materials, providing the interaction of all the constituents of the components of the formulation.

The dipped the dough should ensure the equable kneading of all components, obtaining a dough with homogeneous properties and creating optimal conditions for further stages of the technological process: fermentation, separation, stamping and baking.

Result and discussion

The coloration between the force acting on the dough and the strain caused by its action is investigated.

The yeast dough is a micro heterogeneous disperse system. In the process of processing, raw materials and semi-finished products are stretched, compressed, that is, they are in a complex stressed state. The kneading of the yeast dough is due to the flow of the material, which is described by the relevant laws.

To describe the process of kneading the dough, it is necessary to know the properties of the viscosity and consistency of the dough. Consistency, as a complex term, characterizes the mechanical properties in the material volume – shear rate, shear stress, viscosity, and also the properties of adhesion and adhesiveness.

Structural-mechanical properties characterize the ability of the material to hold and change the shape (deformed) under the influence of external forces.

Depending on its condition and the conditions of loading, various orthogonal properties are manifested in varying degrees.

The obtained results allow us to construct a curve of the dough flow during kneading the yeast dough with different constructive, working elements (Figure 6). The researches have established, within the studied range, the test weight does not change the nature of the flow regardless of the time interval of measurements.

The homogeneous structure of the dough at the stage of plasticization is a stable system and the change in the rate of displacement immediately leads the system to a new structural state. The processes of destruction and restoration of the structure are in the studied range of shear rate in an equally weighted state. The curve of the current with sufficient probability is of a power degree.

The non-Newtonian bodies are characterized by effective viscosity, namely, the coloration of the strain of shear to the shear rate. Scientists argued that effective viscosity acts as a structural and mechanical barrier in the formation and destruction of a foamy porous structure [14]. In the case of insufficient high viscosity, the formation of the gas phase and the gas pores in the volume of the dough occurs during its kneading, and fermentation with low energy consumption.

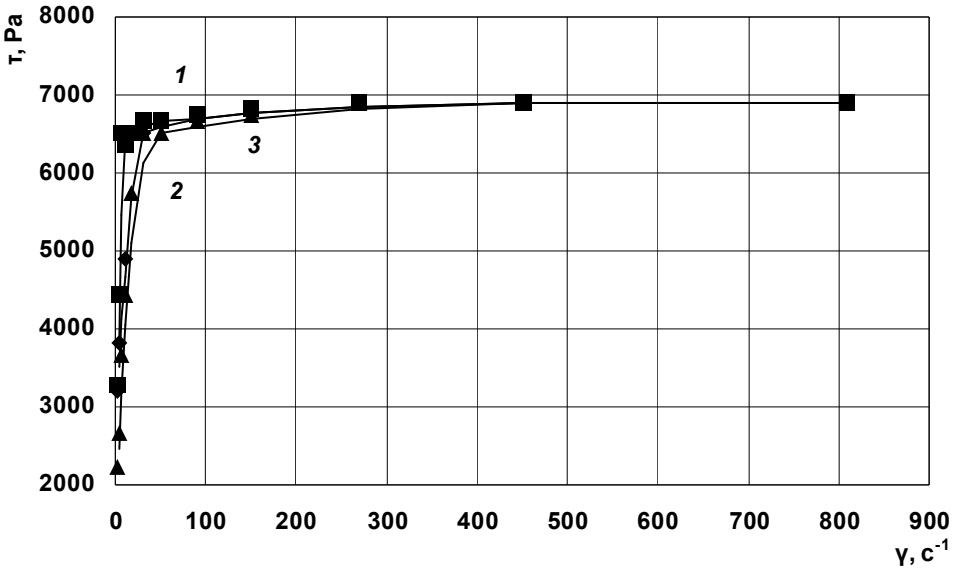

Figure 6. Experimental curve of dough flow during kneading of yeast dough with working elements of various configurations (1-cam element, 2-screw element, 3-pin element)

The obtained experimental data allow us to obtain a change in the effective viscosity of the dough during kneading and its dependence on the shear rate, which confirms the non-Newtonian character of the curve of the dough flow during the kneading of the dough with the working elements of different configurations (Figure 7).

With an increase in the shear rate, the effective viscosity values are significantly reduced. At low viscosity, porous walls are easily destroyed by excessive pressure of gaseous products. The kneading of the yeast dough should be carried out at high viscosity, in this case no fine-grained structure will be observed and the volume of bread is increased.

After 1-2 minutes after kneading, the kneading of the raw material is transferred to the condition of the bound mass. During the subsequent kneading as a result of processes of swelling and action of hydrolytic enzymes, the test substance acquires a certain elasticity. After 4-5 minutes of kneading of the yeast dough as a result of deepening processes of enzymatic and mechanical disaggregation of proteins, which prevail during this period of the processes of swelling, there is a gradual dilution of the consistency of the dough.

The magnitude of the specific work is indicative and does not have a strictly separated number, since it can vary on the same machine depending on the length of the dough and the structural parameters of the working elements.

Determination of the energy is necessary for calculating the dough kneading machine and energy analysis of individual stages of dipping, improving the mechanism of the process and justifying the rational parameters of the individual stages of dipping. In most modern dough kneading machines, the batch is made as a result of the rotational movement of one or more shaft blades.

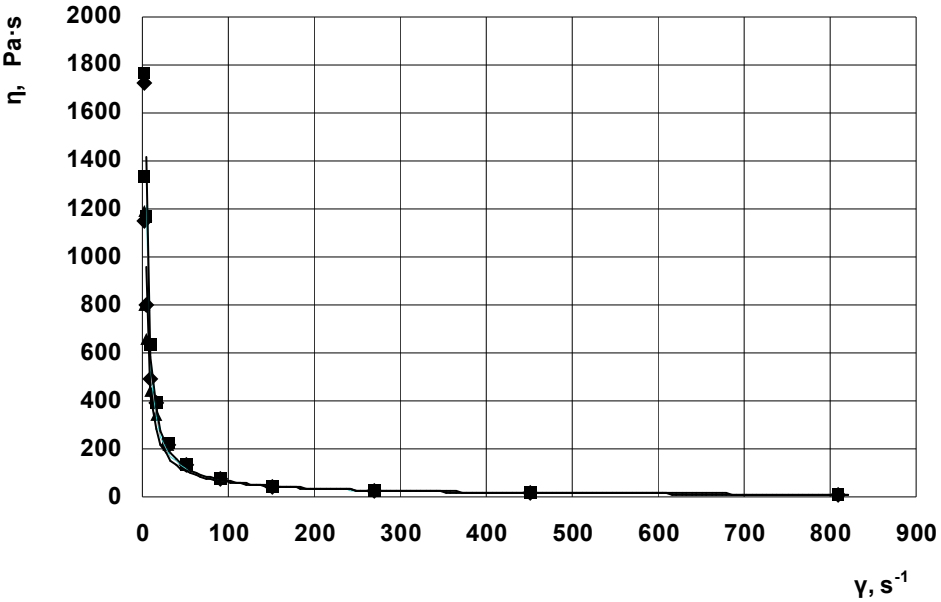

Figure 7. Dependence of the effective viscosity of the dough on the shear rate during kneading the yeast dough with the working elements of different configurations

The obtained experimental data was processed according to the above-mentioned method, calculated according to the formula and reduced to the histogram (Figure 8) depending on the specific work using the working elements of different configurations and the living section of the stabilizing lattice, through which the dense yeast dough is released.

The research was carried out at a living section of the stabilizing grating: 2,5-5,1-7,6% of the total grating area, this is the percentage of the hole through which the bound yeast dough is obtained, to the total grating area.

High indicators of specific work costs are observed during the kneading the yeast dough with the working elements of various configurations for the stabilizing lattice parameter of 2.5%; the performance of the specific work reaches 22-37 J/g. The highest values (37 J/g) are achieved during the kneading the cam operating elements, for such parameters the dough-machine of continuous action can be attributed to super-fast dough machines, intensive action. With the increase in the real section of the stabilizing grate, the costs of the specific work are reduced, this is due to a decrease in the time of kneading and rapid passage of the dough through the stirring chamber. During the using pin work elements there are indicators of specific work in the range of 2 to 7 J/g for such parameters, the dough machine is classified as low-speed, with the exception of kneading with the finger working elements for the value of the live section of the lattice 2,5%, for such parameters the specific work reaches the mark in 22 J/g in this case, the car is classified as high-speed. For use in the dough machine screw working elements, it can be attributed to high-speed, as the performance of the specific work in this case reaches 18-25 J/g.

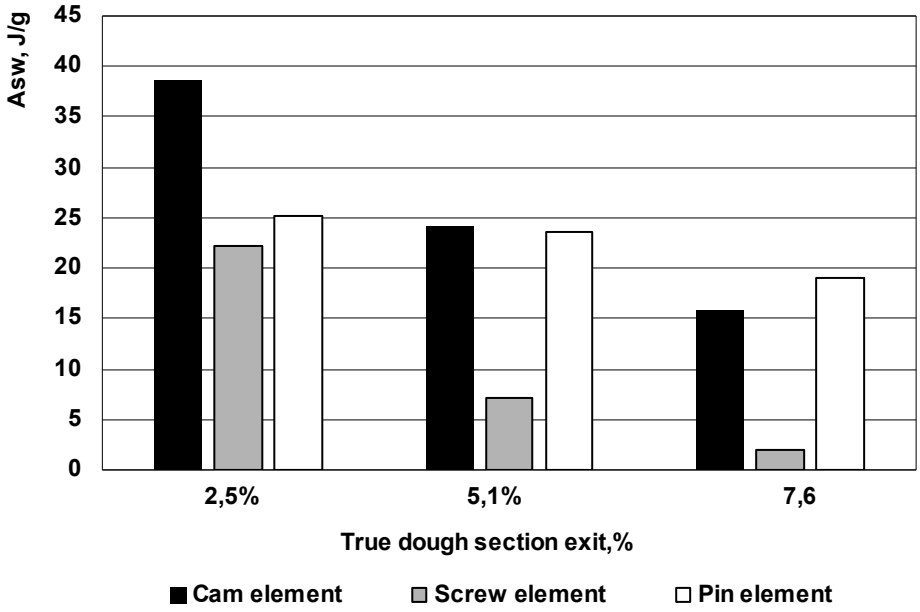

Figure 8. Dependence of specific work on the use of working elements of various configurations and the real section of the stabilizing grate

Thus, the cost of specific work depends on a number of factors that affect the process of kneading the yeast dough, to achieve the necessary values of the cost of specific work, can be achieved by adjusting the variables in the dough machine, such as the working element, the cross section of the stabilizing lattice, the speed of rotation of the working element. The higher the cost of specific work, the better and high-quality the yeast dough after kneading. Strengthened mechanical treatment of the dough while baking causes intensification of maturation of the dough after meal, that is, reducing the duration of maturation of the dough and improving its quality.

The intensity of kneading the dough depends on the design of the dough machine, the rotational speed of the kneading element and its configuration.

The intensity of the kneading (Figure 9) is characterized by the amount of work expended per unit of working time, that is, the average useful power of the drive P, which falls on a batch of 1 g of the test and is determined by the formula:

$$U = A_{sw} / \tau \quad (6)$$

where A_{sw} – specific work, J/G;

τ – the duration of dipping, s.

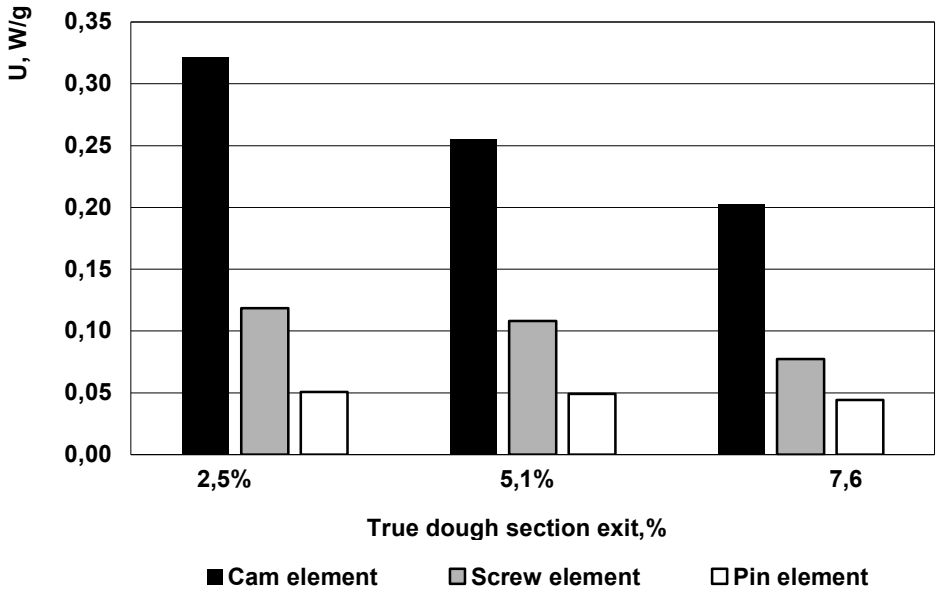

Figure 9. Intensity of the process of kneading using the working elements of different configurations and the living section of the stabilizing grate

During the search the screw working element showed the best intensity of the process of kneading the yeast dough on a continuous machine of continuous action and analyzing the obtained data, it can be argued that the most intensive batch (0,2-0,33 W/g) for the use of cam work elements and in a short time, the semi-finished product is transported quickly. In the case of performance machining by cam operating elements, more energy is consumed, as a result, the quality of the yeast dough improves, due to the fact that the macromolecules of gluten under the influence of stresses occurring in the dough are partially destroyed, but due to the internal restructuring of the structure, the gluten is again restored acquires elasticity and elasticity. In the process of kneading the dough with the cam working elements, there is an accelerated swelling of the proteins and the formation of a gluten-free frame, resulting in the dough gaining elasticity, and its physical properties are improved. Screw working elements are very intense, intensity indicators range from 0.07 to 0.12 W/g. Not intense are considered as pin working elements, the intensity indicator in them at any plane of the living section reaches marks less than 0.05 W/g.

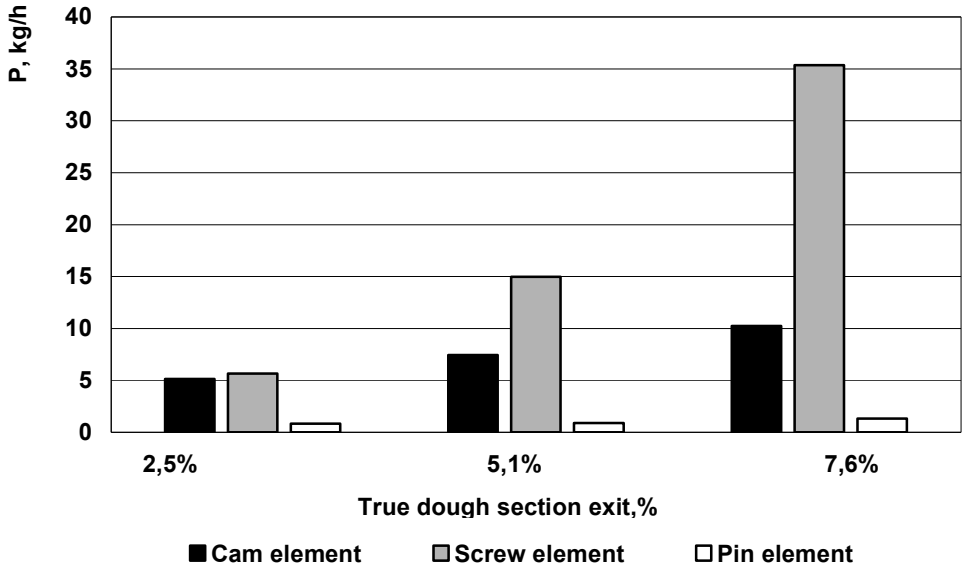

Figure 10. Performance of a dough machine of continuous action for different working constructive elements

During the search, the cam working element was the most productive, indicators at the area of the test section yield 7.6%, reaching the mark of 35.7 kg/h, this pattern is explained by the fact that the structural screw elements have good transporting ability and in a short time transported semi-finished products. The cam elements have a transport capability in the range of 5 to 11 kg/h, due to the fact that most of the work is spent on the batch, rather than on transportation. Pin working elements do not have transporting properties and can only be used in a combined working element, where in the beginning there will be several turns of the screw.

The porosity of the finished product is the volume of pores, expressed as a percentage of the total volume of crumb of bread. Bread with uniform fine porosity, well loosened is better impregnated with digestive juices and therefore is better absorbed.

An important indicator of the quality of the finished product is porosity. The porosity of the bread products is aimed at a large number of pores, even in size and in the nature of the distribution of the product. During wearing out the formation of porosity of products, a significant increase in the amount of gas in the pores of the preform determines the growth of volume during baking. Optimum conditions of production provide a larger volume of products, a soft, well-developed porosity.

The configuration of the working element directly affects the kneading of the yeast dough, and as a result the quality of the finished product: the surface condition and the structure of porosity from the gas-filled dough.

The structure of the bread product was investigated, a detailed analysis of the breadcrumbs of bread was carried out, and after the mathematical processing of the obtained data, porosity was determined (Figure 11) after kneading the yeast dough, working elements of different configurations.

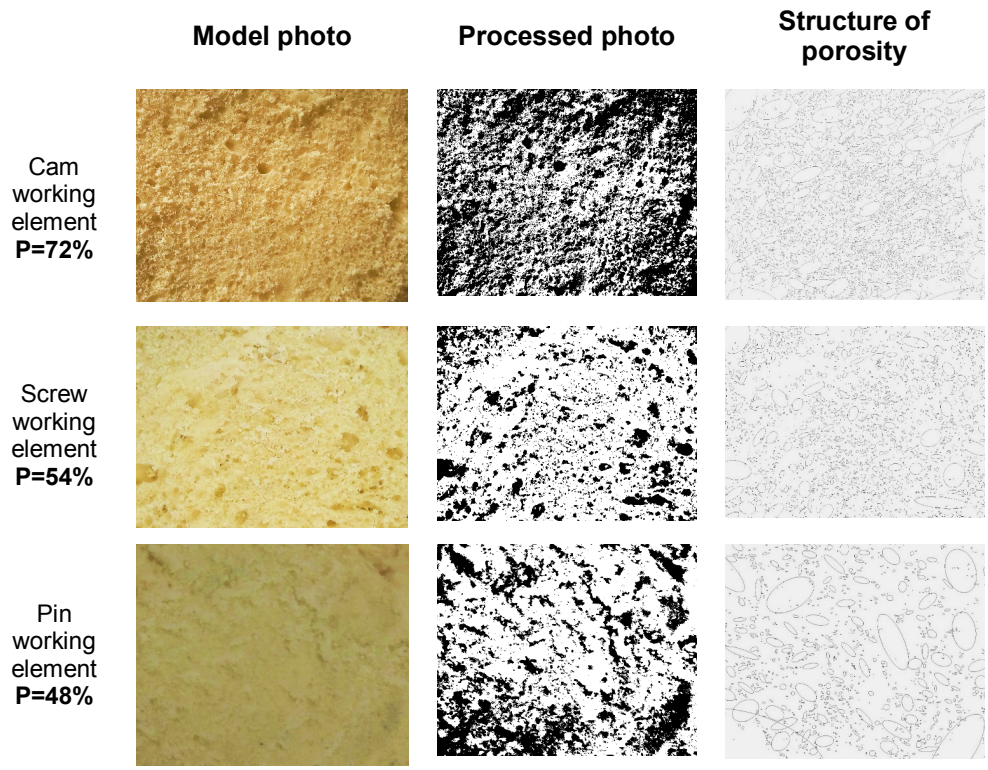

Figure 11. Porosity of the bread product after kneading the yeast dough with various structural elements

The fine grained structure of the porosity of the wheat bread product from wheat yeast dough is observed during the kneading by cam working elements, the percentage of porosity in this case is 72% and is a high indicator for this type of product. After kneading with the screw working element, the porosity is observed in the range of 54%, the index is much lower than in the case of a cam working element, the difference is due to the lower cost of the specific work required for the dough kneading. During the kneading by a screw working element, the number of pores decreases and the existing pores increase in volume. The structure of the bread product mixed by the pin work element is unbalanced and has a low porosity of 48%, the thickness of the pore wall is formed during plasticization, and when porosity develops, only the merging and rearrangement of gas in larger pores occurs with the previous wall thickness, so as the design parameters of the pin working elements do not provide qualitative plasticization, then there is a low porosity of the finished product.

Conclusion

The conducted studies confirm the positive effect of enhanced mechanical processing of the dough during the kneading process. Due to the use of continuous action elements, the process of kneading the yeast dough is intensified, which makes it possible to shorten the dough fermentation period before processing.

The conducted comparative analysis confirms the expediency of using cam-working elements. Screw working elements, have good transporting properties and are highly productive during the use. The use of pin working elements is appropriate in combination with screw working elements at the beginning of the screw, such working element will allow to mix in the beginning and subsequently transport the semi-finished product, then the actual masonry and plasticization will be carried out at the expense of the pin working elements.

In case of application of the cam working elements, an intensive kneading the yeast dough takes place and high porosity indicators of the finished product are observed.

Studies have confirmed that at the same time and intensity and duration of dipping affect the value of the share of specific work. Intensity, in turn, depends on the frequency of rotation of the worm shaft and the mechanism of its impact on the dough, that is, the construction of the dough machine. Thus, at the same intensity, a variety of specific work can be obtained by varying the duration of dipping and achieving the required parameters of the structural and mechanical properties of the dough and the high porosity of the finished product.

References

1. Pareyt B., Brijs K., Jan A. Delcour (2013), Impact of kneading time and sodium stearoyl lactylate on gluten polymerization during baking of wheat flour dough, *Food Chemistry*, 141, pp. 4179–4185.
2. Hailemariam L., Okos M., Campanella O. (2007), A mathematical model for the isothermal growth of bubbles in wheat dough, *Journal of Food Engineering*, (82), pp. 466–477.
3. A.Shehzad, Chiron H., Della Valle G., Lamrini B., Lourdin D. (2012), Energetical and rheological approaches of wheat flour dough kneading with a spiral mixer, *Journal of Food Engineering*, 110, pp. 60–70.
4. Zeppelin Reimelt GmbH (2013), A suitable solution for every kneading task, *Mixing Technology*, Available at: http://www.zeppelin-systems.com/en/products-solutions/mixers.html.
5. Connelly R.K., Kokini J.L. (2007), Examination of the kneading ability of single and twin screw mixers using 2D finite element method simulation with particle tracking, *Journal of Food Engineering*, 79, pp. 956–969.
6. Iedema P.D., Remerie K., M. van der Hamb (2011), Controlled peroxide-induced degradation of polypropylene in a twin-screw extruder: Change of molecular weight distribution under conditions controlled by microkneading, *Chemical Engineering Science*, 66, pp. 5474–5486.
7. Mani K., Eliasson A. C., Lindahl L., Tragardh C. (1992), Rheological properties and bread making quality of wheat flour doughs made with different dough mixers, *Cereal Chem.,* 69(2), pp. 222–225.

8. Mitchell T.A. (1984), Dough mixer controls for the mechanical dough development process, *Proceedings of the International Symposium on Advances in Baking Science and Technology*, Kansas State University, Manhattan.
9. Wooding A.R., Martin R.J., Wilson A.J., MacRitchie F. (1994), Effect of sulphur-nitrogen treat-ments on work input requirements for dough kneading on second season, *Proc. 44th RACI Cereal Chemistry Conference*.
10. Uchida K., Okamoto K. (2008), Measurement technique on the diffusion coefficient of powder flow in a screw feeder by X-ray visualization, *Powder Technology*, 187, pp. 138–145
11. Chin N., Campbell G. (2005), Dough aeration and rheology: Part 1. Effects of kneading speed and headspace pressure on mechanical development of bread dough, *Journal of the Science of Food and Agriculture*, 85, pp. 2184–2193.
12. Shehzad A., Chiron H., Della Valle G., Lamrini B. (2012), Energetical and rheological approaches of wheat flour dough kneading with a spiral mixer, *Journal of Food Engineering*, 110, pp. 60–70.
13. Haraszia R., Larroqueb O.R., Butowb B.J. (2008), Differential kneading action effects on functional properties and polymeric protein size distribution of wheat dough, *Journal of Cereal Science*, 47, pp. 41–51
14. Jekle M., Becker T. (2011), Dough microstructure: Novel analysis by quantification using confocal laser scanning microscopy, *Food Research International*, 44, pp. 984–991.
15. Kudinova O., Kravchenko O., Lytovchenko I. (2014), Modelling of process in twin-screw dough-kneading machines, *Journal of Food and Packaging Science, Technique and Technologies*, 5, pp. 64–68.
16. Telychkun Yu., Telychkun V, Kravchenko O. (2013), Perspective direction of complex improvement of rusk wares, *Journal of Food and Packaging Science, Technique and Technologies*, 2. pp. 67–70.
17. Klemens Kohlgruber (2008), Co-Rotating Twin-Screw Extruders, *Bayer Technology Services*, 347, pp. 152–158.
18. Dobraszczyk B. (2016), *Analysis of Dough Rheology in Breadmaking. Encyclopedia of Food Grains*, Elsevier, pp. 343–353
19. M. Morgensternb O. Campanellacfl N. Larsenb (2000), Rheological Properties of Dough During Mechanical Dough Development, *Journal of Cereal Science*, pp. 293–306
20. P. Kruit, R. G. Hobbs, C-S. Kim (2016), Designs for a quantum electron microscope, *Ultramicroscopy*, 164, pp. 31–45

Determination of rational modes of pumpkin seeds drying

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Keywords:

Pumpkin
Seed
Drying
Germination

Article history:

Received
11.12.2017
Received in
revised form
14.02.2018
Accepted
29.03.2018

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DOI:
10.24263/2304-974X-2018-7-1-12

Abstract

Introduction. Pumpkin seeds are an easily accessible source of protein and other useful substances. A purpose is to determine a rational mode of its drying, which ensures high germinability of the seeds.

Materials and methods. The physical and mechanical properties of pumpkin seeds «Stofuntovyi» of Ukrainian selection with a humidity of 0, 6, 16, 46 % have been investigated. The drying process kinetics have been investigated on a test bench of convective drying at the following conditions: the drying agent temperature in the drying chamber t = 40–80˚C, velocity V = 1,5 m/s, the moisture content of dry air d = 10 g/kg d.a. The biochemical properties of dried pumpkin seeds were determined by the amount of seeds capable of forming normally developed sprouts under optimal conditions on the 5^{th}, $7^{th}$and 10^{th} days of germination.

Results and discussion. The studies of the properties of pumpkin seeds variety have revealed that when the initial moisture content in the material changes from 0 to 46%, there is an increase in the seeds' geometric sizes: the length increases by 38%, width – by 10% and thickness – by 8%. Other parameters change too.

Investigation of the pumpkin seeds drying process has shown that when the temperature of the drying agent increases, the drying intensity increases also. In particular, the drying time reduces 8 times when the drying agent temperature is raised from 40 to 80 °C.

The drying rate curves corresponding to the falling drying rate period with preheating indicate that the highest drying rate at the maximum critical point at a drying agent temperature of 80 °C is 2.32% / min, and the lowest at 40 °C is 0.33 %/min.

The heating of the pumpkin seeds takes 3 to 5 minutes depending on the mode, then the temperature of the material does not change significantly and deviates from the temperature of the drying agent by 0.1–0.5 ºC.

The generalized curve of kinetics of pumpkin seeds drying makes it possible to describe the general process at different drying modes.

Conclusions. The drying agent temperature substantially affects the pumpkin seeds germinability. The most rational mode of drying is at a temperature of 40 °C and an air speed of 1.5 m/s.

Introduction

The consumer properties of pumpkin seeds are widely known in the world market. It is an easily accessible source of protein and other useful substances. A demand for seeds grows under the influence of the trend on healthy eating, the propagation of vegetarianism and the dietetics development.

For the pumpkin seeds processing and storage, it is important to know its geometric parameters and physical and mechanical properties, in particular: length, width, height, weight of 1000 seeds, density and bulk density, which affect the equipment productivity and product losses (Joshi, D.C., and Mukherejee R.K., 1993) [1].

Many researchers studied the technical properties of different crops: melon (Davies R.M, 2010) [2], watermelon (Koocheki, A. et al., 2007) [3], soybeans (Manuwa, S.I and G.G Afuye, 2004) [4], cocoa beans (Bart-plange and Baryeh, 2003) [5], wheat (Tabatabaeefa, 2003) [6].

Usually, the drying of capillary-porous materials is carried out in two or three stages. Drying of pumpkin seeds takes place at the period of the falling drying rate, and, at the end of the period, the drying rate is significantly reduced.

Several scientists had researched the drying process of pumpkin seeds. So in Sacilik, K. (2007) [7], the pumpkin seeds drying by sunlight at an ambient temperature of 10 to 50 ºC is considered. The drying time was 24 hours and the drying occurred during the incident drying rate.

The change in the distribution of equilibrium humidity in pumpkin seeds during drying by sunlight is shown for drying time of 0.5, 1, 2, 5, 10, 15, 20, 25, 30, 34 hours (E.Akyol *et al*., 2015) [8].

Guiné et al. (2011) [9] dried the pumpkin seeds in a drying chamber and showed that the drying air temperature significantly affects the drying time: at an air temperature of 30 °C, drying lasts for 8 hours, with an increase in temperature to 70 °C it takes only 2 hours. Hashim et al. (2014) [10] carried out an experimental study of the drying of pumpkin seeds using a convection dryer with hot air (drying of samples of pumpkin seeds had taken place at a temperature of 50 °C, 60 °C and 70 °C).

The problems of determining the rational modes of drying of pumpkin seeds and their effect on germinability in these works were not considered. Therefore the purpose of this work is to determine the most appropriate drying regimes to ensure a high germinability of the material.

Analyzing the duration of the drying process of seeds, the researchers proceeded from the fact that the layer can be represented as the sum of thin layers. The dependence of moisture evaporation of which approximates the equation of the drying rate of the elementary layer [11, 12, 13].

One of these methods, developed by Hukil [11] and improved by Kofaid [12], makes it possible to determine the change in seeds moisture from drying time at any given time.

The basis of another method for calculating the drying time in a layer of seeds is the equation of the drying rate of the elementary layer [13]. This method is called "stepped". In the mass of the seeds, a thin (elementary) layer may be chosen, so that the air flow, related to the mass of the material, was high enough. Then any mass of seeds can be considered as the sum of elementary layers, passing through which, the air has been saturated of evaporated moisture. The degree of saturation depends on the parameters of the drying agent and the number of passed elementary layers.

Materials and methods

The biochemical properties of pumpkin seeds «Stofuntovyi» of Ukrainian selection, which were dried on a test bench of convective drying, were determined by a method that allows determining the amount of seeds capable of forming normally developed sprouts under optimal germinability conditions.

Method for determining biochemical characteristics of pumpkin seeds

The biochemical properties of seeds include: viability, germinability, germination energy.

The viability is a measure of the percentage of seeds with an alive embryo in the total amount of seeds. The viability test makes it possible to exclude processing of low-quality seeds in a timely manner.

Germinability is the ability of seeds to form normally developed sprouts under optimal conditions. It is determined by the percentage of germinated seeds in the total amount of seeds. Small pumpkin seeds are germinated on moistened filter paper. The quantity of germinating seeds is less than the quantity of viable seeds.

The germination energy characterizes how unanimously the seeds germinate on 5^{th} and 7^{th} days.

Preparation and analysis of pumpkin seeds germinability

1. Thermostats once in 10 days, and the dishes before each test were washed with hot water with detergents and were disinfected with 1% solution of potassium permanganate or alcohol. A pallet with water was placed in the working chamber of the thermostat. Petri dishes were sterilized in a drying chamber at a temperature of (130 + 2) ºC for an hour.
2. The germinability of pumpkin seeds was analyzed. For that purpose, 100 seeds were counted at random by 10 pcs. The seeds were evenly distributed on moistened filter paper. The test was carried out on a single layer of moistened paper placed in Petri dishes covered with glass plates.
3. The germinability of pumpkin seeds under different drying conditions was analyzed at a temperature of 20 °C for 7 days. The germination energy, seed germination and abnormal sprouts (damaged, weak, rotten, undeveloped and dead) were determined on 5^{th}, 7^{th} and 10^{th}days, respectively.

Method of conducting an experiment when drying pumpkin seeds on a test bench of convective drying

The movement speed of the drying agent has been chosen based on the drying efficiency in existing modern dryers (V = 1.5 m/s).

1. Before starting the tests, the initial humidity of pumpkin seeds was determined.

When determining the dry matter or moisture in seeds, a band-and-hook hinge weighing 3–5 g with an uncertainty of not more than 0,01 g was taken from the investigated selected material put in a dry weighing bottle and installed with an open lid in a drying oven at a temperature of 100–105 °C for 3 hours.

After 3 hours of drying, the weighing bottles with seeds were removed from the drying oven and were placed in a desiccator for cooling for 15-30 minutes. It is assumed that a constant mass is achieved if the difference between two successive weighings does not exceed 0.004 g. The cooled weighing bottles with pumpkin seeds were weighed with a closed lid on analytical scales. To calculate the weight of bottle with a band-and-hook hinge has become a rule

The initial moisture content of the pumpkin seeds relative to the dry mass of the substance was determined by the formula:

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

where m_1 – the mass of an empty weighing bottle (with a lid), g;

m_2 – the mass of the weighing bottle with a band-and-hook hinge of the seeds before drying, g;

m_3 – the mass of the weighing bottle with a band-and-hook hinge of the seeds after drying, g.

As a result of tests, the arithmetic mean of two parallel determinations was taken. Calculations were made with an uncertainty no more than 0.001%. Differences between two parallel definitions did not exceed 0.25%.

To determine the current, variable moisture content of the sample, an absolutely dry mass of seeds was determined:

$$G_{a.c.} = G_к - \frac{G_к \cdot W_к}{100}, \quad (2)$$

where $G_{a.c.}$– absolutely dry mass of seeds, g;

G_k– mass of seed sample after drying on the test bench, g;

W_k– residual moisture content of pumpkin seeds,%.

2. A convection drying test bench for pumpkin seeds drying works together with automated system for collecting and processing information.

After setting a drying mode on a drying test bench [15] a mesh saucer by dimension 100×50×4 mm with seeds was installed on the scales bar in the drying chamber 1 (Figure 1) and a thermocouples were inserted in the middle of the sample to measure the material temperature.

At the same time, a computer program for collecting and processing information was turned on.

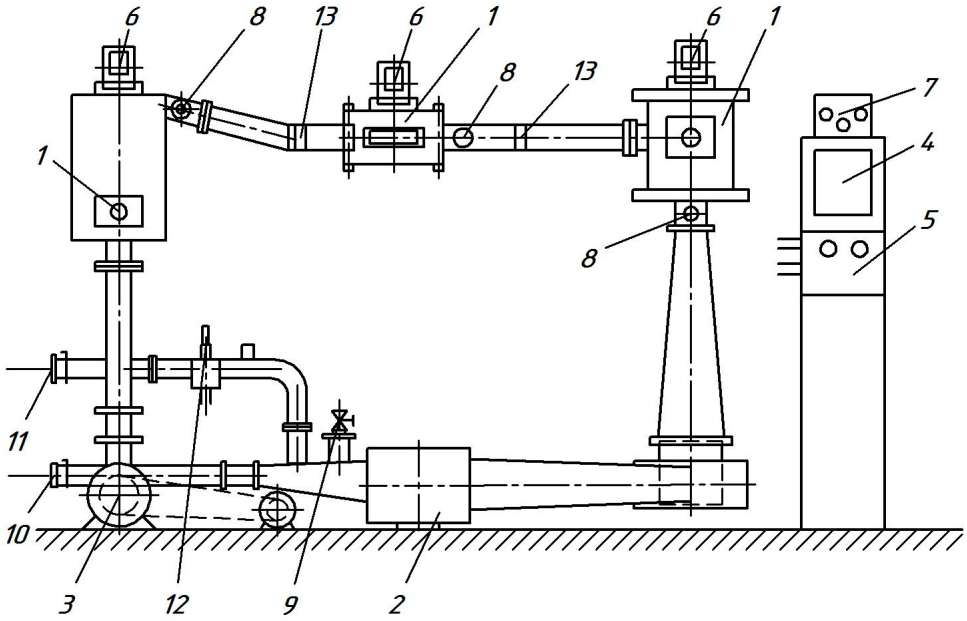


Figure 1. Scheme of the experimental stand of convective drying:
1 – drying chamber; 2 – heater; 3 – fan; 4 – potentiometer; 5 – instrument assembly;
6, 7 – automatic regulating system of temperature; 8 – electric resistance pyrometers;
9, 10, 11 – branch pipes with slide gates; 12 – psychrometer, 13 – express lattices

The automated program provides automatic collection and processing of information that characterizes the process, as well as conducts calculations for plotting the process kinetics. This made it possible to obtain and compare the kinetic and velocity characteristics of pumpkin seeds drying more accurately, promptly and reliably.

3. To determine the biochemical properties of pumpkin seeds, a drying was occurred to an equilibrium moisture content (12%).

4. The dried seeds were divided into two parts:

4.1. The first part was used to determine the biochemical properties of the material.

4.2. The second part was used to determine the residual moisture content of the material (paragraph 1).

5. After determining the absolutely dry mass of the sample, the computer program determined the current moisture content of the material W during drying, carried out calculations and constructed the curves of the drying process kinetics: $W = f(\tau)$, $dW/d\tau = f(W)$.

Results and discussion

Drying of seeds plays an important role in the process of preserving its native properties and is characterized by physical and mechanical properties of the material.

The physical and mechanical properties of pumpkin seeds variety, depending on the change in the moisture content of the material (from 0 to 46%), obtained during the studies, are given in Table 1.

Table 1

The physico-mechanical properties of pumpkin seeds

Characteristic	Value		
Humidity, %	**0**	**16**	**46**
Length, mm	17,4–20,0	20,5–21,0	20–21,5
Width, mm	10–11,0	10,5–11,2	11,7–12,2
Height, mm	2,1–2,2	2,2–2,3	2,6–2,9
Mass of 1000 seeds, g	168–172	210–215	310–316
Density, g/cm^3	0,32 –0,35	0,36–0,40	0,48–0,5
Bulk weight, kg/m^3	265–277	280–300	378–390

So for the seeds there is an increase in the geometric dimensions of the seed: length by 38%, width by 10% and thickness by 8% (Figure 2).

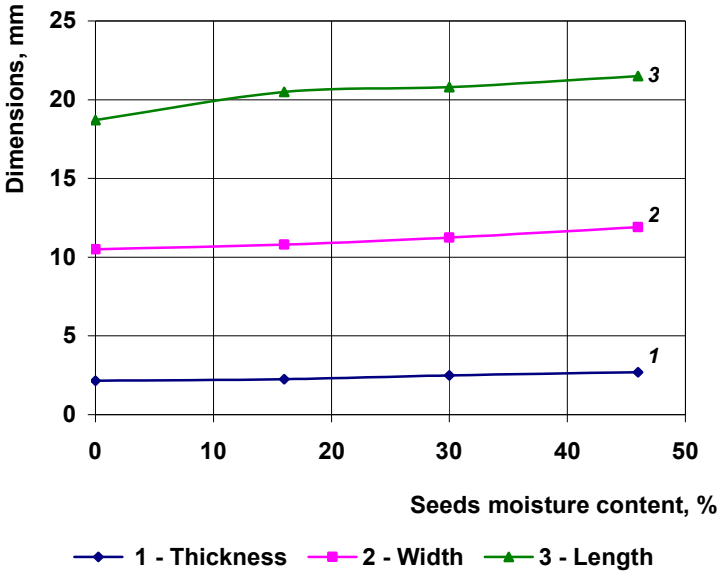


Figure 2. Change of the geometric dimensions of pumpkin seeds depending on the moisture content of the material

Dehydration of plant materials, in particular pumpkin seeds, is one of the most important technological stages, which significantly affects the quality of finished products.

In this paper, the results of a study of pumpkin seeds drying on a test bench of convection drying in the elementary layer are presented.

Experimental studies of the drying process of pumpkin seeds were carried out in the temperature range of the drying agent from 40 to 80 °C and the speed of the drying agent was 1.5 m/s (Figure 3).

The curves of drying kinetics, thermograms and drying rates are built in automatic mode, so there are no points of the process on the presented curves.

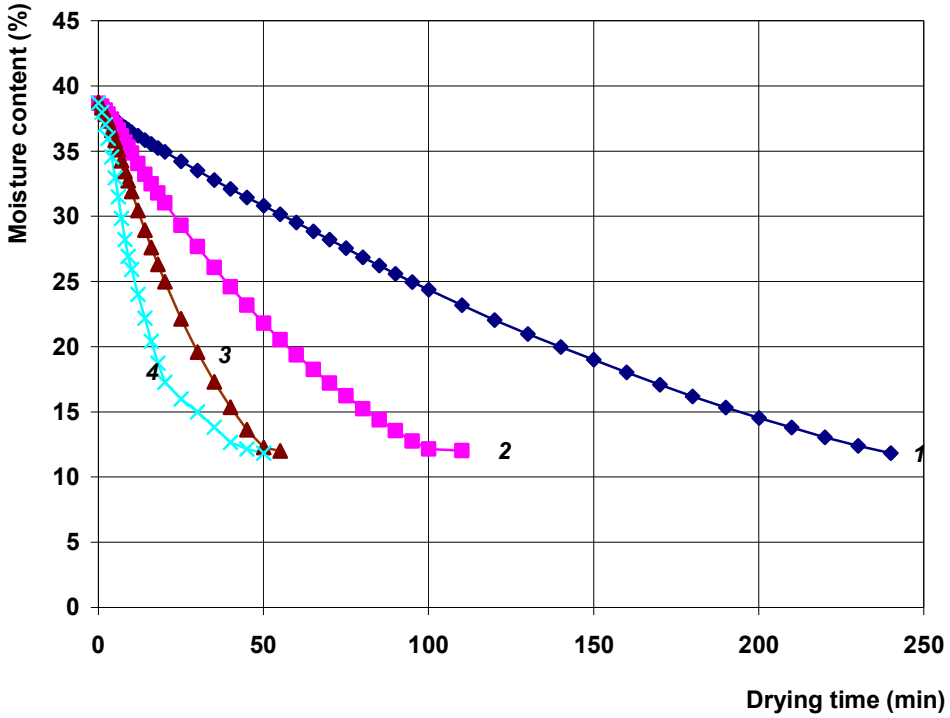


Figure 3. Curves of drying of pumpkin seeds (V = 1.5 m/s, d = 10 g/kg d.a.) at temperature values of the drying agent: 1 – 40 °C, 2 – 50 °C, 3 – 60 °C, 4 – 80 °C

The need to obtain high-quality seedling material (pumpkin seeds) requires a more thorough analysis of the research results. Thus, drying at 40 °C is a long process and takes 240 minutes, which is 2.4 times higher than the drying time at a temperature of 50 °C. At 80°C, the duration is only 32 minutes, which is almost 8 times faster than the drying time at 40 °C.

The rates of drying curves indicate that the highest drying rate at a critical point at 80 °C is 1.6% / min, the lowest at 40 °C is 0.26% / min. (Figure 4).

Thus, with the increase in the drying agent temperature from 40 to 80 °C, the drying rate increases by 6.15 times. The type of the curves of drying speed does not change and

indicates that the drying process of the pumpkin seeds passes the periods of heating to the critical point and the falling drying rate. Drying occurs to an equilibrium moisture content of 12%.

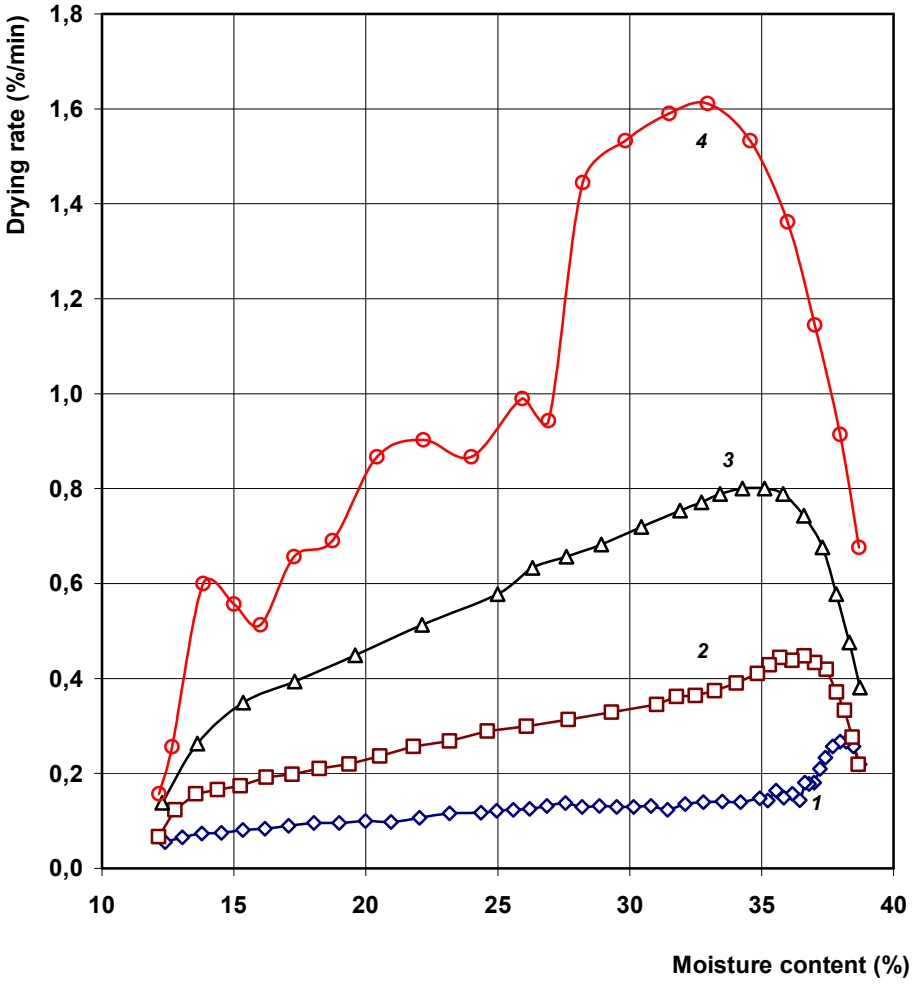


Figure 4. Drying rate curves of pumpkin seeds (V = 1.5 m/s, d = 10 g/kg d.a.) at temperature values of the drying agent: 1 – 40°C, 2 – 50 °C, 3 – 60°C, 4 – 80°C

The thermograms (Figure 5) show the temperature change of pumpkin seeds during the heating at different drying agent temperatures. The seeds are warmed up from 3 to 5 minutes, then the temperature does not change significantly.

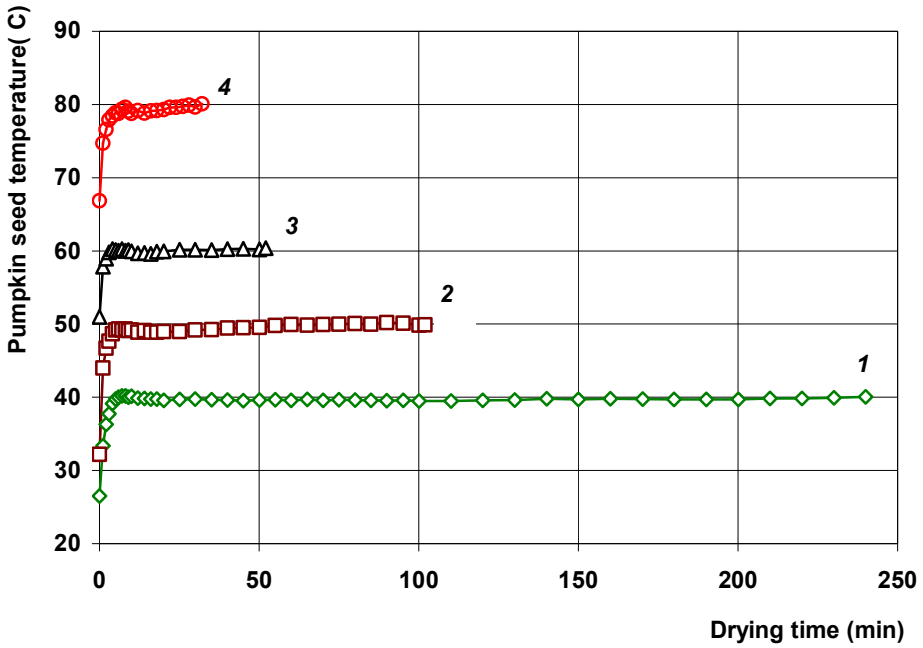


Figure 5. Thermograms of heating of pumpkin seeds depending on the drying temperature: 1 – 40°C, 2 – 50 °C, 3 – 60°C, 4 – 80°C

An increase in the temperature of the drying agent results in an increase in the final temperature of the material – the difference between the temperature of the drying agent and the final seeds temperature is 0.1–0.5 °C. So at a temperature of the drying agent 80 °C the final temperature is 79.5 °C, and at 40 °C is 39.9 °C.

To determine the rational drying mode, it is necessary to determine the quality parameters of the pumpkin seeds, depending on the temperature of the drying agent (Table 2).

Table 2

Influence of drying modes on quality parameters of pumpkin seeds

№	Process parameters			Quality parameters		
	Drying agent temperature t, °C	Speed of movement V, м/с	Drying time τ, min	Germination energy E, %		Germinability on the 10th day, C,%
				5th day	7th day	
1.	Initial seeds			17	99	100
2.	40	1,5	240	15	90	98
3.	50	1,5	102	7	86	96
4.	60	1,5	52	7	69	90
5.	80	1,5	32	-	-	0

The best results of the pumpkin seeds quality correspond to a drying temperature of 40 °C: the germination energy on 7-th day is 90%, and the germinability on 10-th day is 98%. The increase in temperature reduces the germinability on 4% relatively the initial seeds at a temperature of the drying agent of 50 °C, and, accordingly, on 10 °C with an increase to 60 °C. When the temperature of the drying agent increases to 80 °C, the final loss of the seeds germinability occurs.

Visually assess the effect of drying agent temperature on germinability at the initial moisture content of pumpkin seeds 38% it is possible by photos of germination on 5-th, 7-th, 10-th days (Figure 6–8). Thus, active germination occurs of seeds that have been dried at a temperature of 40 °C and almost is absent at a temperature of 80 °C.

From the data of the influence of drying agent temperature on the germinability of pumpkin seeds it is established that the most appropriate mode of drying is: the drying agent temperature 40 °C and the speed of movement 1.5 m/s (the effect of the initial humidity is not significant at that). In this mode, the germinability of pumpkin seeds is 98%.

The mathematical processing of the experimental data obtained was carried out using the method of V.A. Danilov [11].

This method shows that there is a proportionality between the drying rate in the first period N at any mode and the inverse of the length of the process τ_T from the initial moisture Wp to the final Wk, and this proportionality is maintained at all modes of drying.

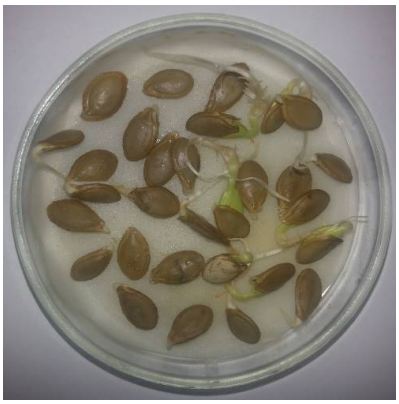
$$N \approx \frac{1}{\tau_T} \tag{3}$$

$$\frac{\tau}{\tau_{T1}} = \frac{\tau}{\tau_{T2}} = ... = \left(\frac{\tau}{\tau_T}\right) = const \tag{4}$$

This means that for a given current moisture content W, if Wp and Wk are unchanged the value $\frac{\tau}{\tau_T}$ remains constant regardless of the drying mode.

In Figure 9 the drying curve of pumpkin seeds is shown, which is transferred to the coordinate system $W - (\tau/\tau_T)$ and is transformed into a single generalized drying curve.

Generalized curves of dry kinetics of pumpkin seeds, constructed by Danilov V.A. method for different regimes, are practically coincide.



Initial seeds
(C = 17%)

Drying agent temperature 40 ºC
(C = 15%)

Drying agent temperature 50 ºC
(C = 7%)

Drying agent temperature 60 ºC
(C = 7%)

Drying agent temperature80 ºC
(C = 0%)

Figure 6. Effect of drying agent temperature on the germ inability of pumpkin seeds on 5-th day of germination

Initial seeds
(C = 99%)

Drying agent temperature 40 ºC
(C = 90%)

Drying agent temperature 50 ºC
(C = 86%)

Drying agent temperature 60 ºC
(C = 69%)

Drying agent temperature80 ºC
(C = 0%)

Figure 7. Effect of drying agent temperature on the germinability of pumpkin seeds on the 7th day of germination

Initial seeds
(C = 100%)

Drying agent temperature 40ºC
(C = 98%)

Drying agent temperature 50 ºC
(C = 96%)

Drying agent temperature 60 ºC
(C = 90%)

Drying agent temperature80 ºC
(C = 0%)

Figure 8. Effect of drying agent temperature on the germinability of pumpkin seeds on the 10th day of germination

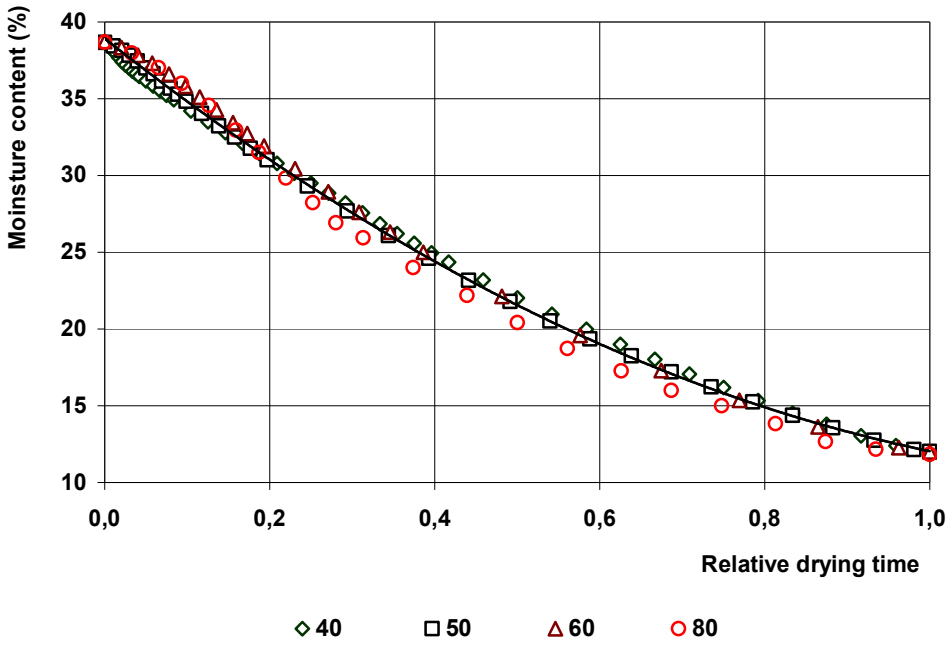


Figure 9. Generalized curve of kinetics of pumpkin seeds drying in the coordinates $W - (\tau/\tau_т)$

The generalized drying curve can be constructed on the basis of one experimental drying curve of pumpkin seeds obtained at any drying mode, which greatly simplifies the study of drying kinetics.

The generalized curve of drying kinetics was differentiated graphically, and a generalized curve of drying rate of pumpkin seeds was received.

In Figure 10 a generalized drying rate curve with a maximum drying rate of 0.45%/min is shown.

The drying process of pumpkin seeds takes place during the periods of heating and falling drying rates with the critical points *Wк1, Wк2* and *Wк3*.

The generalized drying curves of pumpkin seeds constructed in semi-logarithmic coordinates indicate that the drying process, regardless of the drying regime, takes place during the period of the falling drying rate and is divided into three stages with corresponding critical points. So in [7] it is also noted that drying occurs during the period of the falling drying rate. The obtained results of the study showed that when the temperature increases, the drying intensity increases, and the duration decreases by 8 times with the increasing of the drying agent temperature from 40 to 80 °C. While in [9] it is indicated that drying lasts for 8 hours at a temperature of 30 °C and only 2 hours when the temperature increases to 70 °C.

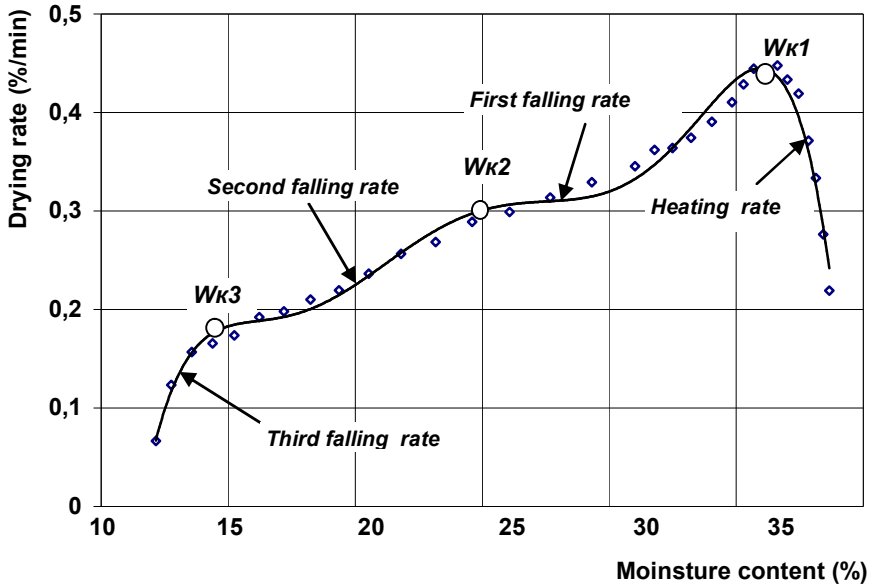


Figure 10. Generalized curve of drying rate of pumpkin seeds

Conclusions

It is recommended such a rational mode of pumpkin seeds drying variety: drying agent temperature 40 ºC, speed – 1,5 m/s. This is due to the biochemical properties of pumpkin seeds, in particular, the germinability, which, at the given drying mode, corresponds to the germinability of the control sample and is 98%.

References

1. Joshi D.C., Mukherejee R.K. (1993), Physical properties of Pumpkin seeds, *J. Agr. Eng.Res*., 54, pp. 219–229.
2. Davies R.M. (2010), Engineering Properties of Three Varieties of Melon Seeds as Potentials for Development of Melon Processing Machines, *Advance Journal of Food Science and Technology*, 2(1), pp. 63–66.
3. Koocheki, A., Razavi S.M.A., Milani E., Moghadan T.M., Abedini M., Alamatiyan and S., Izadikhah S. (2007), Physical properties of watermelonseed as a function of moisture content and variety, *Int. Agrophy*., 21, pp. 349–359.
4. Manuwa S.I., Afuye G.G. (2004), Moisture dependentphysical properties of soyabean (Var-TGx 1871-5E), *Nigeria J. Indust. Stud*., 3(2), pp. 45–54.
5. Bart-Plange A. and Baryeh E.A. (2003), The Physicalproperties of category B cocoa beans, *J. Food Eng*., 60, pp. 219–227.

6. Tabatabaeefa A., (2003), Moisture-dependent physicalproperties of wheat, *Int. Agrophy*., 12, pp. 207–211.
7. Sacilik K. (2007), Effect Of Drying Methods On Thin-Layer Drying Characteristics Of Hull-Less Seed Pumpkin (Cucurbita Pepo L.), *Journal of Food Engineering,* 79, pp. 23–30.
8. Akyol E., Susantez C., Kahveci K., Hacihafizoglu O., Kaya Y. (2015), Drying Simulation of Pumpkin Seed, *Proceedings of the World Congress on Mechanical, Chemical, and Material Engineering (MCM 2015) Barcelona, Spain – July 20–21, Paper No. 320.*
9. Guiné R. P. F., Pinho S., Barroca M. J. (2011), Study of The Convective Drying Of Pumpkin (Cucurbita Maxima), *Food and Bioproducts Processing,* 89, pp. 422–428.
10. Hashim N., Daniel O., Rahaman E. (2014), A Preliminary Study: Kinetic Model Of Drying Process Of Pumpkins (Cucurbita Moschata) İn A Convective Hot Air Dryer, *Agriculture and Agricultural Science Procedia,* 2, pp. 345–352.
11. Hukil W.V. (1954), *Storage ol cereal grains and their products*, Amer Assoc. Cer. Chem.
12. Kofoed S.S. (1964), *Investigations on drying grain with slightly pre-heated air in thick layers*, Copenhagen.
13. McEwen E.R. (1954), Through drying of deep beds of wheat grain, Engineer, 10, pp. 817–819.
14. Petrova Z., Snezhkin Y., Pazyuk V., Samoilenko K. (2015), Drying of Antioxidant Composite Materials based on Table Beet, *Energy engineering and control systems*, 1, pp. 25–28.
15. Vyacheslav Mykhailyk, Sviatoslav Lementar, Roman Yakobchuk, Yevhen Skrynnyk, Roman Semenko (2016), Wheat grain drying kinetics in a thin layer, *Ukrainian Journal of Food Science,* 4(2), pp. 316–326.

Анотації

Анотації

Харчові технології

Антиоксидантні властивості льодяникової карамелі з рослинними екстрактами

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Вступ. Проведено дослідження антиоксидантних властивостей зразків льодяникової карамелі на основі цукрозамінників мальтитолу й ізомальтитолу, збагачених аскорбіновою кислотою та біологічно активними речовинами водних екстрактів сушених листя *Menthae Piperitae* та квіток *Matricariae chamomilla L.*

Матеріали і методи. Загальну антиоксидантну ємність (TAC) і загальний зміст поліфенольних сполук (TPC) зразків карамелі визначали методом кулонометричного титрування в гальваностатичному режимі з електрогенерованим бромом і спектрофотометричним методом за допомогою реактиву Folin-Ciocalteu. Експериментальні величини TAC і TPC були представлені в еквіваленті вмісту галової (GAE) або аскорбінової (AAE) кислоти в одиниці маси відповідного зразка (SW). Вміст аскорбінової кислоти в кінцевому продукті визначали методом гальваностатичної кулонометрії з електрогенерованим йодом.

Результати і обговорення. Визначено загальну антиоксидантну ємність водних екстрактів м'яти та ромашки, що склала 40,0 та 23,3 мг GAE/г SW відповідно, та загальний вмісту поліфенолів – 54,5 та 17,1 GAE/г SW.

Доведено, що в зразках льодяникової карамелі на основі цукрозамінників з додаванням рослинних екстрактів залишається від 48 до 66% початкової маси введеної аскорбінової кислоти.

На основі експериментальних досліджень зразків карамелі з варіацією інгредієнтів рецептури визначені коректні значення загального вмісту поліфенольних сполук для двох зразків льодяникової карамелі за наявностізаважаючих речовин, що дорівнюють 408 мг GAE/100 г зразка для карамелі на основі мальтитолу й екстракту ромашки і 222 мг GAE/100 г для карамелі на основі ізомальтитолу й екстракту м'яти.

Отримано високу позитивну кореляцію між значеннями загальної антиоксидантної ємності TAC і загального вмісту поліфенолів TPC для досліджених об'єктів.

Висновки. Отримані результати свідчать про перспективність технології збагачення льодяникової карамелі на цукрозамінниках натуральними біологічно активними речовинами з антиоксидантними властивостями для виробництва дієтично-функціональних харчових систем.

Ключові слова: *карамель, антиоксидант, поліфеноли, аскорбінова кислота, кулонометрія.*

Вплив сорту і часу зберігання оливок, вирощених у Ахісарському регіоні,Туреччина на якісні показники оливкової олії

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Вступ. Проведені дослідження з метою визначення впливу різних сортів і часу зберігання оливок на якісні показники олії, отриманої екстрагуванням за допомогою системи Абенкор.

Матеріали і методи. Матеріалами досліджень були сорти оливок Едреміт та Услу, які широко вирощуються в районі Ахісара. Ці сорти оливок зберігались у пластикових коробках або нейлонових мішках. Очікуюч 0, 7, 14, 21 дня, Олію екстрагували на 0, 7, 14, 21 дні за допомогою системи Аберкон. В зразках оливкової олії визначалися вільні жирні кислоти, перекисне число, значення ультрафіолетового поглинання (для 232 та 270 нм), кількість опроміненого фенолу, показник заломлення, вміст загального вмісту хлорофілу та каротиноїду, складу жирних кислот та колірних значень. Оцінювалися окислювальна стабільність та органолептичні властивості оливкових олій.

Результати і обговорення. Втрачалася якість зразків, особливо сорту Услу під час зберігання у мішках. Загальний вміст фенолу у оливкових оліях надмірно зменшувався протягом часу проведення обох типів зразків, хоча більшість хімічних параметрів відповідали встановленим вимогам. Зміна вмісту хлорофілу та каротиноїдів складала відповідно від 0,7 до 8,69 мг/кг і від 0,7 до 3,44 мг/кг для оливкової олії з Едреміту і від 0,93 до 2,17 мг/кг та від 0,96 до 1,49 мг/кг для Услу. Олеїнова кислота (C18:1), лінолеві (C18:2), пальмітинові (C16:0) і стеаринові (C18:0) кислоти виявлені переважними жирними кислотами у всіх зразках. Зразки олії, отримані з сорту Едреміт в перший та 7-й дні періоду зберігання у мішках, були класифіковані як екстра чиста оливкова олія. Також, олія, отримана з сорту Uslu в перший день проведення періоду, своїми органолептичними показниками класифікувалася як екстра чиста. У той час як інші зразки були класифіковані як чиста оливкова олія. Початковий індукційний період оливкових олій Едреміт та Услу був 3,9 і 3,8 години. Для сорту Услу спостерігалося його зниження протягом періоду витримування до 21-го дня, а для Едреміту зниження не спостерігалося.

Висновок. Хімічні показники, аналізовані у різних зразках, знаходяться у дозволених межах, але змінюються протягом періоду зберігання та залежно від сорту.

Ключові слова: *оливи, олія, Ахішар, якість.*

Вплив підсолоджувачів на реологічні та якісні показники морозива

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Вступ. Проведені дослідження з метою визначення впливу підсолоджувачів на реологічні та якісні характеристики морозива.

Матеріали і методи. Досліджувались суміші морозива вершкового та ароматичного з цукром, сумішшю паток (глюкозно-фруктозним сиропом і патокою карамельною), еритритолом і сорбітом, а також їх композиціями. Реологічні характеристики вивчали методом ротаційної віскозиметрії.

Результати і обговорення. В'язкість морозива вершкового й ароматичного у разі повної заміни цукру патоками крохмальними збільшувалась. Здатність до відновлення структури таких систем під час вимірювань у режимі ступінчастого зменшення швидкості зсуву підвищувалася і становила від 110,3% до 112,4%, що відповідає реопексній поведінці. Однак ефективна в'язкість морозива з поліолами зменшувалась порівняно з контролем, а відновлення структури цих систем склало лише 46,8 та 55,9%. У разі комбінування суміші паток з еритритолом або сорбітом за рівних співвідношень у морозиві вершковому було зафіксовано підвищення ефективної в'язкості за ступеня відновлюваності структури – 81,9 та 87,0% відповідно.

Виявлено певну кореляцію між ефективною в'язкістю і фізико-хімічними показниками морозива. Так, у діапазоні рекомендованих значень ефективної в'язкості сумішей морозива різного хімічного складу показник збитості становив не нижче 60% за періодичного способу виробництва. Слід відзначити незначне зниження збитості морозива у разі застосування крохмальної патоки, що може бути компенсоване шляхом її комбінуванням з поліолами.

Найвищу збитість виявлено у зразках морозива з еритритолом і сорбітом, а найнижчу у разі використання суміші паток. За комбінування еритиритолу з сумішшю паток технологічний ефект був найвищим.

Опір до танення вершкового морозива з поліолами знижувався до 44,1 хв з еритритолом, та 45,2 хв з сорбітом і підвищувався для морозива із сумішшю паток до 54,1 хв (контроль – 48,2%). Для ароматичного морозива одержано подібну закономірність.

Висновки. Використання поліолів і композиції паток дає змогу корегувати ступінь солодкості готового продукту та формувати задані фізико-хімічні характеристики сумішей і морозива.

Ключові слова: *морозиво, цукор, патока, поліоли, в'язкість.*

Ефективність екстракту розмарину увтехнології м'ясо-містких сардельок з м'ясом мускусної качки

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Вступ. Метою дослідженняє оцінка ефективності застосування екстракту розмарину в технології м'ясо-містких сардельок із м'ясом качки, яке відрізняється високим вмістом поліненасичених жирних кислот.

Матеріали і методи. Моделлю для вивчення ефективності екстракту розмарину була рецептура м'ясо-містких сардельок із м'ясом мускусної качки, до складу якої також було включено яловичину 1 сорту, шпик боковий, соєвий ізолят, молоко сухе, білковий стабілізатор із свинячої шкурки, препарат розчинної клітковини XB Fiber. Під час зберігання м'ясо-містких сардельок визначали кислотне, перекисне числа, тіобарбітурове число.

Результати і обговорення. Отримані результати свідчать про те, що внесений антиоксидант гальмує гідроліз жиру завдяки високій концентрації флавоноїдів екстракту. Найбільш ефективно гальмує гідролітичний розпад ацилгліцеридів екстракт розмарину в концентрації 0,05%. Внесення екстракту розмарину сприяє уповільненню окислювальних процесів. Серед дослідних зразків сардельок перекисне число інтенсивніше зростало у пробі без добавки. Найбільшу стабілізуючу дію мала добавка екстракту в концентрації 0,05%. Перекисне число в цьому зразку в кінці досліджуваного терміну дорівнювало 0,015±0,001%J_2, тоді як у контролі цей показник становив 0,026±0,002%J_2, що на 57,69% вище. Антиоксидантна дія добавок проявляється і в накопиченні моно- й діальдегідів, що реагують з 2-тіобарбітуровою кислотою. Дослідження вмісту вторинних продуктів окислення дало змогуоцінити глибину окислювальних процесів, що відбувалися в зразках сардельок при зберіганні протягом 6 діб при температурі +4ºС. Концентрація вторинних продуктів окислення була найвищою в контрольному зразку, а в дослідних зменшувалась пропорційно концентрації внесеної антиокислювальної добавки. В кінці терміну зберігання кількість продуктів вторинного окислення в контрольному зразку становила 0,269±0,04 мг МА/кг готового виробу, тоді як у дослідних зразках цей показник коливав від 0,231±0,03 до 0,184±0,04 мг МА/кг. Найбільший ефект отриманий при внесенні добавки у кількості 0,05%, що дає змогу знизити показники окислювального псування жиру майже в два рази.

Висновки. Проведені дослідження підтвердили високу антиоксидантну активність екстракту розмарину й ефективне гальмування процесу окислення ліпідів у м'ясо-містких сардельках із м’ясом мускусної качки.

Ключові слова: *антиоксидант, екстракт, розмарин, сардельки, качка.*

Збагачення пива біологічно активними сполуками хмелю

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Вступ. Проведені дослідження з метою вивчення впливу біологічно активних сполук хмелю українських сортів на якісні показники пива, особливостей їх використання в пивоварінні та винайденні способів раціонального вжитку цінних речовин хмелю.

Матеріали і методи. Досліджувались ароматичний сорт хмелю Слов’янка з високим вмістом бета-кислот, хміль спеціальних сортів Руслан і Ксанта з підвищеним вмістом ксантогумолу та пиво, виготовлене з них. Використано високоефективну рідинну хроматографію для визначення кількості та складу гірких речовин і ксантогумолу хмелю та продуктів їх перетворення в процесі пивоваріння, а також спектрофотометричні методи контролю якості гіркоти охмеленого сусла й готового пива.

Результати і обговорення. Для збагачення пива біологічно активними сполуками хмелю оптимальним співвідношенням тонкоароматичного та гіркого хмелю, яке забезпечує високу якість пива є: 40% гіркоти від розрахункової норми за вмістом альфа-кислот, внесеної за рахунок хмелю спеціальних сортів Руслан ті Ксанта та

60%, внесеної з хмелем тонкоароматичних сортів з високим вмістом бета-фракції. Сумісне нормування тонкоароматичного хмелю і хмелю спеціальних сортів згідно із запропонованим способом дає змогу отримати в пиві до 13,0–20,0 мг/дм^3 ізо-альфа-кислот з можливістю досягнення в напої вмісту поліфенольних сполук у діапазоні 160,0–200,0 мг/дм^3. Завдяки цьому досягається більш висока колоїдна стійкість пива та підвищується на 15–20% ступінь використання гірких речовин. Використання яксировини тонкоароматичного хмелю сорту Слов'янка, що має в своєму складі велику кількість бета-кислот і найкраще співвідношення бета-кислот до альфа-кислот від 1,3 до 1,8 у процесі охмеління сусла сприяє утворенню сполук, що мають приємну, м'яку гіркоту. Також використання хмелю Слов'янка з низьким вмістом когумулону в складі альфа-кислот (21,4%) забезпечує невисокий вміст до 5,0–7,0 мг/дм^3 ізокогумулону в пиві, що покращує якість гіркоти. Водночас використання хмелю спеціальних українських сортів Руслан і Ксанта, шишки яких вміщують до 1,2% ксантогумолу, сприяють утворенню в пиві ізоксантогумолу в межах 2,0–5,0 мг/дм^3.

Висновки. Сумісне використання хмелю сортів Слов'янка, Руслан і Ксанта у запропонованому співвідношенні збагачує напій біологічно активними сполуками хмелю, підвищуючи таким чином його функціональні властивості.

Ключові слова: *хміль, ксантогумол, бета-кислоти, поліфеноли, пиво.*

Технологічні особливості біологічного захисту запасів зерна від комплексу лускокрилих-фітофагів (Lepidoptera: Pyralidae, Tineidae, Gelechiidae)

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Вступ. Науково обґрунтовано прийоми біологічного захисту з використанням ентомофагів та ентомопатогенів в умовах зерносховищ щодокомплексу домінуючих популяцій лускокрилих-фітофагів зернових запасів.

Матеріали і методи. Протягом 2010–2017 рр. досліджувались зернові запаси зернових колосових, зернобобових, технічних культур продовольчого, фуражного та насіннєвого призначення, комплекс членистоногих (комахи та кліщі), якітрофічно тй екологічно пов'язані з ними, а також лабораторні культури ентомофагів та ентомопатогенів. Для досліджень використано прийоми візуального (середні проби) та інструментального (харчові принади, феромонні пастки) моніторингу, мікробіологічні, популяційні й статистичні методи.

Результати ті обговорення. В результаті багаторічних досліджень показано принципову можливість ефективного біологічного захисту, а також контролю чисельності домінуючого комплексу лускокрилих-фітофагів зернових запасів. Оптимізовано технологічні параметри та доцільність використання лабораторних культур ентомофагів сумісно з мікробіологічними препаратами. Важливо, що весь арсенал біологічного захисту використовувався в критичні періоди онтогенезу комах-фітофагів, що супроводжувалось не тільки винищувальною дією оперативного характеру, але й регуляторним впливом з подальшимпереведенням популяцій у тривалий депресивний стан. Встановлено специфічну біоценотичну закономірність, яка полягає у тому, що популяції ентомофагів та діючі речовини біопрепаратів характеризувалися вираженою післядією, що проявлялась фізіологічними аномаліями, зокрема порушенням ритміки оогенезу з подальшим зниженням реальної

плодючості самиць і трофічної активності гусениць. Складові частини оригінальної технології проявили виражену ефективність стосовнофітофагів. Так, лабораторні культури ентомофагів уражували відповідні стадії фітофагів на рівні 64,2%. Не менш ефективною була дія та післядія мікробіологічних препаратів у складі технології, що стало причиною загибелі 70,4%. У підсумку, біологічна стратегія захисту зернових запасів забезпечила кінцеву ефективність на рівні 82,7% проти 93,1% в хімічному еталоні. Апробація біологічних прийомів показала їхню технологічність і сприйнятливість практикою захисту рослин за таких специфічних умов.

Висновки. Реалізація технології дає змогу зберегти 96,6 % валового запасу зерна від лускокрилих-фітофагів.

Ключові слова: *зерносховище, елеватор, фітофаги, ентомофаг, ентомопатоген, захист, органіка.*

Біотехнологія, мікробіологія

Особливості синтезу мікробного полісахариду етаполану на змішаних відпрацьованих оліях

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Вступ. Досліджували можливість інтенсифікації синтезу мікробного екзополісахариду (ЕПС) етаполану (продуцент *Acinetobacter* sp. IMB B-7005) на суміші відпрацьованих олій різного виду та якості, а також емульгувальні властивості синтезованого за таких умов ЕПС.

Матеріали і методи. Культивування *Acinetobacter* sp. IMB B-7005 здійснювали на рідкому середовищі, що містило як джерело вуглецю відпрацьовані рослинні олії (соняшникова, кукурудзяна, оливкова) (5%, об'ємна частка). Концентрацію ЕПС визначали ваговим методом після осадження ізопропанолом, ЕПС-синтезувальну здатність – як відношення концентрації ЕПС до концентрації біомаси та виражали у г ЕПС/г біомаси.

Результати і обговорення. Незалежно від виду олії в середовищі для отримання інокуляту (оливкова чи соняшникова), показники синтезу етаполану на суміші відпрацьованих соняшникової й оливкової олій (у співвідношенні 1:4; 4:1; 1:1) були дещо нижчими, ніж за умов росту продуцента на рафінованій соняшниковій олії, але при цьому спостерігали підвищення ЕПС-синтезувальної здатності на 14–41%. Використання змішаної після смаження м'яса, картоплі, цибулі, сиру соняшникової олії як субстрату для отримання етаполану супроводжувалося синтезом такої ж концентрації полісахариду, як і на рафінованій олії. Зниження початкової концентрації змішаної соняшникової олії до 1,25–2% з подальшим дробним внесенням порціями по 1,25–1,5% у процесі культивування до кінцевої концентрації 5% супроводжувалося підвищенням концентрації етаполану на 15–20% порівняно з одноразовим внесенням 5% субстрату. Розчини синтезованого за таких умов полісахариду в концентрації 0,05% емульгували гексадекан, бензин, дизельне паливо (індекс емульгування 48–52%), причому утворена емульсія залишалася стабільною упродовж 20 діб.

Висновок. Одержані результати засвідчують можливість створення універсальної технології одержання мікробного екзополісахариду етаполану на змішаній відпрацьованій соняшниковій олії, незалежної від типу та постачальника цього субстрату.

Ключові слова: *Acinetobacter sp. IMB B-7005, екзополісахарид, відпрацьовані олії, культивування, емульгування.*

Процеси і обладнання

Вплив конструктивних параметрів механічного диспергатора на рівномірність розподілення розчину

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Вступ. Наведені результати експериментальних досліджень впливу конструкції механічного диспергатора на рівномірність розподілення рідини в об'ємі робочої зони.

Матеріали ті методи. Дослідна установка споряджена об'ємними кільцевими комірками для вимірювання витрат рідкої фази по робочій довжині диспергатора. Якмодельна рідина використовувалась вода при температурі 18ºС. З експерименту визначались середні витрати рідкої фази та масові частки їх розподілення за довжиною робочої зони шляхом відведення рідини з комірки кільцевого модуля. Кількість обертів диспергатора вимірювались електронним частотоміром в Гц з точністю ±1Гц. Визначення розміру крапель проводилось за допомогою фото фіксації.

Результати і обговорення. При застосуванні механічного диспергатора конічного типу при 450-кратному перевищені відцентрової сили над силою гравітації на зовнішній поверхні механічного диспергатора конічної форми за рахунок наявності сил поверхневого натягу утворюються струмені рідини, які рухаються до крайки диспергатора та сприяють локальному перезволоженню робочої зони зрошення. Застосування конічного диспергатора із встановленням зовнішніми відбійних кілець збільшило рівномірність розподілення. Запропонований критерій оцінки рівномірності дає змогу провести порівняння будь-яких конструкцій механічних диспергаторів за оригінальною методикою. Окрім цього, визначено раціональний спосіб встановлення живильної трубки подачі робочого розчину. За результатами дослідження визначено параметри, при яких збільшено розміри об'єму розпилення при достатній рівномірності із застосуванням механічного двоконусного диспергатора з перфорованою бічною поверхнею та наявністю зовнішніх відбійних кілець.

Висновки. Теоретично обгрунтовано й експериментально доведено доцільність застосування запропонованих критеріїв оцінювання якості роботи механічного дисператора, які надають можливістьвизначити умови якісного проведення знаводнення та гранулювання рідких систем у псевдозрідженноу шарі.

Ключові слова: *диспергатор, розпилення, псевдозрідження, зневоднення.*

Вплив робочих елементів різної конфігурації на процес замішування дріжджового тіста

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Вступ. Досліджено вплив геометричних параметрів місильних робочих елементів на інтенсивність та якість замішування дріжджового тіста.

Матеріали і методи. Досліджено пшеничне дріжджове тісто, яке замішували в машині безперервної дії за допомогою шнекових, кулачкових і пальцевих робочих елементів. Структурно-механічні властивості тіста визначали методом віскозиметрії. Пористість готового виробу визначали за аналізом зрізу готового виробу та спеціального програмного пакетуaImageJ.

Результати і обговорення. Зі збільшенням показників швидкості зсуву від 0 до 100 $с^{-1}$ відбувається різкий скачок напруження зсуву від 2000 до 6800 Па, далі в діапазоні швидкості зсуву від 100 до 800 $с^{-1}$ повільно збільшується до 6950 Па. Зі збільшенням швидкості зсуву від 0 до 800 $с^{-1}$ в'язкість зменшується за степеневою залежністю.

Показники витрат питомої роботи при замішування дріжджового тіста робочими органами різної конфігурації за параметру стабілізуючої решітки 2,5%, досягають 22-37 Дж/г.

Інтенсивність замішування тіста залежить від конструкції тістомісильної машини, частоти обертання місильного елементу та його конфігурації. Шнекові робочі елементи мало інтенсивні, показники інтенсивності сягають у межах від 0,07 до 0,12 Вт/г.

Пористість хлібного виробу, після замішування кулачковим робочим елементом, складає 72% і є високим показником продукції.

Висновки. Підтверджується позитивний ефект від посиленої механічної обробки шнековими та кулачковими робочими елементами в процесі замішування дріжджового тіста. Пальцеві робочі елементи можуть використовуватися у комбінації з шнековим елементом на початку валу. Порівняльний аналіз підтверджує доцільність використання кулачкових робочих елементів.

Ключові слова: *замішування, дріжджі, тісто, інтенсивність, питома робота, пористість.*

Визначення раціональних режимів сушіння насіння гарбуза

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Вступ. Насіння гарбуза є легкодоступним джерелом білка та інших корисних речовин. Метою дослідження є визначення раціонального режиму його висушування, при якому забезпечується висока схожість матеріалу.

Матеріали і методи. Досліджувались фізико-механічні властивості насіння гарбуза української селекції з вологістю 0, 6, 16, 46 %. Визначення кінетики процесу

сушіння проведені на конвективному сушильному стенді за таких режимів: температура сушильного агента в сушильній камері t = 40–80˚С, швидкість руху V = 1,5 м/с, вологовміст повітря d = 10 г/кг с. п. Біохімічні показники висушеного насіння визначені за кількостю насіння, здатного утворювати нормально розвинуті проростки за оптимальних умов на 5, 7 та 10 день пророщування.

Результати і обговорення. Проведені дослідження властивостей насіння гарбуза сорту «Стофунтовий» показали, що при зміні вологості матеріалу від 0 до 46% відбувається збільшення геометричних розмірів насіння: довжина збільшується на 38%, ширина на 10% і товщина на 8%, а також змінюються й інші показники.

Дослідження процесу сушіння насіння гарбуза показали, що при збільшенні температури сушильного агента інтенсивність сушіння збільшується. Так, тривалість сушіння зменшується у 8 разів при підвищенні температури сушильного агента від 40 до 80 ºС.

Криві швидкості сушіння в період падаючої швидкості сушіння з попереднім прогріванням показують, що найбільша швидкість сушіння в максимальній критичній точці при температурі сушильного агента 80ºС складає 2,32 %/хв, найменша при температурі 40 ºС – 0,33 %/хв.

Прогрівання насіння гарбуза відбувається від 3 до 5 хвилин залежності від режиму, потім температура матеріалу змінюється несуттєво і відрізняється від температури сушильного агента на 0,1–0,5 ºС.

Узагальнена крива кінетики сушіння насіння гарбуза дає можливість описати загальний процес за різних режимів сушіння.

Висновок. Температура сушильного агенту суттєво впливає на схожість насіння гарбуза. Найбільш раціональним режимом сушіння є температура 40 ºС та швидкість руху повітря 1,5 м/с.

Ключові слова: *гарбуз, насіння, сушіння, пророщування.*

Instructions for authors

Dear colleagues!

The Editorial Board of scientific periodical
«**Ukrainian Food Journal**»
invites you to publication of your scientific research.

Requirements for article:
Language – English.
Size of the article – 10–15 pages in Microsoft Word 2003 and earlier versions with filename extension *.doc (!)
All article elements should be in Times New Roman, font size 14, 1 line intervals, margins on both sides 2 cm.

The structure of the article:
1. The title of the article
2. Authors (full name and surname)
3. Institution, where the work performed.
4. Abstract (2/3 of page). The structure of the abstract should correspond to the structure of the article (Introduction, Materials and methods, Results and discussion, Conclusion).
5. Key words.

Points from 1 to 5 should be in English, Ukrainian and Russian.

6. The main body of the article should contain the following obligatory parts:
   - Introduction
   - Materials and methods
   - Results and discussing
   - Conclusion
   - References

   If you need you can add another parts and divide them into subparts.

7. The information about the author (Name, surname, scientific degree, place of work, email and contact phone number).

All figures should be made in graphic editor, the font size 14.

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Figures and EXCEL format files with graphs additionally should submit in separate files.
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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**.**
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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).
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Пункти 2–6 виконати англійською і українською мовами.

7. Основний текст статті. Має включати такі обов'язкові розділи:
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   - Матеріали та методи
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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).
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Рисунки виконуються якісно. Скановані рисунки не приймаються. Розмір тексту на рисунках повинен бути **співрозмірним** (!) тексту статті. **Фотографії можна використовувати лише за їх значної наукової цінності.**

Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

Рисунки та графіки EXCEL з графіками додатково подаються в окремих файлах.

Скорочені назви фізичних величин в тексті та на графіках позначаються латинськими літерами відповідно до системи СІ.

В списку літератури повинні переважати англомовні статті та монографії, які опубліковані після 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.

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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

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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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Наукове видання

Ukrainian Food Journal

Volume 7, Issue 1
2018

Том 7, № 1
2018

Підп. до друку 29.03.2018 р. Формат 70x100/16.
Обл.-вид. арк. 13.06. Ум. друк. арк. 13.23.
Гарнітура Times New Roman. Друк офсетний.
Наклад 100 прим. Вид. № 02н/18.

НУХТ. 01601 Київ–33, вул. Володимирська, 68

Свідоцтво про державну реєстрацію
друкованого засобу масової інформації
КВ 18964–7754Р
видане 26 березня 2012 року.