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Contents

Identification of bacillary microbial contaminants and food poisoning agents from ukrainian plant raw materials and products

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Abstract

Introduction. The characteristics of biological contaminants occurring in plant food products, such as foodborne infections and poisonings, causative agents of spoilage, accelerated indication of potential danger to the consumer are of scientific and practical importance.

Materials and methods. A row of widespread and industrially grown kinds of vegetables, fruits, berries and a number of canned and dried products and spices were investigated. Morphological, cultural and biochemical properties of the isolated cultures were studied by conventional methods. Polymerase chain reaction (PCR) was performed using group-specific and species-specific primers to bacillary sequences with electrophoresis of PCR products in 1.5% agarose gel.

Results and discussion. Bacillary microbial contaminants and potential causative agents of food poisoning and food spoilage, which are common in industrially processed types of vegetable raw materials (vegetables, fruits, berries and products of their processing) in Ukraine, have been investigated. The dominance of the *subtilis-licheniformis* morphotypes of the order *Bacillales* among the detected rod-shaped spore-forming microorganisms is a feature of the Ukrainian vegetative raw materials. The composition of microbiota of various types of vegetable raw materials and products of their processing were studied by the complex of their phenotypic and molecular-genetic properties. The long duration and potential inaccuracy of identification of aerobic and facultative-anaerobic spore-forming bacteria by the complex of their phenotypic properties has been showed. The method of preparation of food samples and PCR with group-specific and species-specific primers for speeding-up diagnostics of *B. cereus, Paenibacillus polymyxa, P. macerans* strains in samples have been tested. Contamination of samples of plant raw materials and products of their processing by epidemiologically significant microorganism *B. cereus* were examined, and showed levels from 16.7% in fresh fruits to 72.7% in spices from the total number of samples.

Conclusions. The bacillary microbial contaminants were identified and a speeded up method of food samples preparation for PCR to detect regulated bacillary microorganisms that affect product safety was tested.

Introduction

The assessment of food safety in modern conditions is relevant all over the world [1,2], as an important characteristic of the quality of nutrition is becoming increasingly important due to increasing pollution [3], and microbiological hazards as a priority in assessing the degree of risk are due to the presence of regulated microorganisms in food. Being criterial in the system of indicators of safety and quality of food, microbiological contaminants also characterize the suitability of products for use [4, 5]. Besides, the qualitative and quantitative composition of the microorganisms of raw materials, along with its biochemical properties, determines the types, methods and regimes of technological processing [6,7].

The deterioration of the man-made environment associated with urbanization, climatic and geographic and environmental conditions of man, reducing its immunoreactivity and affecting the individual microecosystems, actualizes the need for strict control of food safety and the development of modern accelerated methods for detecting microorganisms. When processing vegetable raw materials, particularly canned food, the quality and safety of the finished product depends on the quality of the processed raw materials and is determined by the absence of microorganisms and their toxins that are dangerous to human health or changing their nutritional value [1,8,9]. In the Codex Alimentarius CAC / GL 21 document, a number of EU policy documents - the report of the EU Commission, EU guidance document 2073 - and the documents of the Federal Food and Drug Administration provide general information on the principles for the development and application of microbiological criteria for different types of food products [10, 11, 12].

Among the aerobic and facultative anaerobic spore-forming bacteria of the *Bacillales* order [13], the genus *Bacillus* is one of the largest and most common, currently includes 268 species and 7 subspecies [14], among which are the causative agents of human foodborne illness and food spoilage [15-18]. The study of the quantitative and qualitative composition of the microbial population of fruits, vegetables, berries, and especially their thermally stable species, underlies the development of technological solutions for preserving the native properties of plant raw materials before processing and guaranteeing product safety for the consumer.

The abundance of microorganisms that make up the microbiota of plant raw materials, the duration and inaccuracy of the identification of individual species of bacilli by traditional methods of research, actualize the development of speeded up methods of detecting pathogenic species that affect product safety. Therefore, the characteristics of biological contaminants occurring in plant food products – agents of foodborne infections and poisonings, accelerated indication of potential danger to the consumer, development of speeded up and reliable methods for controlling the safety of products are of scientific and practical interest.

Thus, the *goal of the research* is the identification of aerobic and facultative anaerobic spore-forming bacteria of raw materials - fruits, vegetables, berries and products of their processing, and an accelerated assessment of the safety of plant products in relation to bacillary microbial agents of food poisoning of humans and spoilage of products.

Materials and methods

Microorganisms

Researches of widespread and industrially grown kinds of vegetables, fruits, berries, in particular, green peas, beetroot, tomatoes, carrots, apples, pears, plums, peaches, dill, spinach, parsley, strawberry, a number of canned and dried products, and also spices. Samples of raw materials were selected according to standardized selection rules for the average sample [9, 20] immediately after the raw material was delivered for processing, the processed products in packed, dried or canned form - after inspecting batches, paying special attention to possible defective samples. Each sample was tested in triplicate.

Bacterial strains used in this study were obtained from the National Collection of Type Cultures from Institute of Microbiology and Virology D.K. Zabolotny of NAS of Ukraine, State institution "Ukrainian Centre for Disease Control and monitoring of the Ministry of Health of Ukraine", Scientific Research Institute of preventive toxicology and disinfection of the Ministry of Health of Ukraine, Collections of Type Cultures of Odesa National Academy of Food Technologies and Odesa I. I. Mechnikov National University and were used as a control strains. They are *Bacillus cereus* ATCC 11778, *B. cereus* ATCC 10702, *B. licheniformis C*, *Paenibacillus macerans* B 5803^T, *P. polymyxa* B 5760^T, *B. coagulans* B 5850^T, *Geobacillus stearothermophilus* UCM B 718, and 117 strains isolated from food samples of edible raw material and products.

Determination of phenotypic properties

For the analysis, flushing or shredded samples of an average raw material sample were used which were heated for 20 minutes at a temperature of (80 ± 1) °C and after cooling to room temperature were plated onto meat-peptone agar (MPA) and incubated at a temperature of 30 ± 1°C for 24-48 hours [9, 21]. Samples of dried or canned products were examined without additional heating. To account for the total number of bacteria in the raw material, the samples were also inoculated without heating. Mesophilic aerobic and facultative anaerobic bacteria (MAFAnM) were taken into consideration for inoculation for MPA.

Morphological, cultural and biochemical properties of the isolated cultures were studied by conventional methods on the basis of: the growth pattern on solid and liquid nutrient media (MPB, MPA, MPA enriched with starch, nitrates, etc.), saccharolytic properties – by inoculation of semi-liquid Giss' media, proteolytic properties by inoculation of milk, and meat-peptone gelatin (MPG), determination of indole – by paper indicator impregnated with oxalic acid solution, catalase – by reaction with hydrogen peroxide, production of acetoin – by reaction with egg yolk, hemolytic activity – by the ability of microorganisms to break hemoglobin by direct inoculation of culture on blood agar [7, 9, 20 – 22]. A quantitative characteristic was established as the proportion (%) of bacillary species of microorganisms from the total number of detected contaminants.

DNA extraction and PCR

PCR was performed using group-specific and species-specific primers to bacilli sequences according to Park et al. [23]. DNA was isolated from the samples using the SureFast® PREP Bacteria F1021 (CONGEN, Germany). The composition of the mixture for PCR: 10x PCR buffer (reaction buffer for amplification, optimized for highly specific PCR, designation 10x implies dilution factor by other additive components of the reaction mixture) - 2 µl, $MgCl_2$ solution with a molar concentration of 0.05 mol/l - 0, 8 µl, a solution

of dNTPs with a molar concentration of 0.0025 mol/l of 1.6 µl, a Taq polymerase solution with an enzymatic activity of 5 U/µl is 0.4 µl. Reagents from Fermentas (Latvia) were used. The supernatant containing DNA was introduced into the reaction mixture in a volume of 5 µl.

The following pair of group-specific oligonucleotide primers for the *groEL* gene was used, which is characteristic for all representatives of the *Bacillus cereus* group and 3 pairs of species-specific primers for individual microorganisms, namely:

to *B. cereus* group BCGSH - 1F GTGCGAACCCAATGGGTCTTC *groEL*
BCGSH - 1R CCTTGTTGTACCACTTGCTC;
to *B. thuringiensis* type BTJH - 1F GCTTACCAGGGAAATTGGCAG *gyrB*
BTJH - 1R ATCAACGTCGGCGTCGG;
to *B. cereus* type nhe A F AAGGCGAATGTACGAGAGTGG *nhe A*
nhe A R CTTCTCTCGTTTGACTATCTGCAG;
to *Paenibacillus polymyxa* type 29Pp F GAGCGGGGTTGATTAGAAGC
179Pp R CTTTCCTCCTTCTCCCATGC ;
to Paenibacillus macerans type MAC 1 ATCAAGTCTTCCGCATGGGA
MAC 2 ACTCTAGAGTGCCCAMCWTT.

PCR cycles are primary denaturation at 94 °C for 5 min, 30 cycles of denaturation at 94 °C for 30 s, annealing at 63 °C for 30 s, elongation at 72 ° C for 30 s, final elongation at 72 °C for 5 min (Thermal cycler with BioRad software, USA). Primers were chosen on the basis of literature data [23–25] and synthesized by SPC "Simesta VAAL" (Odesa, Ukraine).

As a negative PCR control, deionized water was used to control the purity of the reagents. A visual evaluation of the size of the formed amplicons was carried out using molecular weight markers.

Electrophoresis of PCR products was carried out in a 1.5% agarose gel. Trisacetate buffer was used (Equipment for electrophoresis of PCR products from BioRad, USA). DNA was stained with ethidium bromide (0.5 µg/ml) and photographed with a video system (BioRad, USA) under UV light (wavelength 312 nm).

Results and discussion

Phenotypic identification of bacillary contaminants

The composition of microorganisms of food raw materials and products characterizes both the possibility of epidemiological risk and high-quality products. Table 1 presents a description of the morphophysiological and biochemical properties of 69 isolated strains of bacilli, the presence of spores in which does not modify the vegetative cell, and utilizing arabinose, mannitol and xylose with acid formation without gas (6 morphotypes). These cultures had the following general properties: medium-sized sticks (0.6-0.8) x (1.5-3.0) - (1.0-1.2) x (3.5-5.0) µm with elliptical spores located centrally and not exceeding the size of the cells. Also of them are gram positive; 25 isolates had pronounced mobility in diurnal culture.

Table 1

Description of the acid-forming bacilli of vegetable raw material and products

Characteristics	Properties of bacilli by morphotypes					
	I	II	III	IV	V	VI
Number of isolates taken for identification	20	16	6	12	10	5
Cell sizes, microns	(0,7–,8)× (2,0–3,0)	(0,6–0,8)× (1,5–2,0)	(0,6–0,7)× 2,0–2,5)	(1,0–1,2)× (3,0–4,0)	(1,0–1,2)× (3,0–4,0)	(1,2–1,5)× (2,5–3,0)
Growth on MPA in anaerobic conditions	–	+	–	+	+	–
Hydrolysis of starch	+	+	–	+	+9 cultures -1 culture	+
Reduction of nitrates	+	+	–	+	+	+
Decarboxylation of tyrosine	–	–	–	+	+8 cultures ±2 cultures	+
Hemolytic activity	–	–	–	+	+	–
Lecithinase activity	–	–	–	+	+	–
The reaction of Voges-Proskauer (production of acetoin)	+	+	+	+	+	–
Production of acid from arabinose, xylose, mannitol	+	A+ G±	+	–	–	+3 cultures –2 cultures
Intended view	*Bacillus subtilis*	*Bacillus licheniformis*	*Bacillus pumilis*	*Bacillus cereus*	*Bacillus thuringiensis*	*Bacillus megaterium*

All cultures have an aerobic type of respiration (catalase-positive), but 38 of them also showed the ability to grow on MPA under anaerobic conditions. Of the other common properties, all isolated cultures with varying degrees of intensity exhibited the ability to liquefy gelatin, hydrolyse casein, assimilate glucose, lactose, sucrose to produce acid without gas production, but only 45 of them developed on media with mannitol, xylose or arabinose. To the utilization of tyrosine, the ability was detected in 27 isolated cultures, for two it was not established reliably. With the exception of six isolates, all reduced nitrates to nitrites. Twenty-two cultures showed lecithinase activity.

Determination of the proportion of isolated acid-forming bacilli from the identified (%) allows them to be arranged in descending order in the following order: *Bacillus subtilis*-*Bacillus licheniformis* > *Bacillus cereus* > *Bacillus megaterium* > *Bacillus pumilis* ≥ *Bacillus thuringiensis*.

According to the totality of the morphological and cultural features of the isolated cultures of the first and second morphotypes studied by us, it can be concluded that, with a common coincidence of most of the individual indices, they differ among themselves by few (the relief of the colonies - representatives of the I morphotype on the MPA formed small grayish shiny colonies and II morphotypes - blurred; representatives of the first

morphotype, when sown with a prick, gave crater-like liquefaction of gelatin, representatives of the second morphotype were saccular, and representatives of the I and II morphotypes opacity and thin film were formed on MPB, but in the second case, the broth was cleared, the representatives of the first morphotype alkalized the milk during peptonization) and can be combined into the group *subtilis-licheniformis*. These cultures accounted for the largest proportion of bacilli found on raw materials. It is these microorganisms that most often constitute the permissible aerobic microbiota of heat-treated benign products intended for long-term storage [20].

From Table 1 description it becomes created that bacillus of the *subtilis-licheniformis* group, six cultures from the third morphological group were distinguished by smoother, whitish shiny colonies on MPA growing into a substrate, formation of a thin film on the MPB, and opacity, peptonization of milk without clotting; crater-like liquefaction of gelatin during inoculation in a stalk, lack of amylase and tyrosinase activity and the ability to reduce nitrates. Presumably they were attributed to the species *Bacillus pumilis*, whose number was insignificant and amounted to no more than 10.8% of the total number of bacilli that contaminated the investigated raw materials.

In the fourth group of cultures, smooth grayish-white colonies formed on the MPA, caused an opacity of the MPB and the formation of a sediment, did not change the kind of milk, did not liquefy gelatin when planted with a prick, forming a brilliant coating on the surface. They split maltose, did not split mannitol. In the early stages of growth on glucose agar, the cells contained fat globules. Disputes formed quickly. All cultures exhibited lecithinase activity on the yolk agar, formed acetoin and characteristic ruby colonies on salt agar with 2,3,5-triphenyltetrazolium chloride, as well as indole, which confirmed their difference from *B. pumilis* and microorganisms of the *subtilis-licheniformis* group. This allowed us to define them as *B. cereus*. On the types of plant raw materials studied, *B. cereus* varieties comprised between 8.5 and 29% of the total number of bacilli.

Colonies of group V bacilli are roundish, greyish-white, with a pasty consistency, a matte surface, like *B.cereus*, with a slightly-wavy margin. Presumably, this group can be formed by strains of *B. thuringiensis*. On the investigated vegetables, *B. thuringiensis* species were small, but prevailed on parsley and spices.

An important reference point in the identification of group VI bacilli was the size, cell structure, folded macrorelief of the colony, which differentiate them from the species described above. Colonies on MPA are round, thick, convex, whole, shiny, slimy. With the age of the culture, the substrate is colored brown. On the MPB, the growth is meager in the form of haze, forming a greyish surface coating on the gelatinous media, when planting with a stab in the column - liquefaction in the form of a crater. Milk does not roll, peptonizes. In old cultures, the growth in MPA revealed fat. Representatives of the sixth group were identified as *B. megaterium*. Reactions of tyrosine cleavage and reduction of nitrates varied depending on the age of the culture. The heat-resistant strains of these bacilli in the samples were also small: 4–14%.

The bacilli described in Table 2, are gram-positive mobile rods whose spores are larger in diameter than the thickness of the cells and are subterminal or terminal. They form catalase, but are able to grow on MPA under anaerobic conditions, and also hydrolyze starch, casein, reduce nitrates to nitrites, do not form indole, lecithinase and tyrosinase. In contrast to the bacilli described in Table. 1, when cultivated on media with arabinose, xylose and mannitol form a gas along with the acid.

The group of bacilli VII is made up of microorganisms that grow poorly on MPA with the formation of thin round beige widespread colonies. They cause turbidity of the MPB and form a mucous precipitate. The Gram-staining of cells during cultivation on different

media showed variability. These bacilli do not decarboxylate tyrosine and do not form acetylmethylcarbinol, liquefy gelatin. On a gelatinous medium, a weak surface coating is formed, they do not cause liquefaction during seeding. Starch hydrolyzed completely - to mono- and disaccharides. Milk coagulate with the formation of gas, utilize glucose, lactose, maltose to form acid. The complex of the revealed properties of this group basically coincides with the description of bacilli of the species *B. macerans* (formerly called *B. aerosporus*), which are currently reported to be of the genus *Paenibacillus* [26].

Table 2

Description of the acid- and gas-forming bacilli of vegetable raw material and products

Characteristics	Properties of bacilli by morphotypes		
	VII	VIII	IX
Number of isolates selected for identification	15	19	14
Cell sizes, microns	(0,5–0,6)× (3,0–4,0)	(0,6–0,7)× (2,0–3,5)	(0,7–1,0)× (2,0–3,0)
Hydrolysis of casein	–	+	+
Gelatin liquefying	+	± weak reaction	±
Production of acetoin	–	+	–
Decarboxylation of tyrosine	–	–	–
Intended view	*Paenibacillus macerans*	*Paenibacillus polymyxa*	*Bacillus circulans*

A distinctive feature of the *Bacillus* group VIII is the formation of mucus on dense and liquid substrates and slow liquefaction of gelatin. On MPA form grayish shiny large colonies, on the MPB – turbidity, sediment, surface film of grayish color. Milk does not coagulate, does not form an indole. The starch is hydrolyzed, gelatin liquefies slightly (bag-like liquefaction). These bacilli can presumably be attributed to varieties of *P. polymyxa*.

Group IX was made up of bacilli, which form thin spreading colonies on the surface of the MPA. Causes mild turbidity of the MPB and mild acid formation in milk (slow coagulation). On gelatinous media grow in the form of a slight surface coating, when inoculation with a prick growth was absent. Glucose, lactose, sucrose is digested with the production of acid. Three isolates in this group after growing on different substrates stained Gram variably, the rest - positively. By the type of respiration they are classified as facultative anaerobic microorganisms. They do not form acetoin, slowly dilute gelatin, hydrolyze casein. According to most of the characteristics, the description corresponds to *B.circulans*, a number of strains which belong to the genus *Paenibacillus* [27]. This species is considered mesophilic, but the literature notes the presence of thermophilic variants [1].

Detection of bacilli VII-IX morphotypes in raw materials draws attention to the need for their control in packaged products and after heat treatment (in particular, preserves, canned food) as potential causative agents of bomb damage.

Acid-forming and gas-forming bacilli on the studied raw materials are represented by a relatively small amount – from 2–4% on strawberries to 15% on green peas from the total number of allocated bacilli.

It should be noted that the morphophysiological, cultural and biochemical properties of the studied cultures did not always show convincingly. On different media, some R-form colonies transformed into S-form colonies, which made it difficult to identify themselves by

culture and tinctorial characters. Identification difficulties prevented the introduction of the characteristics of some crops into tables and clearly determined the proportion of isolates studied in the total number of bacilli found on the raw materials examined. As studies have shown, the precise identification of bacillary species of microorganisms by classical methods is not only time-consuming, laborious, but often difficult to accurately identify.

PCR detection of B. cereus in food samples

Since the microorganisms of the *B. cereus* group cause foodborne illnesses and are potentially enterotoxigenic for humans, the ability to rapidly detect *B. cereus* in food is critical [1, 5–7, 23, 28].

To choose more efficient pretreatment method of raw samples and products for detection of enterotoxin-producing *B. cereus*, samples were inoculated with the culture of each test strain of bacilli and further experiments with DNA release from strains *B. cereus* ATCC 11778, *B. cereus* ATCC 10702, *B. cereus* UCM B 5650 and *B. cereus* UCM B 5671 were carried out in three variants: inoculated bacteria samples without pretreatment (wells 7, 9, 10), and the samples previously centrifuged to remove organic residues and filtered through «Millipore» nitrocellulose membrane filters (wells 1, 4), and the samples centrifugated twice in developed modes (wells 3, 11, 12, Figure 1).

It was revealed that pre-treatment of samples is desirable for the detection of toxin-producing *B. cereus* in plant raw materials and products using PCR: on the electrophoregram the amplicons that were formed in the case of filtering were more clear, however, preliminary preparation with double centrifugation was most effective (Figure 1).

Thus, the method of preliminary treatment of samples of plant raw materials and products with double centrifugation: the first - to remove the residues of organic substances of the product and the second for the concentration of microorganisms. Sampling regimes have been submitted for priority and they have been used for further research.

To confirm the specificity of PCR, the *B. cereus* strain UCM B 5671 was tested with the nhe primer to the enterotoxigenic gene *nhe A* (well 17). The size of the amplicon formed was 553 bp. Thus, by the PCR method, the ability to form an amplicon at 400 bp to the gene *groEL*, which is characteristic for all representatives of *B. cereus* group.

B. cereus causes diarrhea and emetic syndromes, producing various extracellular toxins, including the three main types of enterotoxins, namely hemolysin BL (*hbl*), nonhemolytic enterotoxin (*nhe*) and cytotoxin K (*cyt K*) [13].

Among the strains of *B. cereus*, enterotoxigenic genes *hbl A, nhe A, cyt K* and *Fm* (enterotoxin FM) were widely spread. However, we selected only the *nhe A* gene for PCR, given its greatest prevalence and detectable toxicity, which is associated with a major role in food poisoning. The polymerase chain reaction with specific primers nhe A F and nhe A R, matched to the site of the *nhe A* gene, confirmed the belonging of all tested collection strains of *B. cereus* to the enterotoxigenic species of *B. cereus*, whereas in PCR analysis of the DNA of the collection species *G. stearothermophilus* and *P. polymyxa* and in negative control (PCR mixture without DNA), no amplification products were detected. The size of the amplicons was 553 bp, which indicated the proper specificity of the PCR.

PCR results with product samples containing different combinations of bacterial strains using specific species-specific primers are shown in Figure 2.

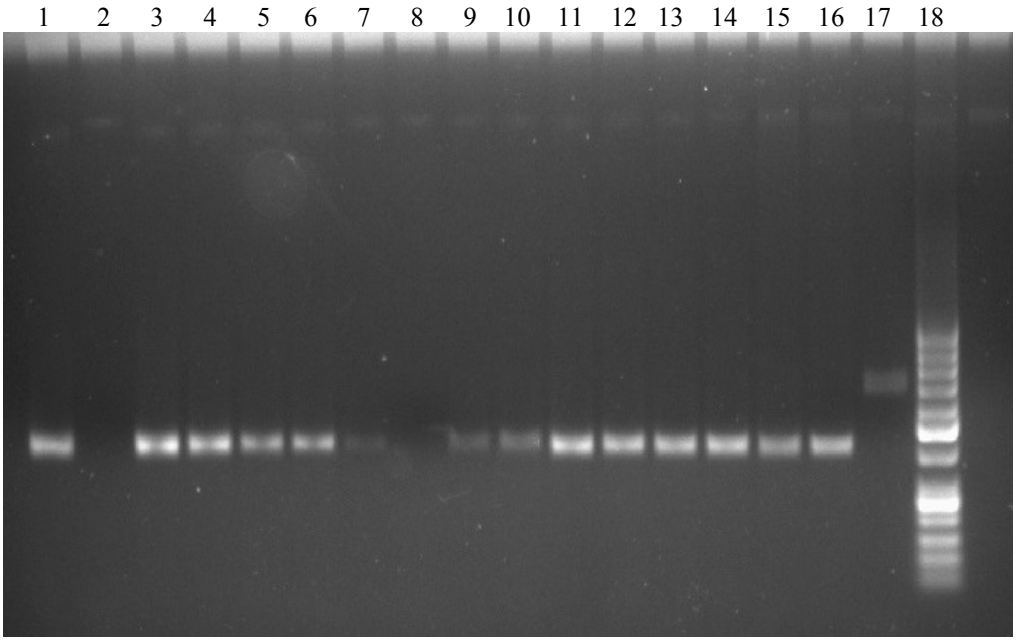

Figure 1. Electrophoregram of PCR products with DNA of strains of *Bacillus* spp. with a pair of specific oligonucleotide primers to the gene *groEL*:

1. *B. cereus* UCM B 5671 (using a membrane filter)
2. Negative PCR control;
3. *B. cereus* ATCC 11778 (using centrifugation)
4. *B. cereus* ATCC 10702 (using centrifugation)
5. *B. cereus* UCM B 5650 (using a membrane filter)
6. *B. cereus* UCM B 5671 (using a membrane filter)
7. *B. cereus* UCM B 5671 (without filtration)
8. Do not inoculate bacteria from cans;
9. *B. cereus* ATCC 11778 (without filtration)
10. *B. cereus* ATCC 10702 (without filtration)
11. *B. cereus* P90-1 (using centrifugation)
12. *B. cereus* P90-4 (using centrifugation)
13. *B. cereus* P90-9 (using centrifugation)
14. *B. cereus* L-3 (using centrifugation)
15. *B. cereus* L-6 (using a membrane filter)
16. *B. cereus* L-7 (using a membrane filter)
17. *B. cereus* UCM B 5671 with the primer nhe A;
18. Molecular weight markers (pBR322 / BsuRI, Fermentas).

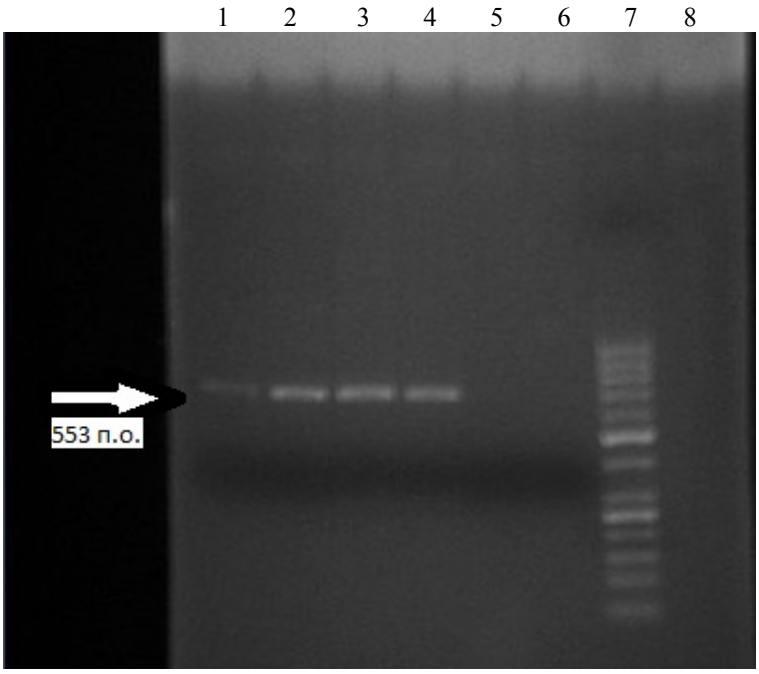

Figure 2. Electrophoregram of PCR products with DNA strains of *B. cereus, P. polymyxa, P. macerans, E. coli, S. aureus, C. perfringens, G. stearothermophilus* species with a pair of specific oligonucleotide primers to the *nhe A* gene:

1. A mixture of *B. cereus* strains (*B. cereus* ATCC 11778, *B. cereus* ATCC 10702, *B. cereus* UCM B 5650, *B. cereus* UCM B 5671);
2. A mixture of strains of *B. cereus*, *P. polymyxa* and *P. macerans* (*P. macerans* B 5803^T, *P. polymyxa* B 5760^T, *B. cereus* ATCC 11778, *B. cereus* ATCC 10702, *B. cereus* UCM B 5650, *B. cereus* UCM B 5671);
3. A mixture of *B. cereus* and *P. polymyxa* strains (*P. polymyxa* B 5760^T, *B. cereus* ATCC 11778, *B. cereus* ATCC 10702, *B. cereus* UCM B 5650, *B. cereus* UCM B 5671);
4. A mixture of *B. cereus* and *P. macerans* strains (*P. macerans* B 5803^T, *B. cereus* ATCC 11778, *B. cereus* ATCC 10702, *B. cereus* UCM B 5650, *B. cereus* UCM B 5671);
5. *C. perfringens* and *G. stearothermophilus* UCM B 718;
6. *Staphylococcus aureus* ONU 223;
7. Molecular weight markers (pBR322 / BsuRI, Fermentas);
8. *Escherichia coli* UCM B 906.

Primers nhe A F and nhe A R formed an amplicon sized 553 bp in PCR with *B. cereus* strains, primers 29Pp F, 179Pp R formed an amplicon with a size of 150 bp with strains of the species *P. polymyxa*, primers MAC 1, MAC 2 formed an amplicon with a size of 100 bp with strains of the species *P. macerans*. In PCR using the DNA of gram-negative bacteria *Escherichia coli* UCM B 906 and gram-positive bacteria *Staphylococcus aureus* ONU 223, *C. perfringens* and *G. stearothermophilus* UCM B 718, which were conducted to verify the authenticity of the results of detection of natural contamination of specimens by food poisoning and product damage agents, no amplification product was obtained. The results of detection of strains of the *B. cereus* species by the presence of the *nhe A* gene in the studied plant products are shown in Table 3.

Table 3

***B. cereus* contamination of plant raw materials and products of their processing**

Product type	Number of samples, n	Number of samples that contain *B. cereus*	Proportion of contaminated samples, %
Fresh fruit	12	2	16,7
Fresh berries	9	3	33,3
Fresh vegetables	34	21	61,8
Canned food with signs of spoilage	9	4	44,4
Dried vegetable mixes	16	7	43,7
Spices	11	8	72,7
Dried herbs	14	10	71,4
Vegetables boiled in vacuum polymer bags	12	2	16,7

Comparing the results with those given for vegetables from the city of Mexico, it is possible to note practically the same trends of detection of *B. cereus* for most types of fresh vegetable raw materials – 61.8% and 57% for the Ukrainian and Mexican regions, respectively [29]. And as noted by Valero et al. [30] in Spain, all samples of fresh raw materials - peppers, cucumbers, tomatoes, carrots, zucchini, onions - were contaminated with *B. cereus*. This, according to INFOSAN [31], leads to an increase in the incidence of foodborne illness.

Conclusions

Bacillary microbial contaminants and agents of food poisoning of plant raw materials and products of the Ukrainian region were identified. The composition of microbiota of various types of vegetable raw materials – vegetables, fruits, berries – and products of their processing were studied. A feature of plant raw materials of Ukraine is the dominance of rod-shaped spore-forming microorganisms of the *Bacillales* order of the group *subtilis-licheniformis*. To accelerate the indication of the potential hazard of products for consumers, a method for preparing food samples was tested and PCR with group-specific and species-specific primers was performed in order to diagnose strains of *B. cereus, P. polymyxa* and *P. macerans* microorganisms in samples. The contamination of samples of plant raw materials and products of their processing with epidemiologically significant microorganism *B. cereus* were examined, and showed levels from 16.7% in fresh fruits to 72.7% in spices from the total number of samples.

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Walnuts Respiration (Juglans regia L) during storage

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Abstract

Introduction. The respiratory rates of English walnut (*Juglans Regia L.*) and factors that may affect it were studied.

Materials and methods. The walnut respiration intensity was determined by the confined atmosphere process. It was used the CO_2 capture method removed from the product with alkaline solution. To assess the influence of temperature on the respiration intensity of unshelled walnuts and walnut kernel, they were kept under four temperature regimes: 6±2, 18±2, 30±2 and 50±2 °C.

Results and discussion. Respiration is one of the oxido-reduction processes that can lead to the oxidative degradation of walnut lipids, respectively their qualitative degradation.

Walnut moisture content is one of the main factors influencing the respiratory rate. Initial respiration intensity of the walnuts is high, but falls sharply in the first 15 days of storage. This decrease being related to the reduction in walnut moisture. The respiration intensity of walnuts decreases slightly after 15 days of storage.

There was established a relationship between the respiration intensity and environmental temperatures. The maximum of respiratory rates were at 30 °C.

Respiration intensity of the walnut kernel is greater than that of the unshelled walnuts, the shell serving as a barrier to the direct contact between the kernel lipids and oxygen. The walnut kernel respiration intensity increaces from 5 mg to 23 CO_2/kg·h at an increase of temperature from 5 to 30 °C. At a further increase of temperature to 60 °C the respiration intensity reduces to 15 CO_2/ kg·h. The unshelled walnut respiration intensity increaces from 5 mg to 17 CO_2/ kg·h at an increase of temperature from 5 to 30 °C. At a further increase of temperature to 60 °C the respiration intensity reduces to 12 CO_2/ kg·h.

It is noted that the walnats lipids acidity index correlates with the storage temperature, but more pronounced in the case of the kernel and slower for unshelled walnuts. The acidity index of the lipids of and unshelled walnut and kernel doesn't change at an increase of temperature from 5 to 15 °C and it is approximately 0.35 mg NaOH/g prod. At a further increase of temperature to 40 °C the lipid acidity index increases to 0.8 NaOH/g prod (for the kernel) and 1.1 (for unpurified walnuts). At a further increase of temperature to 60 °C, the lipid acidity index reduces to 0.6 NaOH/g prod.

Conclusions. Walnut respiration may be limited by low temperatures storage. It is therefore important to ensure storage stability by complying with the limit values for the water content of walnuts. Fruit morphologiacal state also affects the respiration intensity, this parameter being greater for kernels than for unshelled fruits, the differcence being due to shell which servs as a barrier to the direct contact between the kernel and the oxygen.

Introduction

Worldwide walnuts are recommended as a constituent of balanced human nutrition. The high protein and oil contents of the kernels of Juglans regia L. (Juglandacea) make this fruit indispensable for human nutrition [13]. Walnuts contain about 65% lipids with a very high level of unsaturated fatty acids making fruits prone to lipid degradation.

In Moldova, walnuts have been and continue to be a valuable agricultural product. Moldova is favorably positioned from a geographical point of view, on both climatic and pedological conditions for the cultivation of nuts [1], being among the top ten kernel and unshelled walnut producers in the world [2], The volume of production reaching about 30 thousand tons per year [3]. Since the year 2000 the walnut culture has known a substantial evolution in the Republic of Moldova, greatly sustained by the joint efforts of some active promoters and of the Government financial assistance. [12]

Storage of fresh harvested walnut for a certain period of time - is one of the most important processes [4], being paramount importance in quality maintenance. Walnut fruits may be stored either in-shell or shelled. A general belief is that fruits are better preserved when stored in-shell than after shelling. However, the former method has two disadvantages. The first is that in-shell nuts occupy a far greater storage volume. The second is that a larger percentage of nuts are damaged mechanically during shelling since the in-shell nuts are stored at low moisture content (m.c.) to prevent degradation during storage. The higher the level of broken nuts, the lower is the deterioration percentage of the seeds [18].

The main walnut quality concerns are rancidity, mold growth, insect infestation, and stale flavor. Earlier, Prabhakar (1977) reported that development of undesirable odours occurred in walnut kernels when stored at higher humidity and free fatty acid content increased with increase in temperature and storage period [14].

Changes of the chemical compounds of walnuts is carried out in several ways, but the basic direction is respiration, which in fact presents a range of biochemical oxidation - reduction reactions.

Respiration is one of the oxido-reduction processes that can lead to the oxidative degradation of walnut lipids, respectively their qualitative degradation.

In spite of having been removed from the tree, walnuts remain as living organs after harvest. They are living organs in which respiration processes predominate, because their supply of new nutrients has been cut off by separation from the parent plant. Throughout respiration, product nutrients (carbohydrates or lipids) are broken down to their constituent parts to produce energy to run cellular processes, thus keeping the cells and organism alive.

As respiration continues, compounds that affect plant flavor, sweetness, weight, turgor (water content), and nutritional value are lost [11]. It is obvious that the rate or intensity of respiration depends on the chemical composition of the walnut kernel, the degree of maturation and other external factors such as temperature, oxygen concentration in the air, etc [5–6].

There is little the postharvest physiologist can do to alter the internal factors affecting respiration of harvested commodities, since they are largely a function of the commodity itself once harvested. However, a major part of postharvest technology is devoted to reducing respiration and other metabolic reactions associated with quality retention by manipulating the external environment.

Without a doubt, the most important factor affecting postharvest life is temperature. This is because temperature has a profound affect on the rates of biological reactions, eg., metabolism and respiration. Over the physiological range of most crops, ie., 0 to 30 °C (32

to 86 °F), increased temperatures cause an exponential rise in respiration. The Van't Hoff Rule states that the velocity of a biological reaction increases 2 to 3-fold for every 10 °C (18 °F) rise in temperature [15–17]. Additional information on respiration rates at different temperature levels is needed for the solution of practical problems concerned with storage and transportation of fresh.

For this reason, the purpose of this study was to investigate the walnuts respiration intensity, as well as its dependence on the morphological state of stored fruits (nuts in shell or kernel) and on the temperature of the storage medium.

Materials and methods

Materials

Walnult fruits, variety Calarasi, were collected from local walnut plantation, Iargara, Moldova. All chemicals used for experiments were at least analytical grade.

Sample preparation

Each sample was prepared for the experiment by first eliminating unsound or injured specimens.The sample was then divided into two or more weighed lots for the measurement of the rate of respiration at different temperatures. After weighing, each lot of fruit was kept at the temperature at which it was desired to measure the rate of respiration for several hours or overnight before starting the experiment

Method

To assess the intensity of respiration, as well as the influence of temperature on it, were used both nuts in shell and kernel.

To assess the influence of temperature on the respiration intensity of unshelled walnuts and kernel, they were kept under four temperature regimes: 6 ± 2^0C, 18 ± 2^0C, 30 ± 2^0C and 50 ± 2^0C. The respiration intensity was determined by the confined atmosphere process as recommended by Boysen -Jensen [7]. The CO_2 capture method removed from the product with alkaline solution is the most perfect and most commonly used in scientific work.

The apparatus used in the measurement of respiration intensity consists of a desiccator provided with a vertical tube filled with granulated sodium hydroxyde. The air entering the desiccator was first drawn through the tube to free it from carbon dioxid. The dessicator bottom was supplied with a Petri dish containing sodium hydroxide solution, this way the eliminated CO2 through respiration processes is capted by this solution. Then, the method of double titration was used, in which phenolphthalein and methyl orange are employed successively.

Normal hydrochloric acid was added to the alkaline solution, in presence of phenolphthalein, until it was colorless. Methyl orange was then added and the titration finished.

Results and discussion

Respiration is affected by a number of environmental factors such as light, temperature, chemical stress, pathogen attack, the action of radiation, the action of humidity, etc. The most important post-harvesting factors are temperature, atmospheric composition and physiological state.

The process of respiration of the fruit is relatively large topic discussed in the scientific literature and specialist, but the studies on Juglans Regia nuts are very limited [8-10], and on the nuts grown in Modova are totally lacking. The evolution of respiration intensity of fresh nuts (directly after harvesting) stored at 20 °C was monitored for 60 days from storage. Following the conventional method of expressing the degree of respiratory activity, the results of these experiments are reported in terms of carbon dioxide production.

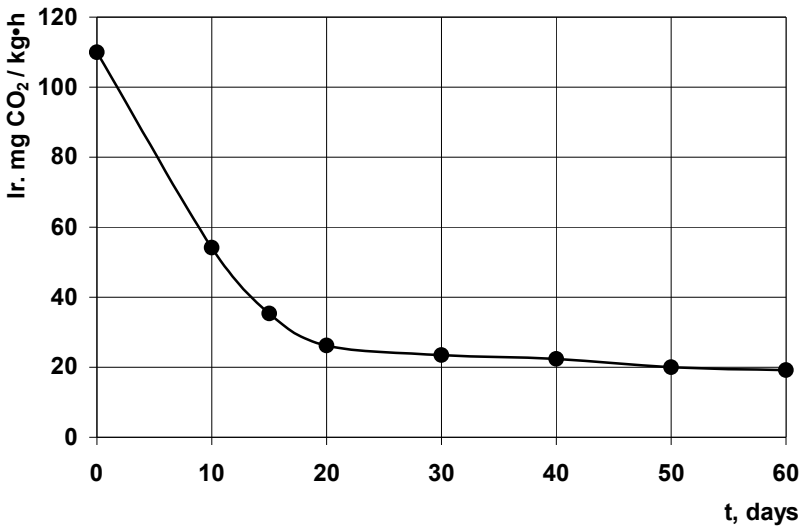

Figure 1. Evolution of respiration intensity of fresh harvested walnuts

Initial respiration intensity of the walnuts is quite high, but falls sharply in the first 15 days of storage. In the following period, the respiration rate continues to decrease at a much lower rate. This decrease is likely (at least in part) related to the reduction in walnut moisture from 20% for fresh walnuts to 12% after 15 days and 8% - towards the end of storage.

In order to identify the impact of the ambient temperature and the walnuts morphological state on the respiration process, the respiration intensity of unshelled nuts (dried up to W = 8%) and of the walnut kernel at different temperatures was studied. The results obtained are shown in Figures 2 and 3.

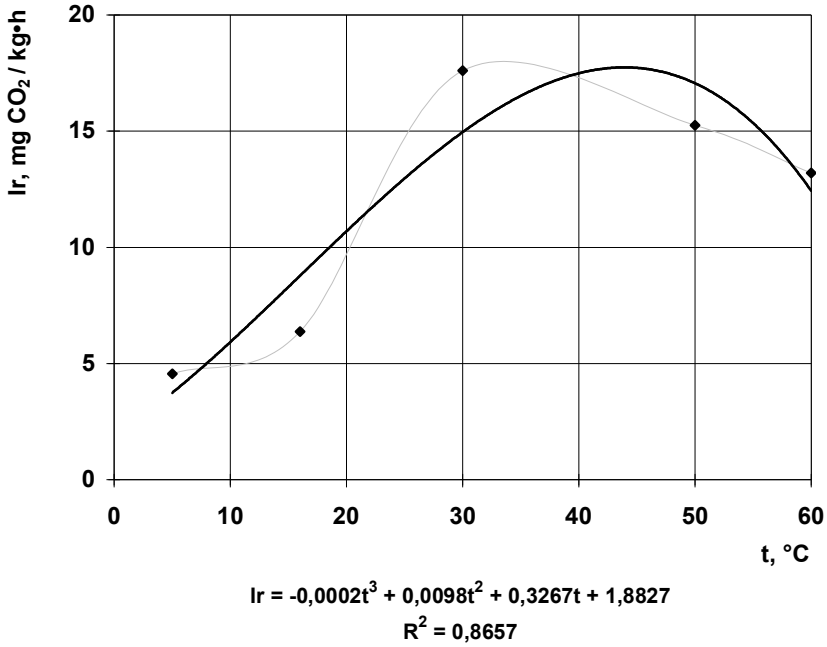

Figure 2. Dependence of the unshelled walnut respiration intensity of the ambient temperature

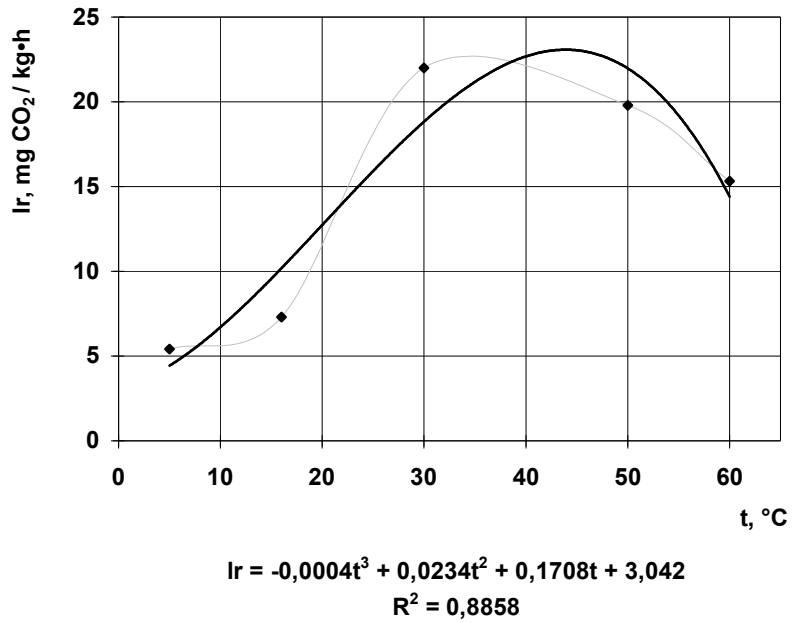

Figure 3. Dependence of the walnut kernel respiration intensity of the ambient temperature

The obtained data reflects the respiration intensity of unshelled walnuts. Maximum values of this indicator were obtained by storing walnuts at 30 °C (17.6 mg CO_2/kg·h), after t> 40 °C the intensity of walnuts tends to decrease.

It has been found that the respiration intensity of the walnut kernel is greater than that of the unshelled fruits. It is worth mentioning that this differcence is probably due to shell which servs as a barrier to the direct contact between the kernel and the oxygen. When shelled, walnut lipids react with atmospheric oxygen which enters into an addition reaction with unsaturated fatty acids through the simultaneous assistance of light, heat and certain fat companion substances. Rancidity caused by oxidative fat cleavage is particularly noticeable in the case of shelled walnuts, because the shelling process results to a certain degree in exposure to atmospheric oxygen.

From the figures and presented equations we deduce that the respiration rate of walnuts depends largely on the temperature of their storage. Respiration intensity in both cases (shelled and unshelled fruits) increases slowly with increasing temperature from 4 to 20 °C, then suddenly rises to the maximum value at temperatures of about 30–40 °C, followed by a decrease in respiration intensity at higher temperatures.

Increased respiration intensity in the temperature range 20–37 °C can be explained by increasing the activity of lipases that induce lipid hydrolysis processes and increase the amount of substrate (fatty acids) for respiratory processes. Endogenous lipids in the walnut kernel hydrolyze lipids to glycerin and free fatty acids, which are then oxidized to produce the energy required for plant biological activity. At temperatures above 40°C enzymes are denatured and inactivated.

Hence, lipid hydrolysis was mentioned, the dependence of the acidity index (expressing the free fatty acid content) of lipids of walnuts held at different temperatures was studied. The obtained results are shown in Figure 4.

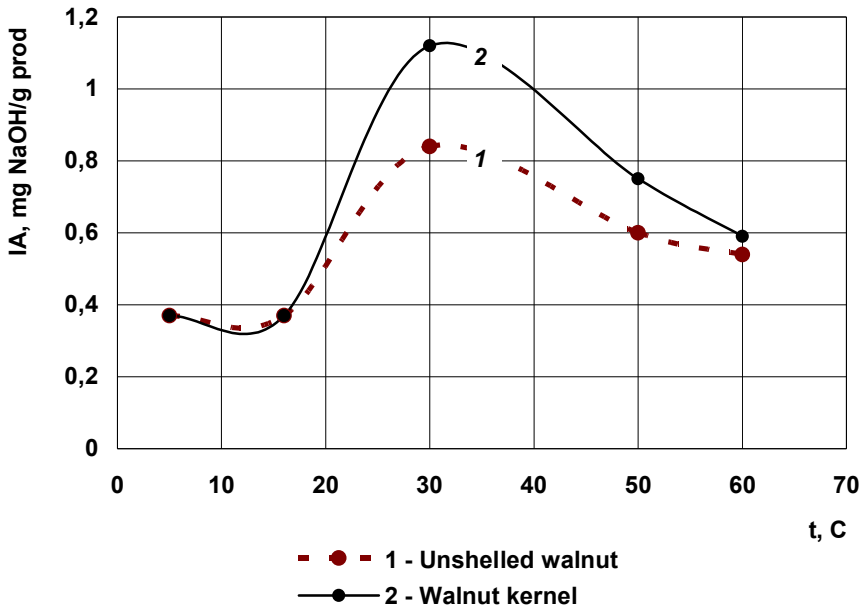

Figure 4. Dependence of acidity index of unshelled walnut and kernel lipids of storage temperature

It is noted that the acidity index correlates with the storage temperature, but more pronounced in the case of the kernel and slower for unshelled walnuts.

Conclusion

In walnuts (particularly when fresh), metabolic processes continue even after harvesting. They absorb oxygen and excrete carbon dioxide (CO_2).

Initial respiratory intensity of walnuts is quite high, but drops sharply in the first 15 days of storage. This decrease is associated with the walnut moisture content, that is why it is therefore important to ensure storage stability by complying with the limit values for the water content of the walnut fruits.

A relationship has been established between respiration intensity and storage temperature, as the temperature increases product respiration rate increases sharply and at 30 °C reaches a maximum.

Storage conditions and fruits morphological state (shelled or unshelled fruits) affect respiration intensity, thus, reducing the rate of respiration is an important consideration in extending the postharvest life of walnut fruits and optimizing postharvest quality.

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Influence of maize germ oilcake on processes of wheat dough ripening and bread quality and nutritional value

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Abstract

Introduction. The influence of maize germ oilcake on processes of wheat dough final ripening, as well as on bread nutritional and biological value was studied.

Materials and methods. The following materials were used in the studies: maize germ oilcake, wheat flour of the first quality, bakery pressed yeast, salt, potable water. The intensity of ethanol fermentation was determined on the basis of gas production rate in the dough and intensity of lactic-acid fermentation – on the basis of change of its titratable acidity. The bread quality parameters, as well as its nutritional value were studied by generally accepted methods.

Results and their discussion. The results of experimental studies have shown that substitution of wheat flour with 10.0 to 20.0% of maize germ oilcake promotes intensification of acid accumulation and gas production in the dough, which is the basis for shortening the interval of its ripening by 6.0 to 17.0%. At the same time, reduction of the dough volume is observed as the additive dosage is increased. The bread manufactured by straight-dough method with addition of the maize germ oilcake has a pleasant corn aftertaste and flavor, more intensively colored crust and soft part, higher moisture and titratable acidity parameters, in comparison with the check sample. Introduction of more than 15% of the additive leads to a substantial decrease of porosity parameters and bread specific volume that makes it impossible to recommend its greater dosage in case of straight method of bread manufacture.

The bread manufactured with the use of 15% of the maize germ oilcake is characterized by a higher content of lysine, cystine, methionine and threonine unsubstituted amino acids, higher content of dietary fibers by 1.7 times, vitamins B_1 – by 1.4 times, E – by 3.0 times, magnesium – by 2.2 times, iron – by 2.3 times.

Conclusion. Use of 15% of maize germ oilcake in case of straight method of bread manufacture makes it possible to obtain the products of high quality and increased nutritional and biological value.

Introduction

One of the global problems of today is propagation among population of the most countries of alimentary diseases caused by unbalanced diet. The modern method of its solution consists in increase of nutritional and biological value of every-day consumption products, including breadstuffs. It is known that traditional bread types having a high energy value are characterized by unbalanced amino acid composition, low content of dietary fibers, low content of many vitamins and mineral substances. Therefore, an important task of bread-making branch consists in forming the range of breadstuffs enriched with physiologically functional ingredients. A promising way of task-oriented change of breadstuff chemical composition is provided by use of in breadstuff technology of products obtained in flour-milling and fat-and-oil industries and during cereals manufacture.

To increase the nutritional and biological value of bread, we proposed to use maize germ oilcake being a byproduct in technology of maize oil manufacture. The maize germ oilcake comprises a finely dispersed powder characterized by a high content of protein (20.0%), starch (25%), as well as dietary fibers (22.5%) which are mainly represented by hemicelluloses and cellulose. It contains 29.7 mg/100 g of vitamin E, 0.73 mg/100 g of vitamin B_1 and 5.6 mg/100 g of vitamin PP, as well as considerable quantity of mineral substances, such as calcium, magnesium, phosphorus and iron [1].

It is known that use of enriching raw materials in bread technology influences not only on nutritional value of finished products but also on progress of processes of dough ripening, including microbiological ones [2-5]. The microbiological processes are one of key factors determining bread quality. Intensity of ethanol fermentation largely determines volume of dough pieces and finished products, and lactic-acid fermentation products play an important role in forming organoleptic, physical and chemical properties of dough and bread.

The objective of these studies, which results are presented below, was determination of influence of the maize germ oilcake on progress of microbiological processes taking place during ripening of wheat dough, as well as on parameters of bread quality and its nutritional and biological value.

Materials and methods

In our studies, we used maize germ oilcake (Table 1), wheat flour, pressed bakery yeast, food-grade cooking salt and potable water.

To obtain the check sample of bread, we kneaded 44% moisture dough of wheat flour with addition of 3.0% of pressed bakery yeast, 1.5% of salt, as well as potable water. To obtain the test samples, the maize germ oilcake was introduced in the stage of dough kneading in dry condition in quantity of 10.0, 15.0 and 20.0% instead of flour. With consideration of the data on water-absorbing capacity of dough in case of introduction of additive [6] obtained earlier, its moisture contents in the test samples were 44.8, 45.3 and 45.7%, respectively. All dough samples were subjected to ripening. The ripened dough was divided to 280 g pieces, which were rounded, placed in baking tins, held there for (30 to 40)×60 s at a temperature of 37 °C and baked for 30×60 s at a temperature of 180 to 220 °C.

Table 1

Quality parameters of maize germ oilcake

Parameter	Description of parameter
Appearance	Finely dispersed dry powder
Taste	Pleasant sweetish corn taste
Flavor	Pleasant corn flavor
Color	Light yellow
Titratable acidity, deg.	7.8
Moisture, %	13.8

The influence of maize germ oilcake on dough ripening microbiological processes was studied by change of parameters of gas production rate and titratable acidity in the dough, as well as by change of its volume during fermentation.

The gas production rate in the dough was determined with the help of Iago-Ostrovsky instrument [7]. To determine quantity of gas released during fermentation, a 500 см^3 conical flask with 100g of dough was put into thermostat at a temperature of 30 ºC. The flask with dough was closer with rubber plug having a tube connecting it with other flask filled with sodium chloride saturated solution. The quantity of gas released during fermentation corresponds to quantity of displaced sodium chloride saturated solution.

To determine change of volume during fermentation, 50 g of kneaded dough was placed in 250 cm^3 graduated cylinder previously lubricated with oil, which was held in thermostat at a temperature of 30 ºC. The initial volume of dough and its changes during fermentation were recorded.

The titratable acidity was determined by method described in [7]. For this purpose, 5 g of dough was rubbed with 50 cm^3 of water, 3-5 drops of 1% phenolphthalein solution were added, and then the obtained solution was titratable with 0.1 mol/dm^3 solution of sodium hydroxide till appearance of pink color not disappearing for one minute. The acidity was calculated with the use of the following formula:

$$X = \frac{a \cdot 100}{G \cdot 10} \cdot K, \tag{1.2}$$

where X – titratable acidity, deg.;

a – quantity of milliliters of 0.1 mol/dm^3 solution of NaOH used for titration;

G – mass of accurately weighed substance, g;

10 – conversion from 0.1 mol/dm^3 to 1 mol/dm^3 of alkali solution;

K – correction coefficient for alkali titer.

The assessment of organoleptic parameters of product quality (appearance, color, condition of crust, condition of soft part, taste and flavor) was carried out after the bread was fully cooled [8]. The physical and chemical parameters of quality, such as moisture, specific volume and porosity, were determined with the use of generally accepted procedures [9–11].

For determination of bread titratable acidity, 25 g of its soft part was placed in a flask having capacity of 500 cm^3, where 250 cm^3 of water having temperature of 20 ºC was added. The flask was closed with plug and vigorously shaken for 2×60 s, settled for 10×60 s, shaken for 2×60 s and settled again for 8×60 s. Then the solution was filtered, 50 cm^3 of the filtrate were taken with pipette and transferred in two 150 cm^3 conical flasks, 2-3 drops

of phenolphthalein solution were added, and titration was carried out with 0.1 mol/dm^3 solution of sodium or potassium hydroxide till appearance of light pink color not disappearing for 1×60 s [11].

The titratable acidity was calculated with the use of the following formula:

$$K = 2 \cdot \nu, \tag{1.3}$$

where ν is the volume of 0.1 mol/dm^3 solution of sodium or potassium hydroxide lost for titration.

The content of protein in bread was determined by modified Kjeldahl's method, content of certain amino acids – by method of ion-exchange liquid-column chromatography on automatic analyzer of amino acids T339 (Mikrotechna, Prague) [12], fat content and total quantity of carbohydrates – by method presented in [13]. The total content of dietary fibers was determined by fermentative methods [12], and that of tanning substance – by titrimetric methods [14], quantity of vitamin B_1 – by special method described in [15], that of vitamin E – by thin-layer chromatography method with a high resolution [16], quantity of mineral substances – by atomic emission spectrometry [17].

The protein amino acid score (AC, %) was calculated with the use of the following formula:

$$AC = \frac{P}{P_i} \cdot 100, \tag{1.4}$$

where P – the content of certain amino acid in 100 g of protein of studied product, mg/g;

P_i – the content of this amino acid in «ideal protein» according to the data of FAO/WHO, (mg/g) [9].

Results and their discussion

The results of determination of influence of maize germ oilcake on gas production process in the wheat dough are presented in Figure 1.

From the data presented, it can be seen that its addition in the entire studied range causes intensification of ethanol fermentation in the dough. In the first stage of fermentation, easily accessible sugars contained in the dough are fermented. Reduction of their quantity in the system leads to decrease of gas production rate. From the Figure, it can be seen that this phenomenon is observed in the check sample after 70×60 s from the beginning of our experiment, while in the test samples – by (10 to 30)×60 s earlier.

Accumulation in the dough of sufficient quantity of maltose as a result of starch amylolysis and also yeast adaptation to its use leads to intensification of ethanol fermentation, which results in increase of rate of carbon dioxide formation to be continued until deficiency of maltose in the dough occurs. Further reduction of gas production rate evidences expediency of completion of dough ripening stage. The maximum gas production rate in the dough samples with added maize germ oilcake takes place in (150 to 170)×60 s from the beginning of experiment, and in the check sample – in 180×60 s, which comprises the precondition for reduction of dough ripening duration by 6 to 17% in case of introduction of the additive.

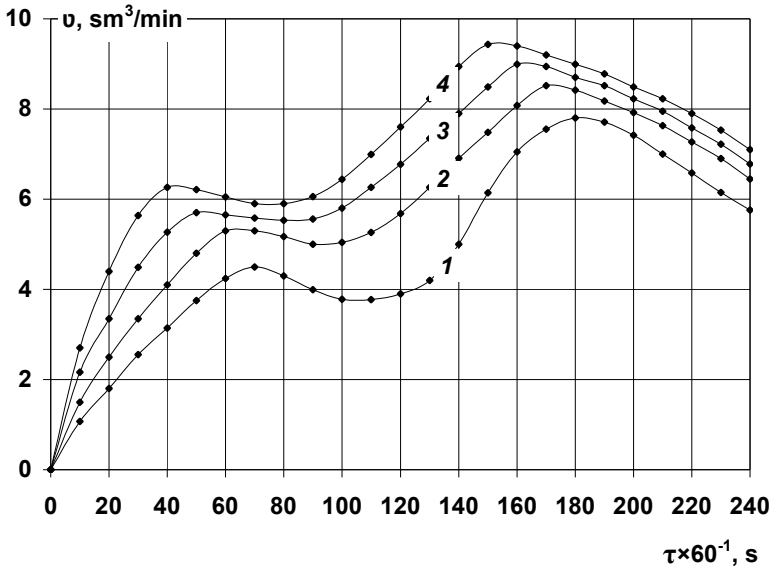

Figure 1. Change of gas production rate in dough with maize germ oilcake:
1 – without additive (check sample);
2, 3, 4 – with introduction of 10.0; 15.0 and 20.0% of additive, respectively

Intensification of gas production in the dough in case of addition of maize germ oilcake is connected, in our opinion, with high content in it of mono- and disaccharides, amino acids, vitamins and mineral substances, which are a nutrient medium for bakery yeast and promote activation of its vital activity. Besides, maize starch is more accessible for amylolytic enzymes, in comparison with wheat one, which promotes more intensive accumulation of maltose in the dough.

The results of study of influence of the tested additive on change of the dough volume during ripening are presented in Figure 2.

It can be see from the Figure that addition of maize germ oilcake in the entire test interval promotes reduction of dough volume in relation to the check sample. For example, in case of decreasing the duration of ripening dough with maize germ oilcake by (10 to 30)×60 s, the dough volume is lesser by 6.0 to 10.5%, in relation to check sample. Such trend is rather expected in case of substitution of wheat flour with gluten-free raw material, which results in loss of CO_2 during dough ripening due to reduction of its gas-retention capacity.

Basing on the results of our study of dynamics of titratable acidity characterizing the dough test and check samples during ripening (Figure 3), we found that addition of 10 to 20% of maize germ oilcake leads to increase of dough initial acidity by 0.8 to 1.3 deg. This is connected with high acidity of the additive (Table 1). However, it is also worth to note that, during the experiment, change of this parameter in the dough with additive is more intensive: for 4×60^2 s of fermentation, the titratable acidity of the check sample is increased by 1.5 deg., and that of the dough sample with maize germ oilcake – by 1.9 to 2.5 deg., which is by 26.6 to 66.7% greater. This is connected with activation of vital activity of lactic acid bacteria due to a high content in the additive of the nutritional and biologically active substances required for their vital activity.

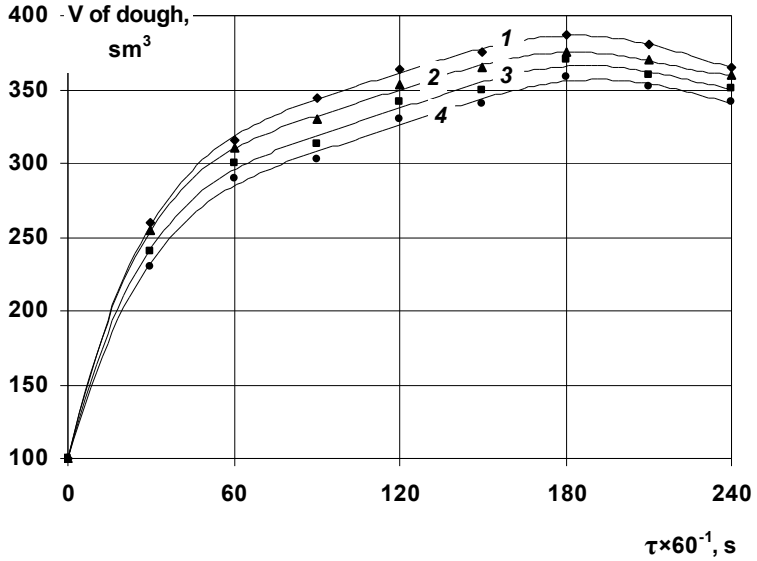

Figure 2. Change of volume in dough samples with maize germ oilcake:
1 – without additive (check sample);
2, 3, 4 – with introduction of 10.0; 15.0 and 20.0% of additive, respectively

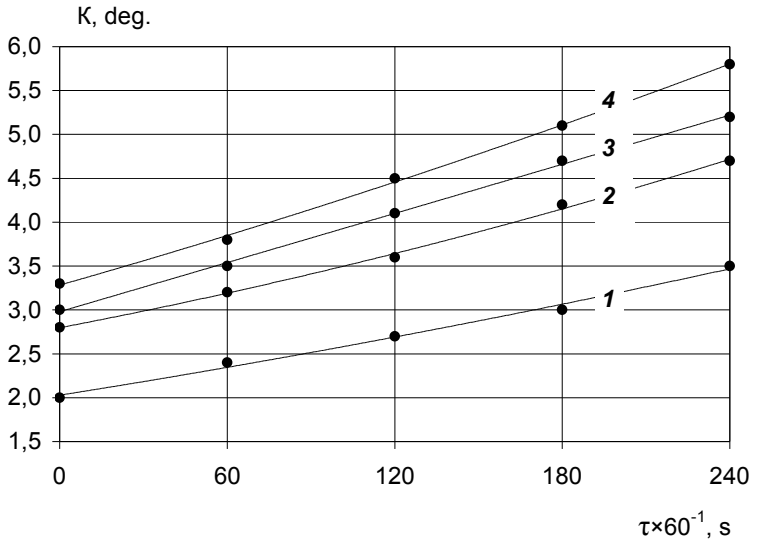

Figure 3. Change of titratable acidity in dough samples with maize germ oilcake: 1 – without additive (check sample); 2, 3, 4 – 2, 3, 4 – with introduction of 10.0; 15.0 and 20.0% of additive, respectively

Addition of maize germ oilcake during obtaining of wheat bread has also influence on organoleptic parameters of the baked bread quality. In particular, the products with maize germ oilcake, in comparison with the check sample, are characterized by brighter color of the crust, which, as the additive dosage increases, changes from light brown to brown. Besides, the bread gets a pleasant corn aftertaste and flavor, as well as yellowish color of its crumb.

The physical and chemical quality parameters of bread with the additive are presented in Table 2.

Table 2

Physical and chemical quality parameters of bread with maize germ oilcake

Parameter	Values of parameters of bread quality			
	Check sample (without additive)	Test samples with additive, %		
		10,0	15,0	20,0
Moisture, %	43.0±1.2	43.9±1.2	44.5±1.3	44.9±1.3
Titratable acidity, deg.	2.8±0.1	3.6±0.2	3.9±0.2	4.4±0.2
Porosity, %	73.0±1.0	71.0±1.0	68.0±1.0	64.0±1.0
Specific volume, cm^3/ g	3.0±0.1	3.0±0.1	2.8±0.1	2.5±0.1

From the data presented in the Table 2, it can be seen that the test samples have greater moisture content by 0.9 to 1.9%, in comparison with the check sample. This is due to increase of dough calculated moisture, as well as to reduction of bread moisture release during baking at the expense of high content of highly hydrophilic polymers at the additive.

The values of titratable acidity of the test samples of bread are greater by 0.8 to 1.6 deg, than that of the check sample, which, on the one part, is connected with more intensive accumulation of acid in the dough with maize germ oilcake, and, on the other part, - with a higher titratable acidity of the additive itself, in comparison with wheat flour.

The porosity and specific volume of bread with introduced additive are decreased, which agrees with the results on change of dough volume presented above. In this case, the values of these parameters in the products with 10 and 15% of additive change substantially, and, in case of addition of 20% of germ oilcake they are reduced by 12.3 and 16.7%, respectively. Therefore, manufacture of bread by straight method with such dosage is not expedient.

The results of nutritional and biological value assessment of bread are represented by products, which are made with addition of rational dosage of maize germ oilcake: that is 15.0% (Tables 3 and 4).

As can be seen from the data of Table 3, in case of introduction of 15% of the maize germ oilcake, the content in bread of protein and fat is inconsiderably increased and that of carbohydrates is decreased by 13.6%.

The products with the said additive is a source of dietary fibers – their content is 4.3 g per 100 g of bread, which is by 1.7 times higher than that in the check sample.

The vitamin value of bread is increased substantially: in case of addition of maize germ oilcake, content of vitamin B_1 in the products is increased by 1.4 times, vitamin E – by 3 times, PP – by1.2 times. Besides, in comparison with check sample, the bread samples have the content of calcium greater by 1.4 times, that of magnesium – by 2.2 times, phosphorus – by 1.5 times and iron – by 2.3 times.

Table 3

Content of nutritional and biologically active substances in bread with maize germ oilcake

Parameter	Content of nutritional and biologically active substances in 100 g of bread	
	Without additive (check sample)	With 15% of corn germ pressed cake
Proteins, g	7.3±0.3	7.8±0.3
Fats, g	0.80±0.02	1.30±0.04
Carbohydrates, g	50.6±2.0	43.8±1.6
Dietary fibers, g	2.5±0.1	4.3±0.1
Tanning substances (calculated as tannin), mg/100g	1.7±0.1	18.1±0.9
Vitamins, mg		
B_1	0.110±0.004	0.150±0.006
E	0.88±0.02	2.65±0.09
PP	1.37±0.05	1.59±0.05
Mineral substances, mg:		
Calcium	13.2±0.6	18.5±0.7
Magnesium	11.7±0.3	25.9±1.1
Phosphorus	63.1±2.1	93.3±3.7
Iron	0.90±0.02	2.10±0.08

For determination of biological value of protein contained in the bread with maize germ oilcake, the amino acid score of unsubstituted amino acids was studied (Table 4). It is known that lysine is a limited amino acid in breadstuffs of wheat flour. The analysis of amino acid score of protein contained in bread with maize germ oilcake indicates increase of biological value of these products. In particular, it is important that content of lysine being deficient in wheat bread increased by 20.8%, cystine and methionine – by 8.0%, threonine – by 11.5%.

Table 4

Biological value of proteins contained in bread with maize germ oilcake

Amino acid	Amino acid score of bread protein, %	
	Without additive (check sample)	With 15% of corn germ pressed cake
Isoleucine	120.6±3.8	107.4±3.3
Leucine	111.8±3.6	114.0±3.4
Lysine	49.0±1.2	59.2±1.6
Cystine + methionine	98.0±3.0	105.5±3.1
Phenylalanine+ tyrosine	113.2±3.4	115.0±3.6
Threonine	70.7±2.1	78.8±2.4
Valine	94.0±4.0	90.0±3.6

The developed products are recommended to be used for traditional, health-giving prophylactic and therapeutic nutrition.

Conclusions

1. Substitution of wheat flour with 10.0–20.0% of maize germ oilcake leads to acceleration of microbiological processes in the dough, which makes it possible to shorten its ripening by 6.0 to 17.0%.
2. To obtain bread with high organoleptic, physical and chemical quality parameters, using straight method of bread manufacture, it is expedient to use up to 15% of maize germ oilcake.
3. Introduction of 15% of the test additive leads to increase of content of unsubstituted amino acids, in particular that of lysine, as well as to increase of content of dietary fibers by 1.7 times, vitamins B_1, E and PP by 1.4, 3.0 and 1.2 times, respectively, mineral substances: calcium, magnesium, phosphorus and iron by 1.4, 2.2, 1.5 and 2.3 times, respectively.

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Determination of oleic acid in the samples of sunflower seeds by method of nir-spectroscopy

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Abstract

Introduction. The possibility of using NIR spectroscopy to determine oleic acid in sunflower seeds has not been studied, so research on this field is perspective.

Materials and methods. The spectra of seed samples of various sunflower varieties with a known content of oleic acid and the same samples additionally enriched with oleic acid were investigated by NIR diffusion reflectance spectroscopy with using the instrument "Infrapid-61". To process the results obtained, the methods of mathematical analysis were applied.

Results and Discussion. In the NIR spectra of samples of dried sunflower seeds, in comparison with the spectra of raw seeds, the expected decrease in the coefficient of diffuse reflection is observed in the range 1920–1940 nm related to the moisture content in the sample. Analysis of NIR spectra of a calibration series of dried seeds enriched with oleic acid shows an increase in the coefficient of diffuse reflection in the wavelength ranges 1920–1940 nm and 2140–2160 nm in proportion to the growth of the mass portion of oleic acid. Corresponding calculations, calibration curves and the obtained equation describing the dependence demonstrate a linear dependence of the reflection coefficient on the mass portion of oleic acid in the sample at the wavelength of 2140 nm with a confidence level of 98%. The dependency found can be used for the quantitative determination of oleic acid in a sunflower seed sample of unknown composition. By the magnitude of the coefficient of diffuse reflection of the sunflower seed sample containing unknown amount of oleic acid, its mass portion in the sample can be determined from the graph. The diffuse reflectance spectra of husked and crushed seed samples and corresponding spectra of crushed sunflower seeds with husks containing the same oleate amount are practically identical with the wavelength range 1330-2370 nm. Therefore, this method can be used for the analysis both intact seeds and seeds separated from husks. The express method of diffuse reflection of NIR spectroscopy can be considered as an alternative to chemical methods for determining the quality indicators of fat-containing raw materials.

Conclusions. The method of NIR spectroscopy is perspective for the determining of other fatty carboxylic acids in sunflower seeds.

Introduction

Near-infrared spectroscopy has been known as a powerful tool for analysis of chemical and physical properties without sample preparation, and it has been applied for the analysis of quality characteristics of complex multi component systems [1]. More then decade, studies on the use of NIR diffuse reflection spectroscopy have been widely carried out to analyze food products and raw materials for their production. Despite the presence of a large number of such data, sufficiently accurate mathematical models, which unambiguously correlate the absorption bands in the NIR region of the spectrum with the quantitative and sometimes qualitative composition of the samples of products under study, have been lacking [2]. The interpretation of the spectral data by the different authors' reports is different, so there are no valid reliable characteristics that could be relied on.

The possibility of using spectroscopy for the quantitative determination of oleic acid in sunflower seeds has not been studied yet, although the NIRS has been successfully used to determine diverse compounds in numerous foods and industrial crops such as sesame, soybean, perilla and peanut, sunflower, rice, maize, and sweet potato [3]. The content of oleic acid in the form of glycerol esters (oleates) in different varieties of sunflower varies from 20 to 90 % and determines the nutritional value of sunflower oil [4]. Modern methods for quantitative analysis of free carboxylic acids in fats and oils are based on chemical transformations, are relatively long, conducted in special laboratories and require the use of chemical reagents. .The purpose of these studies was the development of an express method for the quantitative determination of oleic acid in samples of fat-containing raw materials on the basis of diffuse reflection spectroscopy in the near IR region [5].

Materials and methods

Seed samples of sunflower

Different varieties of sunflower seed were obtained from the Institute of Oilseeds (Zaporizhia). The content of oleic acid in seeds was determined in the factory laboratory. All seed samples were stored at + 10 °C prior to analysis. Standard oleic acid was obtained from the University of Food Technologies [6].

Sample preparation

To carry out the experiment under conditions close to the conveyor regime, the samples were subjected to minimal processing. Two samples of raw sunflower seeds of each variety were taken. One sample of each pair was ground with the husks, the seeds of another sample were separated from the husks and also ground. To ensure the same level of grinding and eliminate the influence of the particle size factor on the resulting spectra, the crushed samples are screened through a sieve with hole diameter of 1 mm. To reduce the influence of moisture on the spectral characteristics of the samples, the crushed seeds without the husks were dried to a constant mass, using an infrared dryer.

Methods

By the method of investigation, a method of diffuse reflection in the near region of the infrared spectrum was chosen for the determination of oleic acid in samples of sunflower oil. The essence of the method consists in comparing the characteristics of the infrared

spectra of the sample that is under investigation, with the spectra of the preliminary investigated calibration series of samples. Infrared spectra of diffuse reflection for samples of sunflower seeds were recorded using the instrument "Infrapid-61" in the wavelength region 1330-2370 nm.

Data processing

The equations for NIRS prediction, calibration coefficients and statistical parameters characterizing the calibration of the instrument were developed with the regression method.

Preparation of the calibration series of raw material samples

The use of diffuse reflection spectroscopy involves conducting a procedure for preliminary calibration of the instrument using standard methods [7]. Samples for the calibration series were prepared by adding free oleic acid to the ground seeds characterized with known content of oleates [8]. For this purpose, a solution of oleic acid in a volatile organic solvent was evenly sprayed over the surface of the sample stirring it. The increase in the mass fraction of oleic acid was controlled by measuring the mass of the sample after a short drying term at a temperature of 35 ^{o}C.

Spectra collection and pretreatment

Prepared samples of ground seeds were loaded into the cuvette compartment of the instrument and their spectra were recorded. The procedure for analyzing all samples involves recording the spectrum of the standard that is in the instrument, recording the spectrum of the prepared samples that are under the study, and processing the obtained results with the appropriate software [8]. The time for recording of the spectrum of one sample does not exceed 2 minute. The reflectance data were recorded as a reflectance coefficient R at 10 nm intervals, and 3 scans were averaged for each sample.

Results and discussion

The results of computer processing of the obtained spectra of samples of crushed seeds with husks containing oleic acid from 79 to 90% are shown in Figure 1. Comparative analysis of spectra of samples series of crushed seeds demonstrates their similarity in that wave region (from 1370 to 2370 nm) [9]. Spectra of samples of crushed seeds without husks with the corresponding content of oleic esters are shown in Figure 2 and they also seem to be similar. The experiments show that the method is suitable for the analysis both intact seeds and seeds separated from husks [10].

To compare the spectra of diffuse reflection of seed samples with husks and without husks, two sunflower varieties, exactly “Smak” and “KP1 1B” containing high (73.6 %) and low (29.78 %) amount of oleates, were investigated. The results are shown in Figure 3.

As a result of the analysis of these IR spectra, no significant differences were found in the NIR region. Spectra of dried seed samples are shown in Figure 4.

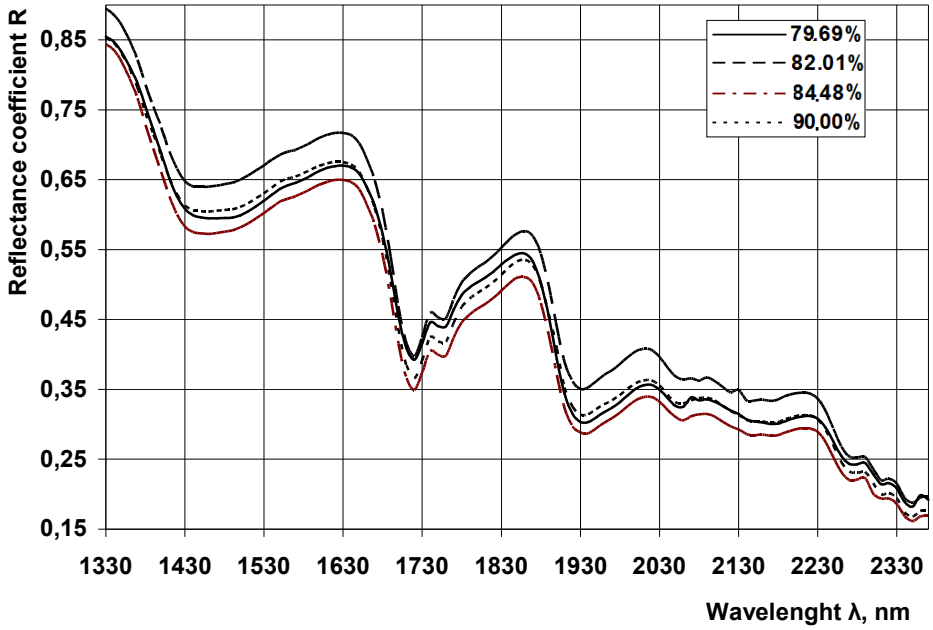

Figure 1. Diffuse reflection NIR spectra of samples of crushed sunflower seeds with husks containing oleic acid from 79 to 90%.

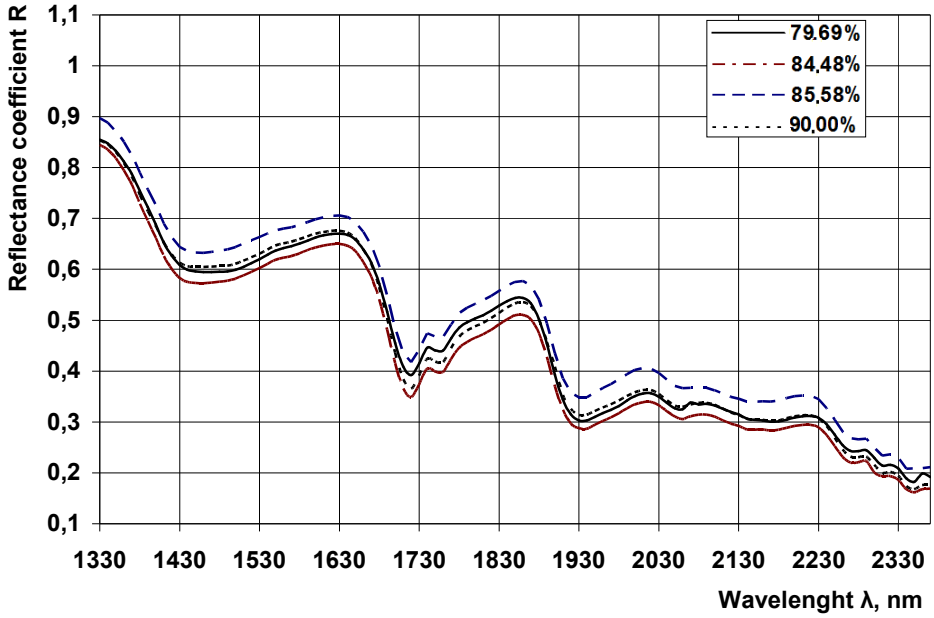

Figure 2. Diffuse reflection NIR spectra of samples of crushed sunflower seeds without husks containing oleic acid from 79 to 90%.

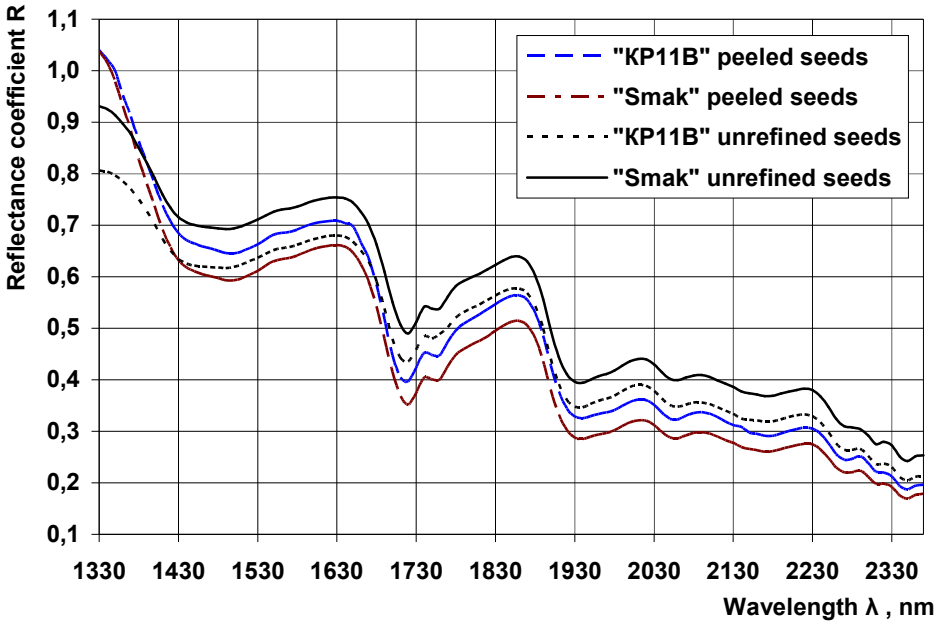

Figure 3. Diffuse reflection NIR spectra of samples of sunflower seed varieties "Smak" and "KP1 1B"

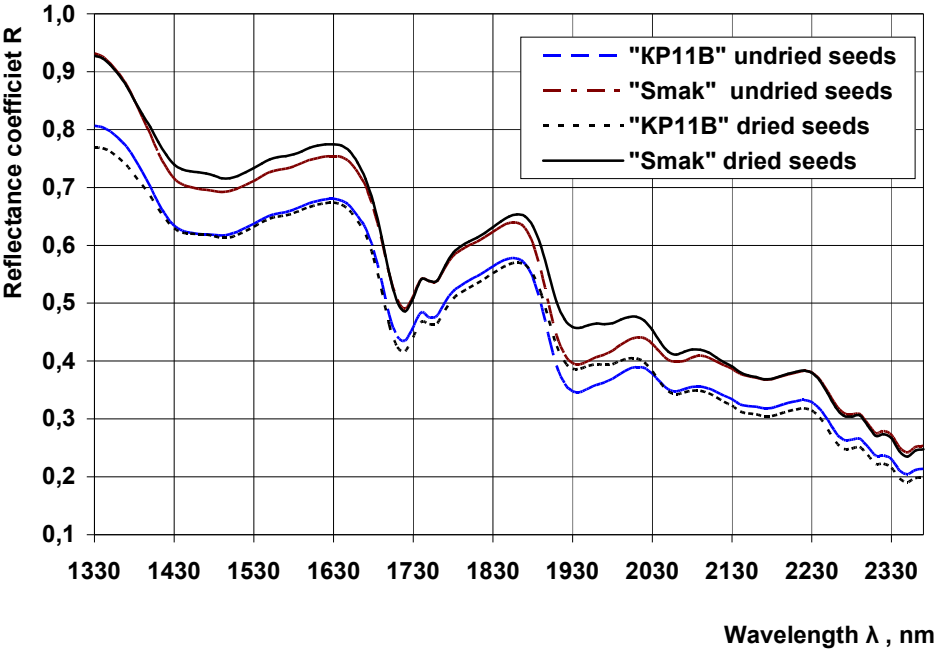

Figure 4. Diffuse reflection NIR spectra of dried samples of sunflower seed varieties "Smak" and "KP1 1B"

When the spectra of dry and undried samples were compared, the expected differences in the intensity of diffuse reflection were found in the region 1910-1940 nm that is responsible for the water content.

Development of calibration curve

Analysis of the spectra of calibration series of sunflower seed samples enriched with free oleic acid showed the appearance of characteristic minima of the reflection intensity in the range of 2140-2160 nm (See Figure 5). The coefficient of diffuse reflection in this range increases proportionally to the growth of the mass portion of oleic acid in the sample. Calculation and construction of calibration curves and determination of linear equations on the basis of regression analysis show the dependency of the diffuse reflection coefficient on the mass portion of oleic acid at the wavelength of 2240 nm at a confidence level of 98 % (See Figure 6).

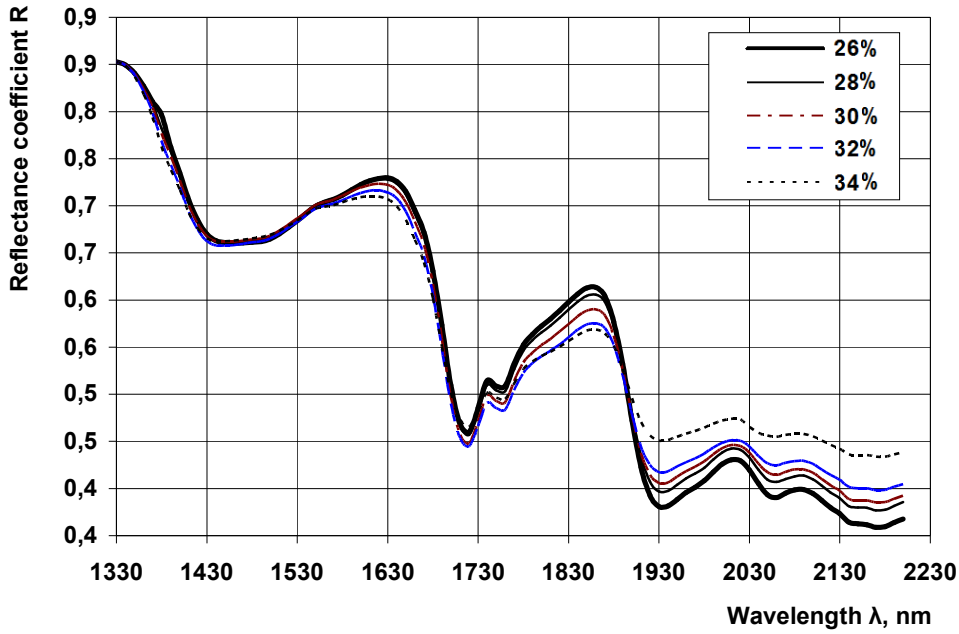

Figure 5. Diffuse reflection NIR spectra of samples of sunflower seed enriched with oleic acid

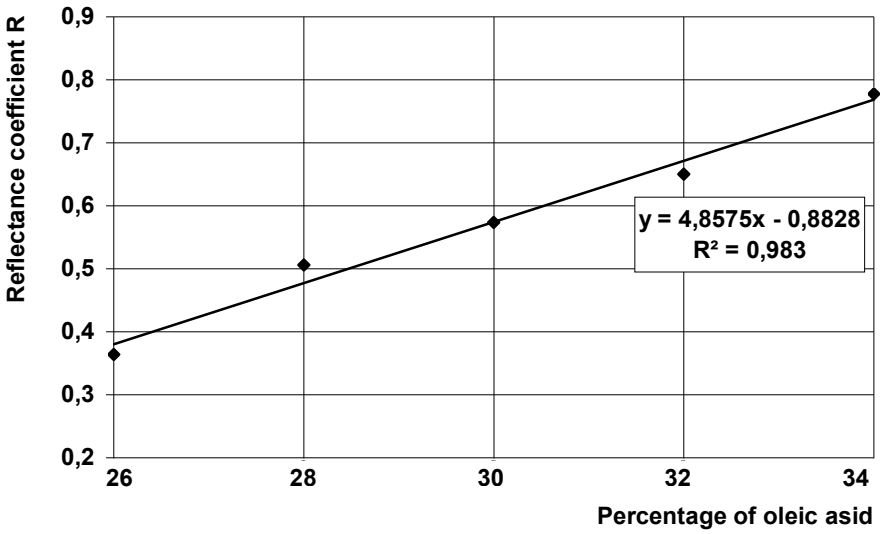

Figure 6. Calibration curve and the linear equation of dependency of the diffuse reflection coefficient on the mass portion of oleic acid at 2240 nm

Differences in the spectra of diffuse reflection of seed samples with different amounts of free oleic acid and changes in the values of the diffuse reflection coefficient in certain regions of the spectrum are explained by the increase in the number of functional groups, that able to enter into weak interactions with both the same groups and with others [11].

Using the dependency found and knowing the value of the coefficient of diffuse reflection in the NIR range from a sample with an unknown content of oleic acid, it is possible to determine from the graph its mass portion in a given sample.

Conclusions

This non-destructive NIRS method could simplify the analysis of qualitative components, because extraction steps with organic solvents were not required and instrumental analysis was completed in a few minutes. This method for studying systems with multi component chemical composition is perspective because of the low level of light absorption in this spectral region. The method can be used to determine the wanted components over a wide range of concentrations For the analysis of numerous samples, the NIRS method can replace chemical methods and chromatographic methods such as GLC. The development of these NIR equations for individual fatty acids is only a first step though the NIRS is a practical method. The results of the comparative analysis of diffuse reflectance spectra of seed samples with husks and without husks and the same samples enriched with free oleic acid, lead to the conclusion that the method is perspective for detection of other fatty carboxylic acids in sunflower oil.

The express method of diffuse reflectance NIR spectroscopy can be considered as an alternative method for determining the quality of fat-containing materials in the processes of their storage, sorting or processing.

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Qualimetric assessment of diets

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Abstract

Introduction. The work's objective is to analyze quality rating of diets from the standpoint of physiological need norms of a person and a daily ration, to further determine the balance of nutrition.

Materials and methods. The daily ration of human nutrition (breakfast, lunch, dinner) and the norms of the physiological needs of the average person – to determine the complex quantitative assessment of the quality of diets. An additive mathematical model as most widespread in a qualimetry is used for joining the quality rating into the generalized (complex) index. Methods – qualimetric.

Results and discussion. Taking into account the norms of physiological needs of a common person, the complex-quantitative estimation of quality of one meal is calculated, the three-level hierarchical structure of the system of qualitative indexes is developed: the third level simple indexes are grouped in the qualitative indexes, which form the second level of structure systems hierarchy, which, in turn, form the first level, and then - in the complex index of zero level, which characterizes quality rating of diets.

Basic qualitative indexes (P^{basic}) of macronutrients, mineral matters and vitamins are the following: for proteins – 0,15; fats – 0,17; carbohydrates – 0,68; sodium – 0,45; potassium – 0,34; calcium – 0,07; magnesium – 0,03; phosphorus – 0,11; thiamine – 0,02; ribofflavinum – 0,02; perydoxine – 0,02; cevitamic acid – 0,94. Weight coefficients (m) are the following: proteins – 0,50; fats – 0,40; carbohydrates – 0,10; sodium – 0,03; potassium – 0,05; calcium – 0,25; magnesium – 0,50; phosphorus – 0,17; thiamine – 0,36; ribofflavinum – 0,32; perydoxine – 0,31; cevitamic acid – 0,01.

The biggest value of the complex index (K_0) is obtained in breakfast – 1,60, the lowest value is typical for supper – 1,09.

Conclusion. For the set daily ration, the complex qualitative indexes for the group of macronutrients, mineral matters and vitamins are determined. The most balanced values of qualitative index are set, that is typical for a supper №2 with the estimation – 1,09.

Introduction

A qualitative index of a product is a quantitative characteristic of one or several properties of a product, which characterize its quality, and is considered in terms of certain conditions of its creation, exploitation or consuming (Azgaldov et al, 2011, 2015; Topol'nik, Ratushnyj, 2008; Zinchenko, Koretska, 2013) [1, 2, 4, 11].

According to the amount of characterized properties the indexes are divided into simple and complex (Topol'nik, Ratushnyj, 2008; Koval, Guts, 2013) [4, 9]. Simple qualitative index identifies one of its properties, for example contents of water, sugar, fat etc (Sébédio, 2017; Kuzmin et al, 2014-2016) [3, 5-8]. They are determined by the industry regulatory document.

Complex index identifies several properties of a product. It can be related to both set of properties, which determine quality, and certain group of properties (Topol'nik, Ratushnyj, 2008) [4]. If ever one index is equal to zero, complex index is also equal to zero (Azgaldov et al, 2011; Topol'nik, Ratushnyj, 2008) [1, 4].

There are two methods of a product quantitative estimation - differential and complex. A product quantitative estimation is a set of operations, which includes: qualitative indexes' nomenclature selection of a product, value determination of these indexes and their comparison with basic indexes (Koval, Guts, 2013; Niemirich, Novosad, 2013; Zinchenko, Koretska, 2013) [9-11].

Qualimetric methods can be used in any food as well as the results of their research. Method of a product quantitative estimation is based on comparison of the set of simple indexes' values of an estimated product with a certain set of base indexes' values, called differential (Topol'nik, Ratushnyj, 2008) [4].

Complex method of a product quantitative estimation is based on expressing of the estimation rate by one number, which is a result of grouping of selected simple indexes to one complex index (Azgaldov et al, 2011, 2015; Topol'nik, Ratushnyj, 2008) [1, 2, 4].

Complex method of a product quantitative estimation is prevailing (Wang et al, 2016; Rodgers, 2017; Perng, Oken, 2017; Grassi et al, 2017; Kim et al, 2017; Carbonneau et al, 2017; Kufley et al, 2017) [12-18]. But, a complex estimation of food products is not exclusive of differential estimation, because in some cases high value of complex qualitative index can disguise the low level of product's quality according to some simple indexes.

Each qualitative index, being a quantitative characteristic (extent) of one of object's quality model (fact) should reflect (to greater or lesser extent) the ability (property) of the object (fact), meet public demands (interests, values) in certain conditions. Therefore, in order to form a qualitative index we should take into account following qualitative components: public demand, certain conditions, object and extent of its meeting. Qualitative index should provide an answer to the question: to what extent is this object (fact) able to meet public demand (interest, value) (Topol'nik, Ratushnyj, 2008) [4].

It is better to represent the properties of food in a form of an hierarchical tree. Hierarchical structure of qualitative indexes of a product, manufactured by the industry regulatory document, is represented on the figure 1.

During the modeling of a product quality in the form of properties' hierarchical structure we decide that a quality, as the most generalized complex product property, is considered on the highest, null rate of an hierarchical set of properties (complex qualitative index), and its components – less generalized properties – are considered on the lowest, first hierarchical level (nutritive index). Nutritive indexes, in their turn, consist of an amount of even less generalized properties, situated on the even lower level – second

level (macronutrients, vitamins, mineral matters) (Tsapanou et al, 2017; Ramsay et al, 2017; Nguyen et al, 2017; Roy et al, 2017; Bruce et al, 2017; Hoerster et al, 2016) [19-24].

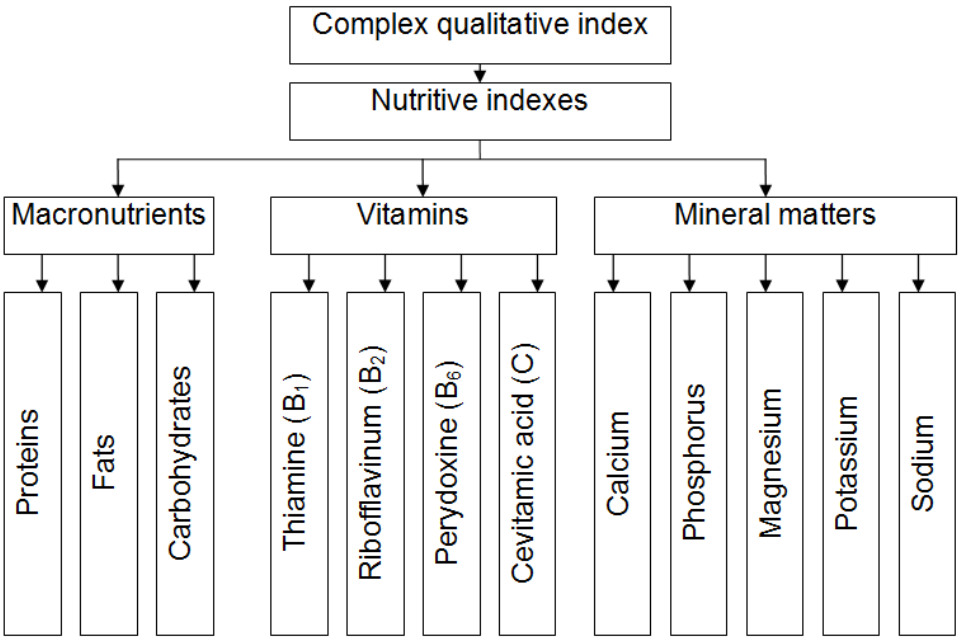

Fig. 1. Hierarchical structure of qualitative indexes of a diet

On the third level each group of properties also consists of several indexes: macronutrients (proteins, fats, carbohydrates); vitamins (thiamine, ribofflavinum, perydoxine, cevitamic acid); mineral matters (calcium, phosphorus, magnesium, potassium, sodium) (Moubarac et al, 2017; Zuniga et al, 2017; Andrade et al, 2016; Pham-Short et al. 2016; Nansel et al, 2016; Hu et al, 2016) [25-30].

Subordinate, so-called hierarchical, structure of properties appears which can be considered from increasing amount of levels (Kim et al, 2017; Nansel et al, 2016) [16, 29]. Building the hierarchical structure of properties we have gone down to the low level, where there are so-called simple properties. These simple properties can be measured by the certain method, and then, used as simple qualitative indexes.

Well grounded choice of production indexes in estimating its qualitative rate has high priority. In order to make this choice, we should have at hand the nomenclature of qualitative indexes' groups which meets demands of need and sufficiency.

Materials and methods

The daily ration of human nutrition (breakfast, lunch, dinner) and the norms of the physiological needs of the average person – to determine the complex quantitative

assessment of the quality of diets. An additive mathematical model as most widespread in a qualimetry is used for joining the quality rating into the generalized (complex) index. Methods – qualimetric (Azgaldov et al, 2011, 2015; Topol'nik, Ratushnyj, 2008) [1, 2, 4].

Method of a diet complex quantitative estimation (Topol'nik, Ratushnyj, 2008) [4]:

1. Index values for set diets are determined from the formula:

$$P_{ij} = \frac{M_{ij}}{\sum M_{ij}}, \tag{1}$$

M_{ij} – content of nutrient materials in group j in nutrition products included in the diet.

2. Analogously, due to recommended norm, basic indexes are determined;

$$P_{ij}^{basic} = \frac{M_{ij}}{\sum M_{ij}}, \tag{2}$$

M_{ij} – regulatory i nutrient material in group j of daily ration material.

3. Simple indexes'estimation of proteins, fats, carbohydrates is calculated by the formula:

$$K_{ij} = \left(\frac{P_{ij}}{P_{ij}^{basic}} \right)^{z}, \tag{3}$$

P_{ij} – index of a nutrient material in daily ration;
Pij^{basic} – basic (balanced) value of index of a nutrient material in daily ration (according to norms of physiological needs);
z – index, that considers the influence of changing index value on qualitative rate of an object, that is equal to plus 1 in proteins and carbohydrates content estimating and minus 1 in fats content estimating.

4. Weight coefficient value of nutrient materials m_{ij} is calculated by the formula:

$$m_{ij} = \frac{\frac{\sum P_{ij}^{basic}}{P_{ij}^{basic}}}{\sum \left(\frac{\sum P_{ij}^{basic}}{P_{ij}^{basic}} \right)}. \tag{4}$$

Complex qualitative index of meal due to nutrient materials equation for two-level structure is determined from the adaptive model:

$$K_o = \sum_{i=1}^{t} M_j \cdot \sum_{j=1}^{n_i} m_{ij} \cdot K_{ij}, \tag{5}$$

M_j – weight coefficient value of nutrients.

Results and discussions

According to norms of physiological needs of a common person we have developed complex qualitative index of meal (Table 1).

1. Complex quality rating of breakfast

Due to norms of macronutrients, mineral matters and vitamins content, included in breakfast dishes, the calculation of nutrient materials found in canteen menu is provided (Table 2).

Table 1

Norms of physiological needs of a common person at the age from 18 to 59

Nutrient material	Norm
Proteins, g	88,00
Fats, g	107,00
Carbohydrates, g	422,00
Total amount of nutrient materials, g:	**617,00**
Sodium (Na), mg	5000,00
Potassium (K), mg	3750,00
Calcium (Ca), mg	800,00
Magnesium(Mg), mg	400,00
Phosphorus (P), mg	1200,00
Total amount of mineral matters, mg	**11150,00**
Thiamine (B_1), mg	1,60
Ribofflavinum (B_2), mg	1,80
Perydoxine (B_6), mg	1,90
Cevitamic acid (C), mg	85,00
Total amount of vitamins, mg	**90,30**

Absolute values of qualitative indexes of macronutrients, mineral matters and vitamins calculated by the formula (1) are the following: for proteins – P_p= 0,20; fats – P_f = 0,15; carbohydrates – P_c =0,65; sodium – P_{Na} = 0,48; potassium – P_K = 0,20; calcium – P_{Ca} = 0,09; magnesium – P_{Mg} = 0,03; phosphorus– P_P = 0,20; thiamine – P_{B1} = 0,02; ribofflavinum – P_{B2} = 0,08; perydoxine – P_{B6} = 0,07; cevitamic acid– P_c = 0,83. Obtained results are brought in the Table 3.

Analogously to the recommended norms of physiological needs (Table 1) basic values have been determined from the formula (2). Basic qualitative indexes of macronutrients, mineral matters and vitamins are the following: for proteins – P_p^{basic} = 0,15; fats – P_f^{basic} = 0,17; carbohydrates– P_c^{basic} = 0,68; sodium– P_{Na}^{basic} = 0,45; potassium – P_K^{basic} = 0,34; calcium– P_{Ca}^{basic} = 0,07; magnesium– P_{Mg}^{basic} = 0,03; phosphorus– P_P^{basic}= 0,11; thiamine – P_{B1}^{basic}= 0,02; ribofflavinum – P_{B2}^{basic} = 0,02; perydoxine – P_{B6}^{basic} = 0,02; cevitamic acid – P_c^{basic}= 0,94. Obtained results are brought in the Table 3.

Table 2

Calculation of macronutrients, mineral matters and vitamins content included in breakfast dishes

Nutrient materials	Name of the dish							Total
	Diary butter	Fried liver	Dutch cheese	Buckwheat porridge	Wheat bread from first grade flour	Tea with sugar	Tomato	
Weight, g	20	75	30	150	100	200	100	675
Macronutrients, g:								
proteins	0,12	17,40	8,04	14,81	7,60	0,20	1,10	49,27
fats	16,50	7,65	8,19	3,90	0,90	0,00	0,20	37,34
carbohydrates	0,18	10,35	0,00	76,35	49,70	16,00	3,80	156,38
Mineral matters, mg:								
Na	14,80	456,00	330,00	988,50	488,00	0,00	40,00	2317,30
K	4,60	199,50	39,00	256,50	127,00	6,00	290,00	922,60
Ca	4,40	13,50	312,00	81,00	26,00	1,00	14,00	451,90
Mg	0,60	16,50	0,00	94,50	35,00	1,00	20,00	167,60
P	3,80	319,50	163,20	351,00	83,00	0,00	26,00	946,50
Vitamins, mg:								
B1	0,00	0,24	0,01	0,36	0,16	0,00	0,06	0,83
B2	0,02	1,97	0,11	0,20	0,08	0,00	0,04	2,41
B6	0,00	1,19	0,06	0,29	0,06	0,00	0,53	2,12
C	0,00	0,00	0,84	0,00	0,00	0,00	25,0	25,84

Table 3

Calculation of absolute values, basic values, weight coefficients and simple qualitative indexes

Absolute values		Basic values		Weight coefficients		Simple qualitative indexes	
Macronutrients							
P_p	0,20	P_p^{basic}	0,15	m_p	0,50	K_p	1,42
P_f	0,15	P_f^{basic}	0,17	m_f	0,40	K_f	1,13
P_c	0,65	P_c^{basic}	0,68	m_c	0,10	K_c	0,94
Mineral matters							
P_{Na}	0,48	P_{Na}^{basic}	0,45	m_{Na}	0,03	K_{Na}	1,08
P_K	0,20	P_K^{basic}	0,34	m_K	0,05	K_K	0,57
P_{Ca}	0,09	P_{Ca}^{basic}	0,07	m_{Ca}	0,25	K_{Ca}	1,31
P_{Mg}	0,03	P_{Mg}^{basic}	0,03	m_{Mg}	0,50	K_{Mg}	0,97
P_P	0,20	P_P^{basic}	0,11	m_P	0,17	K_P	1,83
Vitamins							
P_{B1}	0,02	P_{B1}^{basic}	0,02	m_{B1}	0,36	K_{B1}	1,50
P_{B2}	0,08	P_{B2}^{basic}	0,02	m_{B2}	0,32	K_{B2}	3,88
P_{B6}	0,07	P_{B6}^{basic}	0,02	m_{B6}	0,31	K_{B6}	0,31
P_c	0,83	P_c^{basic}	0,94	m_c	0,01	K_c	0,88

Weight coefficient value of nutrient materials m_{ij} has been calculated due to the recommended norms of physiological needs (Table 1) by the formula (4). Weight coefficients are the following: proteins – m_p = 0,50; fats – m_f = 0,40; carbohydrates – m_c = 0,10; sodium– m_{Na} = 0,03; potassium – m_K = 0,05; calcium– m_{Ca} = 0,25; magnesium– m_{Mg} = 0,50; phosphorus– m_P = 0,17; thiamine – m_{B1} = 0,36; ribofflavinum – m_{B2} = 0,32; perydoxine – m_{B6} = 0,31; cevitamic acid – m_c = 0,01.

Simple indexes'quality rating of proteins, fats, carbohydrates has been calculated by the formula (3) using data from Table 3. Simple indexes'estimation is the following: from proteins – K_p = 1,42; fats – K_f = 1,13; carbohydrates– K_c = 0,94; sodium– K_{Na} = 1,08; potassium– K_K = 0,57; calcium– K_{Ca} = 1,31; magnesium– K_{Mg} = 0,97; phosphorus– K_P = 1,83; thiamine – K_{B1} = 1,50; ribofflavinum – K_{B2} = 3,88; perydoxine – K_{B6} = 0,31; cevitamic acid – K_c = 0,88.

Complex qualitative index of meal due to nutrient materials equation for two-level structure has been determined from formula (5), in which weight coefficient values (M) are for macronutrients– 0,35; vitamins – 0,55; mineral matters– 0,1.

Due to the calculation results breakfast has complex quality rate K_o = 1,60.

2. Complex quality rating of dinner

Due to norms of macronutrients, mineral matters and vitamins content, included in dinner dishes, the calculation of nutrient materials found in canteen menu is provided (Table 4).

Table 4

Calculation of macronutrients, mineral matters and vitamins content included in dinner dishes

Nutrient materials	Name of the dish							Total
	Pickled cucumbers	Borshch with cabbage and potato	Dumplings	Wheat porridge	Rye bread	Pastry gingerbread	Compote	
Weight, г	50	250	115	150	150	50	200	965
Macronutrients, g:								
proteins	0,40	2,45	19,40	7,50	11,40	4,80	0,40	46,39
fats	0,05	5,15	17,70	0,66	1,65	2,80	0,00	28,02
carbohyd-rates	0,80	13,10	0,00	32,10	61,10	77,70	29,60	214,35
Mineral matters, mg:								
Na	0,00	782,00	656,60	585,00	874,50	11,00	24,00	2933,15
K	70,50	424,50	244,90	177,00	309,00	60,00	86,00	1371,95
Ca	11,50	41,50	16,10	33,00	57,00	9,00	17,00	185,10
Mg	7,00	29,50	21,85	36,00	73,50	0,00	9,00	176,85
P	12,00	47,20	166,70	153,00	234,00	41,00	12,00	665,95
Vitamins, mg:								
B_1	0,01	0,06	0,30	0,12	0,27	0,08	0,06	0,84
B_2	0,01	0,05	0,15	0,06	0,17	0,04	0,04	0,47
B_6	0,05	0,21	2,65	0,21	0,09	0,06	0,53	3,26
C	2,50	6,85	0,00	0,00	0,00	0,00	25,0	9,35

Absolute values of qualitative indexes of macronutrients, mineral matters and vitamins calculated by the formula (1) are the following: for proteins – P_p = 0,16; fats – P_f = 0,10; carbohydrates – P_c =0,74; sodium– P_{Na} = 0,55; potassium – P_K = 0,27; calcium– P_{Ca} = 0,03; magnesium– P_{Mg} = 0,03; phosphorus– P_P = 0,12; thiamine – P_{B1} = 0,06; ribofflavinum – P_{B2} = 0,04; perydoxine – P_{B6} = 0,23; cevitamic acid – P_c = 0,67 (Table 5).

Table 5

Calculation of absolute values of qualitative indexes and estimation of simple indexes of nutrient materials

Absolute values		Basic values		Weight coefficients		Simple qualitative indexes	
Macronutrients							
P_p	0,16	P_p^{basic}	0,15	m_p	0,50	K_p	1,13
P_f	0,10	P_f^{basic}	0,17	m_f	0,40	K_f	1,79
P_c	0,74	P_c^{basic}	0,68	m_c	0,10	K_c	1,09
Mineral matters							
P_{Na}	0,55	P_{Na}^{basic}	0,45	m_{Na}	0,03	K_{Na}	1,23
P_K	0,27	P_K^{basic}	0,34	m_K	0,05	K_K	0,76
P_{Ca}	0,03	P_{Ca}^{basic}	0,07	m_{Ca}	0,25	K_{Ca}	0,48
P_{Mg}	0,03	P_{Mg}^{basic}	0,03	m_{Mg}	0,50	K_{Mg}	0,92
P_P	0,12	P_P^{basic}	0,11	m_P	0,17	K_P	1,16
Vitamins							
P_{B1}	0,06	P_{B1}^{basic}	0,02	m_{B1}	0,36	K_{B1}	3,40
P_{B2}	0,04	P_{B2}^{basic}	0,02	m_{B2}	0,32	K_{B2}	1,71
P_{B6}	0,23	P_{B6}^{basic}	0,02	m_{B6}	0,31	K_{B6}	0,09
P_c	0,67	P_c^{basic}	0,94	m_c	0,01	K_c	0,88

Quality rating of simple indexes for a group of nutrient materials has been determined from the formula (3), as a result the values are the following: for proteins – K_p = 1,13; fats– K_f = 1,79; carbohydrates– K_c = 1,09; sodium– K_{Na} = 1,23; potassium – K_K = 0,76; calcium – K_{Ca} = 0,48; magnesium– K_{Mg} = 0,92; phosphorus – K_P = 1,16; thiamine – K_{B1} = 3,40; ribofflavinum – K_{B2} = 1,71; perydoxine – K_{B6} = 0,09; cevitamic acid – K_c = 0,88.

Complex qualitative index of meal due to nutrient materials equation for two-level structure has been determined from formula (5). Due to the calculation results breakfast has complex quality rate – K_o=1,57.

3. Complex quality rating of supper №1

Due to norms of macronutrients, mineral matters and vitamins content, included in supper №1, the calculation of nutrient materials found in canteen menu is provided (Table 6).

Absolute values of qualitative indexes of nutrient materials calculated by the formula (1) are the following: for proteins – P_p = 0,13; fats – P_f = 0,12; carbohydrates– P_c =0,75; sodium – P_{Na} = 0,42; potassium – P_K = 0,28; calcium – P_{Ca} = 0,08; magnesium– P_{Mg} = 0,04; phosphorus– P_P = 0,18; thiamine – P_{B1} = 0,04; ribofflavinum – P_{B2} = 0,03; perydoxine – P_{B6} = 0,10; cevitamic acid – P_c = 0,83 (Table 7).

Table 6

Calculation of macronutrients, mineral matters and vitamins content included in supper №1

Nutrient materials	Name of the dish						
	Green peas	Milk rice soup	Natural minced schnitzel	Cooked noodles	Wheat bread from first grade flour	Waffles	Total
Weight, g	50	250	75	150	100	50	675
Macronutrients, g:							
proteins	2,50	6,15	7,92	15,60	7,60	1,70	41,47
fats	0,10	7,85	11,28	1,35	0,90	15,10	36,58
carbohydrates	6,40	23,20	4,56	112,8	49,70	32,35	229,01
Mineral matters, mg:							
Na	1,00	455,50	199,80	15,00	488,00	3,50	1162,80
K	142,50	191,50	88,80	186,00	127,00	21,50	757,30
Ca	13,00	150,50	8,40	27,00	26,00	4,00	228,90
Mg	19,00	20,50	12,00	24,00	35,00	1,00	111,50
P	61,00	122,50	67,80	130,50	83,00	16,50	481,30
Vitamins, mg:							
B1	0,17	0,05	0,04	0,26	0,16	0,02	0,69
B2	0,10	0,16	0,07	0,12	0,08	0,01	0,53
B6	1,00	0,08	0,17	0,09	0,06	0.18	1,58
C	12,50	0,65	0,00	0,00	0,00	0,00	13,15

Quality rating of simple indexes of nutrient materials has been determined from the formula (3), as a result the values are the following: for proteins – K_p = 1,0; fats – K_f = 1,46; carbohydrates – K_c = 1,09; sodium – K_{Na} = 0,95; potassium – K_K = 0,82; calcium – K_{Ca} = 1,16; magnesium– K_{Mg} = 1,00; phosphorus – K_P = 1,63; thiamine – K_{B1} = 2,44; ribofflavinum – K_{B2} = 1,71; perydoxine – K_{B6} = 0,20; cevitamic acid – K_c = 0,88.

Complex qualitative index of meal due to nutrient materials equation for two-level structure has been determined from formula (5). Due to the calculation results supper №1 has complex quality rate – K_o=1,35.

4. Complex quality rating of supper №2

Due to norms of macronutrients, mineral matters and vitamins content, included in supper №1, the calculation of nutrient materials found in canteen menu is provided (Table 8).

Absolute values of qualitative indexes of nutrient materials calculated by the formula (1) are the following: for proteins – P_p = 0,11; fats – P_f = 0,32; carbohydrates – P_c = 0,57; sodium – P_{Na} = 0,06; potassium– P_K = 0,47; calcium– P_{Ca} = 0,17; magnesium – P_{Mg} = 0,05; phosphorus– P_P = 0,25; thiamine– P_{B1} = 0,01; ribofflavinum – P_{B2} = 0,06; perydoxine – P_{B6} = 0,10; cevitamic acid – P_c = 0,83 (Table 9).

Table 7

Calculation of absolute values of qualitative indexes and estimation of simple indexes of nutrient materials

Absolute values		Basic values		Weight coefficients		Simple qualitative indexes	
Macronutrients							
P_p	0,13	P_p^{basic}	0,15	m_p	0,50	K_p	1,0
P_f	0,12	P_f^{basic}	0,17	m_f	0,40	K_f	1,46
P_c	0,75	P_c^{basic}	0,68	m_c	0,10	K_c	1,09
Mineral matters							
P_{Na}	0,42	P_{Na}^{basic}	0,45	m_{Na}	0,03	K_{Na}	0,95
P_K	0,28	P_K^{basic}	0,34	m_K	0,05	K_K	0,82
P_{Ca}	0,08	P_{Ca}^{basic}	0,07	m_{Ca}	0,25	K_{Ca}	1,16
P_{Mg}	0,04	P_{Mg}^{basic}	0,03	m_{Mg}	0,50	K_{Mg}	1,00
P_P	0,18	P_P^{basic}	0,11	m_P	0,17	K_P	1,63
Vitamins							
P_{B1}	0,04	P_{B1}^{basic}	0,02	m_{B1}	0,36	K_{B1}	2,44
P_{B2}	0,03	P_{B2}^{basic}	0,02	m_{B2}	0,32	K_{B2}	1,71
P_{B6}	0,10	P_{B6}^{basic}	0,02	m_{B6}	0,31	K_{B6}	0,20
P_c	0,83	P_c^{basic}	0,94	m_c	0,01	K_c	0,88

Table 8

Calculation of macronutrients, mineral matters and vitamins content included in supper №2

Nutrient materials	Name of the dish		Total
	Chocolate covered curd cheese bar	Apple juice	
Weight, g	100	200	300
Macronutrients, g:			
proteins	8,50	1,00	9,50
fats	27,80	0,00	27,80
carbohydrates	32,00	18,20	50,20
Mineral matters, mg:			
Na	43	12,0	55,0
K	181	240,0	421,00
Ca	137	14,0	151,0
Mg	35	8,0	43,00
P	213	14,0	227,00
Vitamins, mg			
B_1	0,03	0,02	0,05
B_2	0,31	0,02	0,33
B_6	0,35	0,20	0,55
C	0,50	4,00	4,50

Table 9

Calculation of absolute values of qualitative indexes and estimation of simple indexes of nutrient materials

Absolute values		Basic values		Weight coefficients		Simple qualitative indexes	
Macronutrients							
P_p	0,11	P_p^{basic}	0,15	m_p	0,50	K_p	0,76
P_f	0,32	P_f^{basic}	0,17	m_f	0,40	K_f	0,55
P_c	0,57	P_c^{basic}	0,68	m_c	0,10	K_c	0,84
Mineral matters							
P_{Na}	0,06	P_{Na}^{basic}	0,45	m_{Na}	0,03	K_{Na}	0,14
P_K	0,47	P_K^{basic}	0,34	m_K	0,05	K_K	1,40
P_{Ca}	0,17	P_{Ca}^{basic}	0,07	m_{Ca}	0,25	K_{Ca}	2,35
P_{Mg}	0,05	P_{Mg}^{basic}	0,03	m_{Mg}	0,50	K_{Mg}	1,34
P_P	0,25	P_P^{basic}	0,11	m_P	0,17	K_P	2,35
Vitamins							
P_{B1}	0,01	P_{B1}^{basic}	0,02	m_{B1}	0,36	K_{B1}	0,52
P_{B2}	0,06	P_{B2}^{basic}	0,02	m_{B2}	0,32	K_{B2}	3,00
P_{B6}	0,10	P_{B6}^{basic}	0,02	m_{B6}	0,31	K_{B6}	0,20
P_c	0,83	P_c^{basic}	0,94	m_c	0,01	K_c	0,88

Quality rating of simple indexes of nutrient materials has been determined by the formula (3), as a result the values are the following: for proteins – K_{p0} = 0,76; fats – K_f = 0,55; carbohydrates – K_c = 0,84; sodium– K_{Na} = 0,14; potassium– K_K = 1,40; calcium – K_{Ca} = 2,35; magnesium – K_{Mg} = 1,34; phosphorus– K_P = 2,35; thiamine – K_{B1} = 0,52; riboflavinum – K_{B2} = 3,00; perydoxine – K_{B6} = 0,20; cevitamic acid – K_c = 0,88.

Complex qualitative index of meal due to nutrient materials equation for two-level structure has been determined from formula (5). Due to the calculation results supper №2 has complex quality rate – K_o=1,09.

5. Complex quality rating of dialy ration

According to the canteen menu original data is calculated for determination of daily ration (Table 10).

Absolute values of qualitative indexes of nutrient materials are the following: for proteins – P_p = 0,16; fats – P_f = 0,14; carbohydrates – P_c =0,70; sodium – P_{Na} = 0,47; potassium – P_K = 0,25; calcium– P_{Ca} = 0,07; magnesium– P_{Mg} = 0,04; phosphorus– P_P = 0,17; thiamine – P_{B1} = 0,04; riboflavinum – P_{B2} = 0,06; perydoxine – P_{B6} = 0,11; cevitamic acid – P_c = 0,79. The results are brought in the Table 11.

Quality rating of simple indexes of nutrient materials has been determined by the formula (3), as a result the values are the following: for proteins – K_p = 1,06; fats – K_f = 1,21; carbohydrates – K_c = 1,03; sodium – K_{Na} = 1,04; potassium– K_K = 0,74;calcium – K_{Ca} = 1,00; magnesium – K_{Mg} = 1,00; phosphorus– K_P = 1,53; thiamine – K_{B1} = 2,00; riboflavinum – K_{B2} = 3,00; perydoxine – K_{B6} = 0,18; cevitamic acid – K_c = 0,85.

Complex qualitative index of meal due to nutrient materials equation for two-level structure has been determined from formula (5). Due to the calculation results daily ration has complex quality rate K_o=1,39.

Table 10

Calculation of macronutrients, mineral matters and vitamins content for daily ration

Nutrient materials	Name of the dish				
	Breakfast	**Dinner**	**Supper №1**	**Supper №2**	**Total**
Weight, g	675	965	675	300	2615
Macronutrients, g:					
proteins	49,27	46,39	41,47	9,50	146,62
fats	37,34	28,02	36,58	27,80	129,74
carbohydrates	156,38	214,35	229,01	50,20	649,94
Mineral matters, мг:					
Na	2317,30	2933,15	1162,80	55,0	6468,25
K	922,60	1371,95	757,30	421,0	3472,85
Ca	451,90	185,10	228,90	151,0	1016,90
Mg	167,60	176,85	111,50	43,0	498,95
P	946,50	665,95	481,30	227,0	2320,75
Vitamins, mg:					
B_1	0,83	0,84	0,69	0,05	2,41
B_2	2,41	0,47	0,53	0,33	3,75
B_6	2,12	3,26	1,58	0,55	7,51
C	25,84	9,35	13,15	4,50	52,84

Table 11

Calculation of absolute values of qualitative indexes and estimation of simple indexes of nutrient materials

Absolute values		**Basic values**		**Weight coefficients**		**Simple qualitative indexes**	
Macronutrients							
P_p	0,16	P_p^{basic}	0,15	m_p	0,50	K_p	1,06
P_f	0,14	P_f^{basic}	0,17	m_f	0,40	K_f	1,21
P_c	0,70	P_c^{basic}	0,68	m_c	0,10	K_c	1,03
Mineral matters							
P_{Na}	0,47	P_{Na}^{basic}	0,45	m_{Na}	0,03	K_{Na}	1,04
P_K	0,25	P_K^{basic}	0,34	m_K	0,05	K_K	0,74
P_{Ca}	0,07	P_{Ca}^{basic}	0,07	m_{Ca}	0,25	K_{Ca}	1,00
P_{Mg}	0,04	P_{Mg}^{basic}	0,03	m_{Mg}	0,50	K_{Mg}	1,00
P_P	0,17	P_P^{basic}	0,11	m_P	0,17	K_P	1,53
Vitamins							
P_{B1}	0,04	P_{B1}^{basic}	0,02	m_{B1}	0,36	K_{B1}	2,00
P_{B2}	0,06	P_{B2}^{basic}	0,02	m_{B2}	0,32	K_{B2}	3,00
P_{B6}	0,11	P_{B6}^{basic}	0,02	m_{B6}	0,31	K_{B6}	0,18
P_c	0,79	P_c^{basic}	0,94	m_c	0,01	K_c	0,85

Obtained values of complex qualitative index of breakfast, dinner, supper №1, supper №2 and daily ration are brought in the Table 12.

Table 12

Complex quality rating of daily rations

Name	Breakfast	Dinner	Supper № 1	Supper № 2	Daily ration
K_0	1,60	1,57	1,35	1,09	1,39

Due to the data (Table 12), we can draw a conclusion that the biggest value of the complex index K_{0max}=1,60 is obtained in breakfast, the lowest value is typical for supper №2 K_{0min}=1,09. Whereas, supper №2 is considered to be the most balanced meal with value K_0=1,09, which is close to the optimal value of complex quantitative rating K_0=1,00. Quality rating of daily rations in hotels and restaurants provides an opportunity to determine diet balance due to the norms of physiological need for daily ration.

Conclusions

Method of quality rating of daily rations in hotels and restaurants is considered. The structure of qualitative indexes and results of experimental research of complex diet quantitative rating are represented. Taking into account the norms of physiological need of a common person, complex qualitative rate of one meal and daily ration in a canteen is calculated. For this daily ration, complex qualitative indexes for group of macronutrients, mineral matters and vitamins are identified. The most balanced values of the complex qualitative index are determined which are common to super №2 with rate K_0=1,09.

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FTIR spectroscopy combined with chemometric: a versatile tool for quality evaluation of fried vermicelli

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Abstract

Introduction. Snacks are common food throughout the world including subcontinent. Most of the snack foods are prepared in oil and fat. In current study, fried vermicelli (common snack food) was selected to evaluate the quality as it is largely consumed in many countries.

Materials and methods. Fried vermicelli was subjected for the extraction of total oil by applying Soxhlet extraction method using hexane as a solvent. Fatty acid composition of extracted fried vermicelli oil was checked on GC-MS. Similarly, FTIR spectroscopy was also used to record the spectra of same oil for the development of simple methodology to quantify fatty acid groups and ratios.

Results and discussion. High percentage of oil content was observed in all fried vermicelli samples (19.77–32.99%). Fatty acid composition exposed that palmitic (34.6–47.5%), stearic (4.76 to 10.6%), oleic (27.2–37.0%) and elaidic acid (12.0–24.3%) were predominant fatty acids among saturated and monounsaturated fatty acids. While polyunsatured fatty acids were observed comparatively in less quantity in fried vermicelli (0.66 to 5.99 %). The presence of higher *trans* fatty acids indicated that fried vermicelli was prepared in hydrogenated oil. Fatty acid ratios of some important groups were observed in the range of 0.72–1.92 SFA/UFA, 0.013–0.130 cis PUFA/SFA, 0.1 to 1.81 *trans* FA/cis FA, 0.01 to 0.097 cis PUFA/SFA + TFA, 27.7–37.05 cis MUFA + cis PUFA/SFA + TFA. The obtained results of groups and ratios by GC-MS were used to develop different calibration models for the quantification of fatty acid groups and fatty acid ratios using PLS chemometric approach. The developed PLS models using selected wavelength regions showed higher correlations (>0.99) with GC-MS results.

Conclusions. It can be concluded that quality of fried vermicelli marketed locally is worrisome matter for the consumers and quality control authorities. FTIR provided complete profiling of groups and ratios in fried vermicelli very accurately with negligible difference in the results. The proposed methodology serves as a rapid and simple quantitative tool for quality evaluation of major groups and ratios.

Introduction

Nutritionists are interested in the fatty acid intake, as the oil and fats play an essential role in human nutrition as energy source and metabolic activities since it is a major research focus in nutritional sciences. They regulate the physiological process in human body structure and produce energy [1].

Currently, nutritionists recommend intake of saturated fatty acids (SFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) in a balanced amount for a nutritious diet because higher intake of SFA has been associated with cardiovascular diseases (CVD), whereas MUFA and PUFA consumption is related with beneficial health effects [2]. MUFA and PUFA substituted SFA [3] because MUFA lower the risk factors of CVD [4]. PUFA can be linked to negative or beneficial health effects [5]. The epidemiological research on clinical role of n-6/n-3 ratio of PUFA was studied and found an increased risk of cardiovascular and coronary heart diseases [6]. Conversely, PUFA/SFA ratio is associated with CVD which can be lower by replacing SFA with PUFA in a balanced diet [7] as the increased intake of PUFA has beneficial effects [8]. However, some detrimental properties are also there, unsaturated FA can be reacted with oxygen especially in air which makes them rancid [9]. The process of partial hydrogenation is used to avoid the rancidity of unsaturated FA [10]. Before hydrogenation process, unsaturated FA present in cis configuration, whereas partial hydrogenation converts some of the cis double bonds into its *trans* configuration and relocate the position of double bonds [11]. WHO scientific review committee on *trans* fat recommend daily intake of partially hydrogenated oil should be less than 1% [12]. FDA proposed nutritional facts labeling rules to separate the *trans* fat from total fat content, which was effective from 1st January 2006 [11]. FDA remove partial hydrogenated oil which is the primary source of *trans* fat, from the list of GRAS (Generally recognized as safe) and allow food companies to eliminate the partially hydrogenated oils by reformulating their products by 2018 [13].

In Pakistan, no any study has been reported on the fatty acids as well as *trans* fatty acid contents of fried vermicelli, as it is a very popular snack food in sub-continent. GC-MS is considered as an authentic technique for the quantification of fatty acid composition. The current study is conducted to investigate the main classes of fatty acid present in different fried vermicelli samples collected from different locations of Hyderabad, Sindh. The results of GC-MS correlated with the specific regions of FTIR spectra using PLS chemometric technique.

Materials and methods

Chemicals and reagents

Solvents and chemicals, such as hexane, methanol and potassium hydroxide (analytical grade) purchased from Merck (Darmstadt, Germany).

Sample collection

18 samples of fried vermicelli were collected from different local shops of Hyderabad, Pakistan.

Oil extraction

Fried vermicelli samples were subjected for the extraction of total fat and oil by applying Soxhlet extraction method using hexane as a solvent [14]. Total oil content was calculated as percentage mass of the sample. Extracted fried vermicelli oil was transferred into vials and kept at -4 °C until further analysis.

Determination of fatty acid composition

Fatty acid composition of fried vermicelli was analyzed by preparing Fatty acid methyl ester (FAME) using IUPAC standard method [15]. GC-MS chromatograms of fried vermicelli were recorded via Agilent GC-MS. Obtained data was analyzed using ChemStation software. For identification of fatty acids in fried vermicelli, NIST and Wiley libraries were used to compare the fatty acids by matching >90% similarity.

Gas chromatography – mass spectrometry conditions

FAME were analyzed on gas chromatography (Agilent 6890 N) coupled with a mass selective detector (Agilent MS-5975) and an auto sampler injector (Agilent 7683-B) (Little Fall, NY, USA). For the separation of FAME, 5% phenyl methylsiloxane (HP-5MS) capillary column having 30 m length with internal diameter of 0.25 mm from Agilent Technologies (Palo Alto, CA, USA) was used. Initial oven temperature 150 oC was set for 2 min and ramped at 4 C/min up to 230 °C and hold for 5 min. Helium was used as a carrier gas with flow rate of 1ml/min and a split ratio 1:50. Temperature of injector and detector was set at 240 °C and 260 °C, respectively. Electron impact (EI) ionization source at 70 ev in mass spectrometer was used with the scan range of 50–550 m/z as reported in earlier study [16].

Statistical analyses and calculations

Peaks were identified by GC-MS libraries of NIST and Wiley and percentage of fatty acids were quantified by area percent method.

Fourier Transform Infrared spectroscopy

All the infrared spectra of Fried vermicelli samples were recorded using Nicolet 320 Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Analytical Instruments) Madison, WI, USA with ZnSe Single bounce ATR accessory (Spectra-Tech, Shelton, CT) with KBr beam splitter and deuterated triglycine sulphate (DTGS) detector. OMNIC software (version 7.3) was used for the instrumental control and acquisition of data. 24 accumulated scans with the resolution of 4 cm^{-1} in the range of 4000–650 cm^{-1} were set for recording spectra. Background spectrum was collected before acquiring each spectrum of sample. Soft tissue and hexane were used for the cleaning of ZnSe crystal after every sample.

Results and discussion

Snack food products are of wider interest for food researchers because of its high consumption. Fried vermicelli is one of the common snack food in sub-continent especially in Pakistan. It is a type of pasta, round in section and somewhat thinner than

spaghetti. It is prepared using different recipes and looks like thin vermicelli usually roasted/fried in oil/fat until light brown color appears. Initially, the samples were subjected to oil extraction using Soxhlet extractor to know the exact oil content. High percentage of oil content was observed in all fried vermicelli samples (19.77 and 32.99%). The highest amount of oil was extracted from fried vermicelli-14 and minimum quantity was found in fried vermicelli-18. Table 1 shows the fatty acids composition of fried vermicelli expressed in percentage. In analyzed samples, palmitic (C-16:0) and stearic acid (C-18:0) were present in higher amounts, whereas dodecanoic (C-12:0), myristic (C-14:0) and arachidic acid (C-20:0) found in relatively low quantities. Among SFA, palmitic acid in fried vermicelli was present in the range of 34.6–47.5%. The stearic acid in fried vermicelli was present in the range of 4.76–10.6%. Oleic acid was observed as main contributor among MUFA in fried vermicelli samples. The percentage of oleic acid was found between 27.2–37.0% in fried vermicelli. Among MUFA, elaidic acid (*trans* fatty acid) was also detected in all fried vermicelli samples. The *trans* fatty acids in fried vermicelli was quantified in the range of 12.0–24.3%, highest and lowest value was found in fried vermicelli-17 and vermicelli-2, respectively, which indicated that fried vermicelli prepared in hydrogenated oil. Nutritional values of PUFA are very important because of essential FAs. The amount of PUFA in fried vermicelli samples was observed comparatively in less quantity (0.66–5.99 %). Linoleic acid (C18:2) was the main fatty acid in PUFA group.

Table 2 shows the fatty acid ratios and nutritive values of the fried vermicelli. SFA/UFA ratio showed co-relation of two main fatty acid groups. The value of this ratio was found between 0.72 – 1.92, indicated that SFA proportion present in higher amount. It has been reported that high ratio increases plasma very low density lipoprotein (VLDL) lipids and reduces the hepatic hypertriglyceridemic effect [17]. The minimum value of cis PUFA/SFA ratio set as 0.45 by British Department of Health, UK [18]. In this study, cis PUFA/SFA ratio were found lower than recommended limits in fried vermicelli samples which are not good for health in terms of CVD. Highest value of cis PUFA/SFA was found in fried vermicelli-12 (0.103) and minimum in fried vermicelli-3 (0.013). Trans FA/cis FA ratio is also a very important parameter which shows the degree of conversion of cis to *trans* configuration. In current study the ratio was found between 0.1 and 1.81. Higher values of this ratio indicated higher proportion of hydrogenated oil. cis PUFA/SFA + TFA and cis MUFA + cis PUFA/SFA + TFA are commonly used to express nutritional value of edible oils and fats [19]. In this study the values of cis PUFA/SFA + TFA were found between 0.01 and 0.097, whereas cis MUFA + cis PUFA/SFA + TFA ratio were found in the range of 27.7 to 37.05 in fried-vermicelli.

Table 1

Fatty acid composition of fried vermicelli

Fried vermicelli Sample No.	C 12:0	C 14:0	C 16:0	C18:2	C18:1 Cis	C18:1 trans	C18:0	C 20:0
1	-	0.14 ±0.01	41.5 ±0.00	2.73 ±0.00	37.0 ±0.01	12.2 ±0.00	6.38 ±0.00	-
2	-	0.54 ±0.01	41.7 ±0.01	2.14 ±0.02	35.1 ±0.07	12.0 ±0.01	8.49 ±0.01	-
3	0.03 ±0.01	0.25 ±0.03	41.6 ±0.01	0.66 ±0.01	33.0 ±0.04	13.8 ±0.01	10.6 ±0.07	0.07 ±0.00
4	-	0.52 ±0.02	37.3 ±0.01	3.22 ±0.05	30.6 ±0.01	19.4 ±0.01	8.91 ±0.02	-
5	-	0.66 ±0.01	38.8 ±0.02	5.99 ±0.02	32.5 ±0.00	14.5 ±0.01	7.54 ±0.01	-
6	0.02 ±0.01	0.26 ±0.05	34.6 ±0.01	1.97 ±0.01	32.0 ±0.01	23.4 ±0.05	7.60 ±0.01	0.12 ±0.01
7	0.18 ±0.01	0.86 ±0.00	40.6 ±0.00	3.92 ±0.00	30.2 ±0.01	15.4 ±0.01	8.58 ±0.00	0.24 ±0.05
8	0.16 ±0.01	0.89 ±0.01	42.1 ±0.00	3.90 ±0.01	28.8 ±0.03	17.2 ±0.01	6.73 ±0.00	0.27 ±0.01
9	0.30 ±0.01	0.79 ±0.01	40.8 ±0.06	3.58 ±0.04	29.3 ±0.00	16.7 ±0.06	8.60 ±0.02	-
10	0.55 ±0.01	-	47.5 ±0.00	1.56 ±0.01	27.2 ±0.01	18.4 ±0.01	4.76 ±0.05	-
11	-	0.68 ±0.02	39.6 ±0.01	2.81 ±0.03	28.3 ±0.05	22.9 ±0.01	5.78 ±0.01	-
12	-	0.40 ±0.02	38.5 ±0.01	4.74 ±0.01	30.0 ±0.01	19.3 ±0.03	6.94 ±0.00	0.15 ±0.04
13	-	0.48 ±0.01	38.8 ±0.04	2.86 ±0.01	28.5 ±0.00	23.9 ±0.01	5.43 ±0.01	-
14	-	0.15 ±0.05	40.4 ±0.05	1.40 ±0.00	31.6 ±0.05	20.5 ±0.02	5.88 ±0.01	-
15	-	0.37 ±0.01	37.0 ±0.00	2.15 ±0.01	31.6 ±0.01	22.0 ±0.00	6.74 ±0.05	0.18 ±0.05
16	0.02 ±0.01	0.26 ±0.06	37.3 ±0.02	1.91 ±0.05	33.6 ±0.02	20.4 ±0.01	6.49 ±0.01	0.06 ±0.00
17	0.03 ±0.01	0.38 ±0.01	39.1 ±0.01	1.30 ±0.02	28.5 ±0.02	24.3 ±0.04	6.38 ±0.06	0.07 ±0.01
18	-	0.69 ±0.01	41.9 ±0.00	2.48 ±0.02	29.4 ±0.01	16.5 ±0.01	9.06 ±0.01	-

Table 2

Fatty acid groups and fatty acids ratios of fried vermicelli (SFA, cis MUFA, trans MUFA, total MUFA, cis PUFA, SFA+TFA, MUFA+PUFA, cis MUFA+PUFA, SFA/UFA, cis PUFA/SFA, trans MUFA+ cis MUFA, cis PUFA / SFA+TFA, cis MUFA+PUFA/SFA+TFA)

Fried vermicelli Sample No.	cis MUFA+PUFA/ SFA+TFA	cis PUFA/ (SFA+TFA)	trans / cis	cis PUFA/ SFA	SFA/UFA	cis MUFA+PUFA	MUFA+PUFA	SFA+TFA	cis PUFA	Total MUFA	trans MUFA	cis MUFA	SFA
1	37.05	0.045	0.308	0.057	0.923	39.74	51.99	60.26	2.73	49.30	12.26	37.01	48.00
2	35.15	0.034	0.322	0.042	1.030	37.26	49.25	62.72	2.14	47.1	11.99	35.12	50.73
3	33.04	0.010	0.410	0.013	1.105	33.69	47.50	66.31	0.66	46.8	13.81	33.03	52.50
4	30.70	0.049	0.571	0.069	0.878	33.87	53.23	66.12	3.22	50.0	19.36	30.65	46.76
5	32.59	0.097	0.377	0.128	0.887	38.48	53.00	61.51	5.99	47.0	14.52	32.49	46.99
6	32.05	0.030	0.688	0.046	0.743	33.99	57.36	66.01	1.97	55.4	23.37	32.02	42.64
7	30.22	0.059	0.452	0.078	1.020	34.08	49.49	65.92	3.92	45.6	15.41	30.16	50.51
8	28.81	0.058	0.528	0.078	1.004	32.66	49.89	67.34	3.90	46.0	17.23	28.75	50.11
9	29.36	0.053	0.507	0.071	1.018	32.89	49.55	67.11	3.58	46.0	16.67	29.31	50.45
10	27.27	0.022	0.638	0.030	1.118	28.81	47.20	71.19	1.56	45.6	18.39	27.25	52.80
11	28.30	0.041	0.736	0.061	0.854	31.08	53.94	68.92	2.81	51.1	22.86	28.26	46.06
12	30.04	0.072	0.557	0.103	0.850	34.71	54.05	65.29	4.74	49.3	19.34	29.97	45.95
13	28.52	0.042	0.764	0.064	0.809	31.34	55.28	68.66	2.86	52.4	23.94	28.49	44.72
14	31.67	0.021	0.619	0.030	0.868	33.05	53.53	66.95	1.41	52.1	20.47	31.64	46.47
15	31.60	0.032	0.652	0.048	0.795	33.72	55.71	66.28	2.15	53.6	21.98	31.57	44.29
16	33.64	0.030	0.573	0.043	0.790	35.52	55.88	64.48	1.91	53.9	20.35	33.61	44.12
17	28.50	0.018	0.814	0.028	0.850	29.78	54.04	70.22	1.30	52.7	24.26	28.48	45.95
18	29.43	0.036	0.518	0.048	1.067	31.87	48.37	68.13	2.48	45.9	16.50	29.40	51.63

ATR-FTIR spectra of fried vermicelli

The representative FTIR spectra of extracted oil of fried vermicelli are shown in Figure 1A. The assignments of the bands corresponding to the stretching vibration modes are usually easier than the assignments of the bands corresponding to the bending vibration modes due to overlap [20]. The stretching vibration band at 3004 cm^{-1} and two intense bands at 2920 cm^{-1} and 2851 cm^{-1} correspond to the cis double-bonds and asymmetric and symmetric stretching vibration of aliphatic C-H_2 functional groups, respectively.

Intense band of carbonyl functional group of triglycerides appear at 1742 cm^{-1}, the aliphatic groups of the CH_2 and CH_3 shows a band near 1465 cm^{-1} because of the bending vibrations, whereas the rocking vibrations of CH band at 1418 cm^{-1} appeared due to the cis-olefins and 1377 cm^{-1} band is due to bending vibrations of CH_2 groups. Stretching vibrations of C–O ester group typically shows four bands at 1235, 1161, 1116 and 1097 cm^{-1} along with CH_2 group associated with bending vibrations at first two frequencies i.e.

1235 cm^{-1} and 1161cm^{-1}. Characteristic band of isolated *trans* olefins at 966 cm^{-1} appears due to the bending vibrations of C-H out of plane deformation, while the band at 721 cm^{-1} is due to the rocking vibration of out of plane cis olefins overlapping of CH_2.

FTIR spectral pre-treatment and data correction

For the FTIR quantification of various fatty acid groups and their ratios, different regions of the mid IR range were used to construct suitable model using 1st and 2nd derivative spectra in order to improve regression values as compare to the pure absorbance signal. Figure 1A, 1B and 1C shows normal, 1st derivative and 2nd derivative spectra of extracted fried vermicelli oil, respectivley.

PLS models

Table 3A and Table 3B illustrates the quality parameters based on Fig 2A and Fig 2B including selected spectral region, baseline type, factors, R2 value and RMSEC of models to predict groups such as SFA, MUFA, cis-MUFA, PUFA, TFA and fatty acid ratios. The number of factors used in PLS models were auto selected by TQ software in regression analysis based on attaining minimum predicted residual error of sum of squares (PRESS) value. For the development of calibration model partial least square (PLS) regression was applied, whereas the obtained GC-MS values of SFA, MUFA, cis-MUFA, PUFA, TFA and their ratios were used as reference to establish correlation between actual GC-MS and predicted FTIR values. For each PLS model 18 samples were used as calibration points. It was found that difference between actual and predicted values of SFA, MUFA, cis-MUFA, PUFA, TFA and their ratios were very small which indicates successfulness of developed PLS models.

Minimum three models were developed by selecting different spectral regions for each fatty acids groups and ratios. For SFA model best results were achieved in the regions of 2970–2820 & 1400–1200 cm^{-1} with R2 and RMSEC value of 0.999 and 0.112, respectively. Model developed for total MUFA showed higher R2 value 0.99916 in the region of 3000–3050 cm^{-1} using linear removed baseline with RMSEC 0.132. On the other hand, individually cis and *trans* MUFA models demonstrated good results with linear removed baseline in the region of 3050–2850 cm^{-1} and 2nd derivative in the spectral range of 980–945 cm^{-1}. The high R2 values were achieved in both models 0.999 and 0.991 with minimum RMSEC value 0.00984 and 0.504, respectively. For the quantification of cis PUFA in fried vermicelli, best model was developed in the range of 2989–2869 cm^{-1} using linear removed baseline type with R2 and RMSEC values of 0.999 and 0.031, respectively. The developed PLS model for fatty acid ratios including SFA+TFA (2880–2815 & 980–945), MUFA+PUFA (3010–2880), cis MUFA+PUFA (3050-2650 & 1650-1800), SFA/UFA (3010–2880), cis PUFA/SFA (2950–2800 & 679–786), *trans* MUFA/cis MUFA (2950–2880 & 980–945) and cis MUFA+PUFA/SFA+TFA (3050–2800 & 1520–1000) showed R2 values of 0.999 except in cis PUFA/(SFA+TFA) (2950–2800 & 980–945) model which has R2 value of 0.997 with the maximum RMSEC value of 0.092 in SFA+TFA model and minimum RMSEC was found to be 0.11e-3 in cis PUFA/ SFA model. Table 4A and Table 4B show the results of fatty acids groups and fatty acids ratios respectively, obtained from GC-MS and FTIR with difference between them. In all the developed FTIR models, there is very little difference compared to GC-MS results.

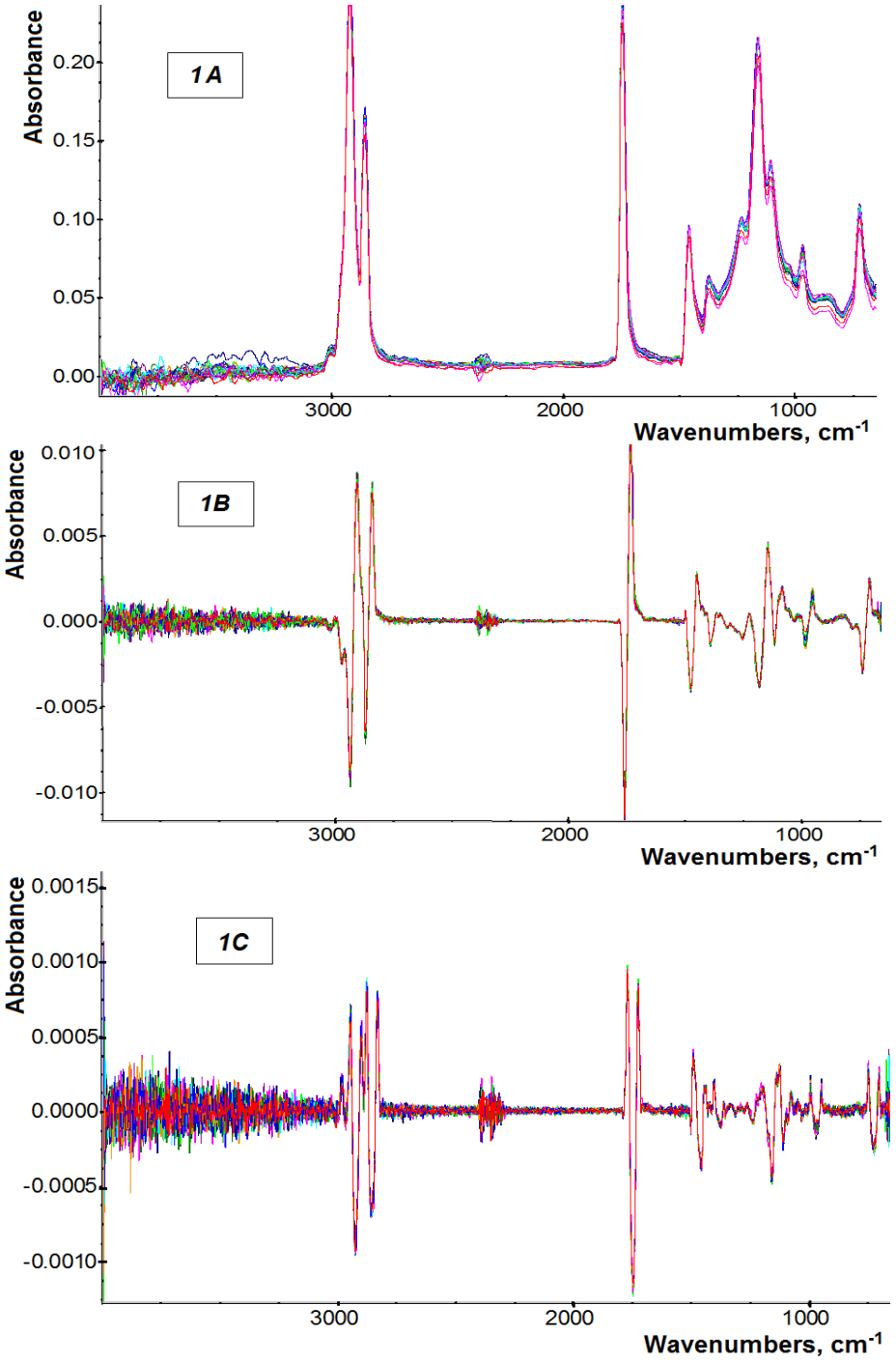

Figure 1.
A - Normal FTIR spectra of fried vermicelli; B - 1st derivative spectra;
C - 2nd derivative spectra of all the samples

Table 3A

FTIR PLS correlation model of fatty acid groups

Fatty acid	Spectral region cm^{-1}	Baseline type	Factors	R^2	RMSEC
SFA	3050–650	None	2	0.818	1.74
	2950–2820&1125–1080	None	4	0.956	0.888
	2970–2820&1400–1200	**None**	**7**	**0.999**	**0.112**
cis MUFA	3050–2950	None	8	0.999	0.0357
	3020–650	None	3	0.885	1.15
	3050–2850	**Linear removed**	**10**	**0.999**	**0.009**
trans MUFA	980–945	None	4	0.984	0.674
	980–945	1st Derivative	4	0.988	0.605
	980–945	**2nd Derivative**	**5**	**0.991**	**0.504**
Total MUFA	3050–650	None	3	0.958	1.04
	4000–650	None	2	0.959	1.03
	3050–3000	**Linear Removed**	**9**	**0.999**	**0.132**
cis PUFA	2989–2869	None	5	0.984	0.229
	4000–650	None	1	0.759	0.839
	2989–2869	**Linear Removed**	**8**	**0.999**	**0.031**

Table 3B

FTIR PLS correlation model of fatty acid ratios

Fatty acid ratios	Spectral region cm^{-1}	Baseline type	Factors	R^2	RMSEC
SFA+TFA	**2880–2815 & 980–945**	**None**	**9**	**0.999**	**0.092**
	3010–750 & 990–945 3050–2950	None	2	0.808	1.570
		None	7	0.999	0.101
MUFA+PUFA	**3010–2880**	**None**	**7**	**0.999**	**0.091**
	3015–2835	None	6	0.999	0.122
	3040–2830	None	4	0.992	0.383
Cis MUFA+PUFA	3050–2700 & 1650–1800	None	3	0.984	0.480
		None	3	0.839	1.480
	3050–2870 & 1650–1800 **3050–2650 & 1650–1800**	**1st Derivative**	**4**	**0.999**	**0.060**
SFA/UFA	3030–2880	None	6	0.999	0.006
	3040–2880	None	6	0.998	0.006
	3010–2880	**None**	**7**	**0.999**	**0.003**
cis PUFA/ SFA	**2950–2800 & 679–786**	**None**	**8**	**0.999**	**$0.11e^{-3}$**
	2950–2800 3000–2800	None	5	0.992	0.003
		None	3	0.929	0.009
trans MUFA/ cis MUFA	2950–2830 & 980–945	None	5	0.994	0.015
		None	3	0.975	0.031
	3050–2950 & 980–945 **2950–2880 & 980–945**	**Linear removed**	**7**	**0.999**	**0.006**
cis PUFA/(SFA+TFA)	3050–2800 & 980–945	None	4	0.980	0.003
		None	5	0.992	0.002
	2950–2800 **2950–2800 & 980–945**	**Linear removed**	**6**	**0.997**	**0.001**
Cis MUFA+PUFA/ SFA+TFA	3050–2800 & 1000–900	None	7	0.998	0.053
	3050–2800 & 1520–1000	**None**	**8**	**0.999**	**0.006**
	3050–2800 & 1830–920	None	4	0.961	0.681

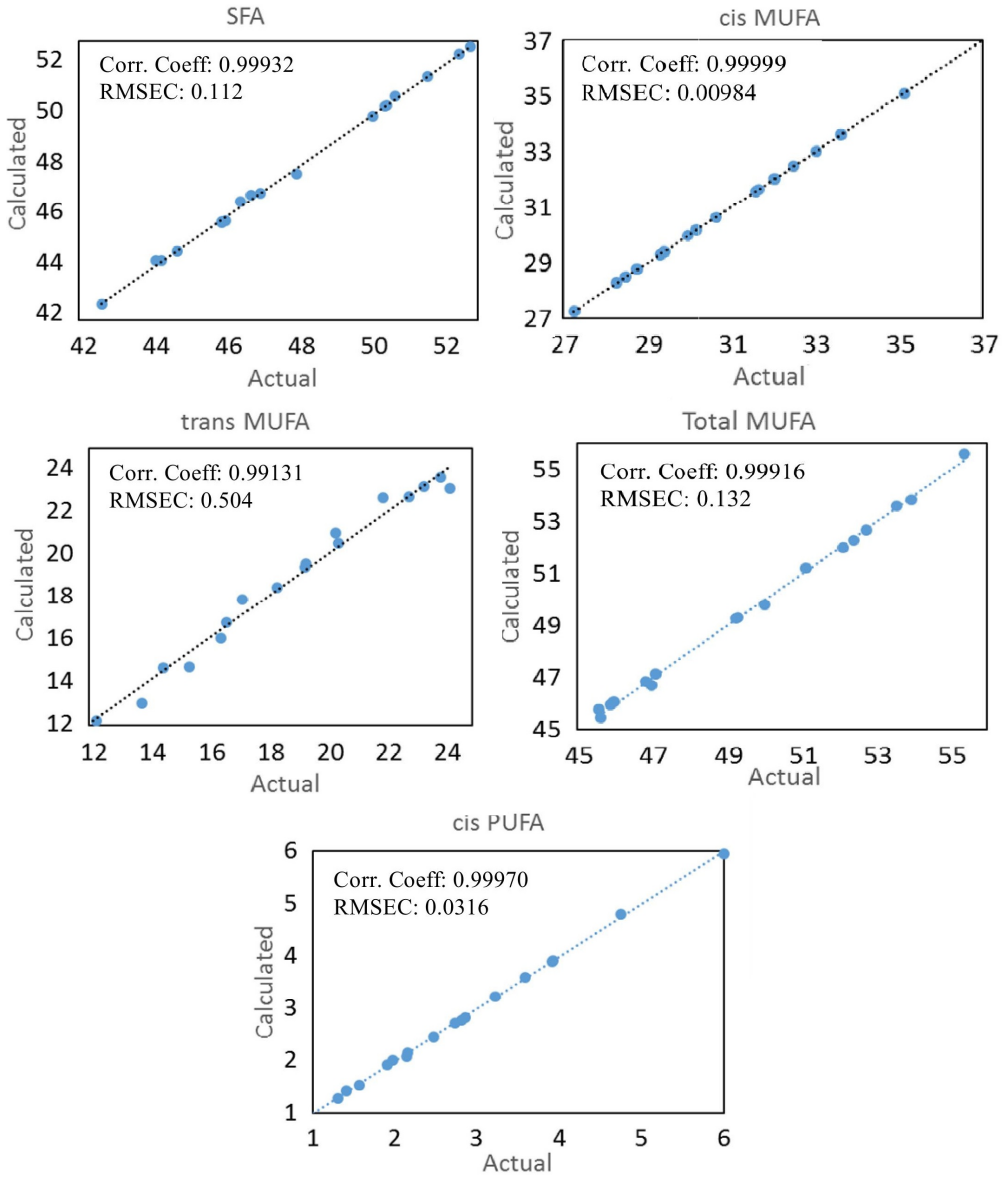

Figure 2A. PLS models for SFA, cis-MUFA, *trans*-MUFA, total-MUFA and total PUFA.

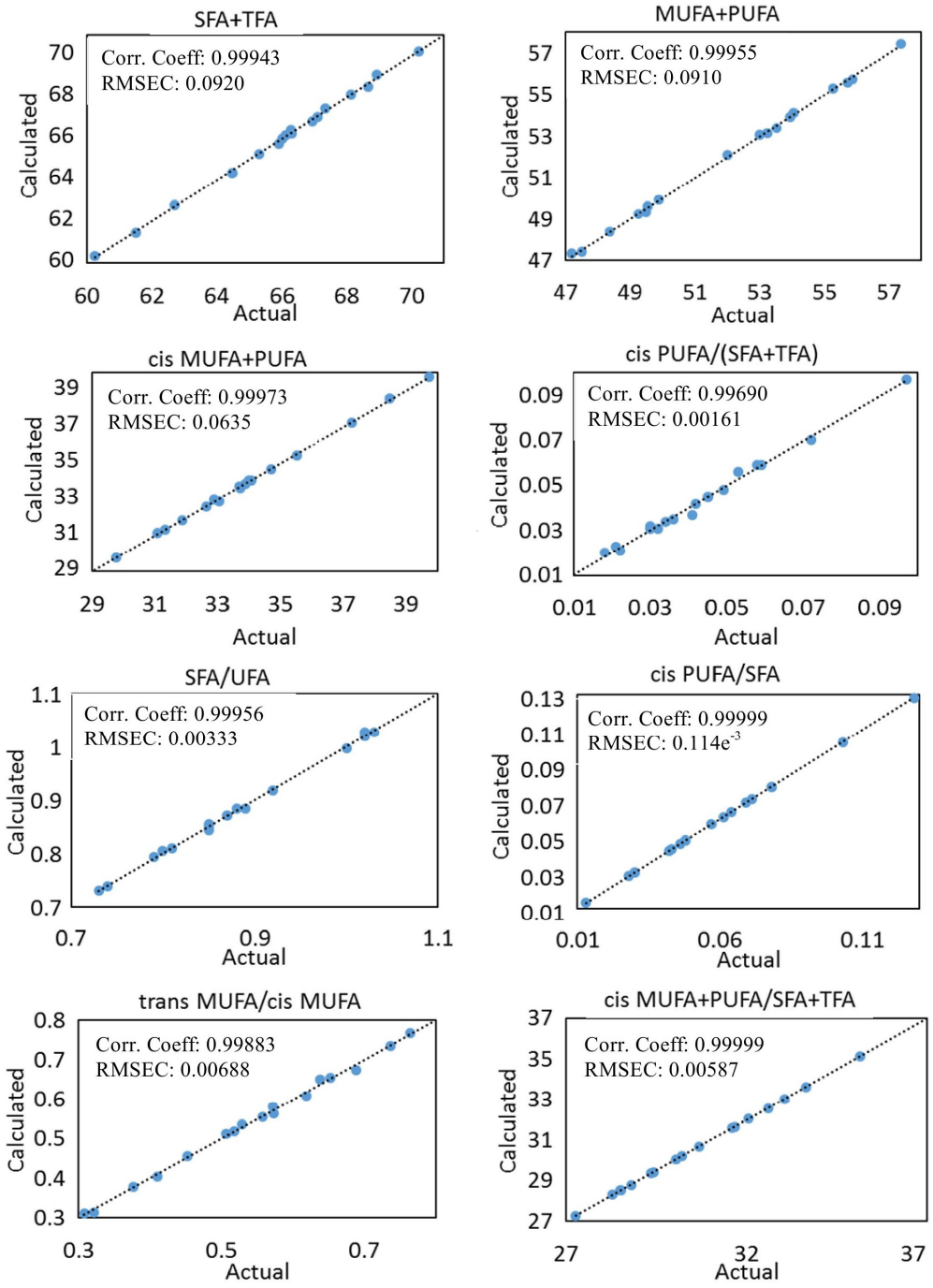

Figure 2B. PLS models for SFA+TFA, MUFA+PUFA, cis-MUFA+PUFA, SFA/TFA, cis PUFA/SFA, trans MUFA/ cis MUFA, cis PUFA/SFA+TFA and Cis MUFA+PUFA/ SFA+TFA.

Table 4A

Comparative results of FTIR and GC methods for fatty acid groups

Fried vermicelli Sample No	SFA			cis MUFA			*trans* MUFA		
	GC	FTIR	Diff	GC	FTIR	Diff	GC	FTIR	Diff
1	48.003	47.769	-0.234	37.010	37.017	0.007	12.255	12.235	-0.020
2	50.730	50.860	0.130	35.120	35.116	-0.004	11.990	12.596	0.606
3	52.498	52.504	0.006	33.030	33.024	-0.006	13.808	13.075	-0.733
4	46.760	46.921	0.161	30.650	30.634	-0.016	19.360	19.597	0.237
5	46.999	47.006	0.006	32.492	32.493	0.001	14.516	14.696	0.180
6	42.641	42.606	-0.036	32.016	32.022	0.006	23.369	23.222	-0.147
7	50.508	50.492	-0.016	30.165	30.156	-0.008	15.412	14.737	-0.675
8	50.113	50.051	-0.062	28.755	28.758	0.003	17.228	17.927	0.699
9	50.447	50.450	0.002	29.310	29.303	-0.007	16.666	16.838	0.172
10	52.798	52.803	-0.017	27.248	27.264	0.016	18.392	18.465	0.073
11	46.062	45.915	-0.147	28.265	28.255	-0.009	22.859	22.747	-0.112
12	45.950	45.845	-0.105	29.970	29.963	-0.007	19.340	19.428	0.088
13	44.721	44.683	-0.037	28.487	28.495	0.009	23.935	23.659	-0.276
14	44.293	44.327	0.034	31.573	31.579	0.006	21.984	22.679	0.695
15	44.124	44.319	0.195	33.614	33.606	-0.008	20.354	21.051	0.698
16	45.955	45.867	-0.088	28.480	28.467	-0.013	24.262	23.108	-1.154
17	46.473	46.675	0.202	31.646	31.663	0.018	20.474	20.562	0.089
18	51.627	51.611	0.005	29.398	29.409	0.012	16.499	16.081	-0.418

Fried vermicelli Sample No	Total MUFA			cis PUFA		
	GC	FTIR	Diff	GC	FTIR	Diff
1	49.265	49.281	0.016	2.730	2.713	-0.017
2	47.110	47.131	0.021	2.140	2.077	-0.063
3	46.838	46.867	0.029	0.663	0.698	0.035
4	50.010	49.810	-0.200	3.220	3.236	0.016
5	47.007	46.735	-0.272	5.993	5.962	-0.031
6	55.386	55.595	0.209	1.973	2.011	0.038
7	45.576	45.791	0.215	3.916	3.920	0.004
8	45.983	46.093	0.110	3.905	3.910	0.005
9	45.976	46.091	0.115	3.576	3.598	0.023
10	45.640	45.476	-0.164	1.561	1.539	-0.022
11	51.124	51.237	0.113	2.814	2.767	-0.047
12	49.310	49.317	0.007	4.740	4.803	0.063
13	52.422	52.288	-0.134	2.858	2.823	-0.034
14	53.557	53.612	0.055	2.149	2.162	0.013
15	53.968	53.884	-0.084	1.908	1.927	0.019
16	52.742	52.706	-0.035	1.304	1.294	-0.010
17	52.119	52.037	-0.082	1.407	1.431	0.024
18	45.897	45.978	0.081	2.476	2.459	-0.016

Table 4B

Comparative results of FTIR and GC methods for fatty acid ratios

Sample No	SFA+TFA			MUFA+PUFA			Cis UFA+ PUFA			cis PUFA/ (SFA+TFA)		
	GC	FTIR	Diff	GC	FTIR	Diff	GC	FTIR	Diff	GC	FTIR	Diff
1	60.258	60.345	0.087	51.995	52.093	0.098	39.740	39.752	0.012	0.045	0.045	-0.000
2	62.720	62.770	0.050	49.250	49.225	-0.025	37.260	37.219	-0.041	0.034	0.034	0.000
3	66.306	66.257	-0.049	47.501	47.419	-0.082	33.693	33.733	0.040	0.010	0.009	-0.001
4	66.120	66.173	0.053	53.230	53.171	-0.059	33.870	33.864	-0.006	0.049	0.048	-0.001
5	61.515	61.469	-0.046	53.000	53.071	0.071	38.485	38.549	0.064	0.097	0.097	0.000
6	66.011	66.035	0.024	57.358	57.466	0.108	33.989	34.060	0.071	0.030	0.031	0.001
7	65.920	65.759	-0.161	49.492	49.334	-0.158	34.080	34.069	-0.011	0.059	0.059	0.000
8	67.341	67.464	0.123	49.888	49.936	0.048	32.659	32.632	-0.027	0.058	0.059	0.001
9	67.114	67.062	-0.051	49.552	49.583	0.031	32.886	33.034	0.148	0.053	0.056	0.003
10	71.190	71.178	-0.012	47.201	47.333	0.132	28.809	28.797	-0.012	0.022	0.021	-0.001
11	68.921	69.090	0.169	53.938	53.941	0.003	31.079	31.162	0.083	0.041	0.037	-0.004
12	65.290	65.258	-0.032	54.050	54.153	0.103	34.710	34.666	-0.044	0.072	0.070	-0.002
13	68.656	68.530	-0.125	55.279	55.301	0.022	31.344	31.357	0.013	0.042	0.042	-0.000
14	66.277	66.446	0.169	55.707	55.578	-0.128	33.723	33.647	-0.076	0.032	0.031	-0.001
15	64.478	64.372	-0.106	55.876	55.735	-0.141	35.522	35.443	-0.079	0.030	0.032	0.002
16	70.216	70.202	-0.014	54.045	54.129	0.083	29.784	29.758	-0.026	0.018	0.020	0.002
17	66.947	66.874	-0.073	53.527	53.417	-0.110	33.053	32.930	-0.123	0.021	0.023	0.002
18	68.127	68.122	-0.005	48.373	48.378	0.006	31.873	31.889	0.015	0.036	0.035	-0.001

Sample No	SFA/UFA			Cis PUFA / SFA			Trans MUFA/ cis MUFA			Cis MUFA+PUFA/ SFA+TFA		
	GC	FTIR	Diff	GC	FTIR	Diff	GC	FTIR	Diff	GC	FTIR	Diff
1	0.920	0.917	-0.003	0.057	0.057	-0.000	0.308	0.311	0.003	37.050	37.057	0.007
2	1.030	1.027	-0.003	0.042	0.042	0.000	0.322	0.313	-0.009	35.150	35.151	0.001
3	1.100	1.104	0.004	0.013	0.013	-0.000	0.410	0.405	-0.005	33.040	33.039	-0.001
4	0.880	0.883	0.003	0.069	0.069	0.000	0.572	0.581	0.009	30.700	30.696	-0.004
5	0.890	0.883	-0.007	0.128	0.128	-0.000	0.377	0.379	0.002	32.590	32.589	-0.001
6	0.740	0.738	-0.002	0.046	0.046	-0.000	0.688	0.675	-0.013	32.050	32.049	-0.001
7	1.020	1.027	0.007	0.078	0.078	0.000	0.452	0.456	0.004	30.220	30.215	-0.005
8	1.000	0.996	-0.004	0.078	0.078	-0.000	0.528	0.536	0.008	28.810	28.800	-0.010
9	1.020	1.019	-0.001	0.071	0.071	0.000	0.507	0.513	0.006	29.360	29.360	-0.000
10	1.120	1.119	-0.001	0.030	0.030	-0.000	0.638	0.651	0.013	27.270	27.270	0.000
11	0.850	0.850	-0.000	0.061	0.061	-0.000	0.736	0.734	-0.002	28.300	28.316	0.016
12	0.850	0.855	0.005	0.103	0.103	-0.000	0.557	0.556	-0.001	30.040	30.044	0.004
13	0.810	0.810	0.000	0.064	0.064	0.000	0.764	0.768	0.004	28.520	28.516	-0.004
14	0.730	0.730	0.000	0.048	0.048	-0.000	0.652	0.656	0.004	31.600	31.596	-0.004
15	0.800	0.805	0.005	0.043	0.043	-0.000	0.573	0.564	-0.009	33.640	33.640	-0.000
16	0.790	0.793	0.003	0.028	0.028	0.000	0.814	0.809	-0.005	28.500	28.509	0.009
17	0.850	0.843	-0.007	0.030	0.030	0.000	0.619	0.610	-0.009	31.670	31.663	-0.007
18	0.870	0.871	0.001	0.048	0.048	-0.000	0.518	0.519	0.001	29.430	29.431	0.001

Conclusion

In the present study, fried vermicelli was completely analyzed for their fatty acid profile including various groups and ratios by GC-MS. Based on results, it was concluded that fried vermicelli contain high percentage of oil ranging from 19.77 and 32.99%. Fatty acid composition revealed that SFA and MUFA present in higher amount as compare to PUFA in fried vermicelli. All fried vermicelli samples showed higher *trans* fatty acids which indicated that samples were prepared in hydrogenated oil. Furthermore, fried vermicelli also showed less nutritional values in comparison to recommended values of *trans* fat and cis PUFA/SFA ratio set as 0.5% and 0.45, respectively. FTIR spectroscopy successfully applied to quantify fatty acid groups and ratios in fried vermicelli using chemometric. The developed PLS models showed higher correlations (>0.99) with less calibration error. The selected wavelength regions can be used to quantify the fatty acid group and their ratios using FTIR with least analysis time without using organic solvents.

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Features of using hops and CO_2-extract in brewing

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Abstract

Introduction. Beer that is made from hops or hop products of certain breeding varieties, varies considerably in the nature of bitterness, taste and aroma. This is due to the peculiarity of the biochemical composition of bitter substances, polyphenolic compounds and essential oil of hop of aromatic and bitter varieties. The aim of the study is to use in brewing the CO_2-extract and hop with a low content of alpha-acids, which can be the waste in the production of pellets 45, and to invent methods for its rational using.

Materials and methods. Aromatic hops varieties with low alpha-acids, CO_2-extract and beer made from them were investigated. High-performance liquid chromatography to determine the amount and composition of the bitter substances of hops, CO_2-extracts and their conversion products in the brewing process and spectrophotometric quality control methods for the bitter taste of hopped wort and finished beer were used.

Results. When we use in brewing CO_2-extract and a thin-aromatic hop with a low content of alpha-acids in optimal proportions, polyphenols of low-hops help to remove high-molecular polypeptides from the wort by coagulation with the formation of complexes. Thanks to this, a higher colloidal resistance of beer is achieved and the degree of use of bitter substances is increased by 15–20%. Beer that was prepared with the using of 40% wort, bitterness of aromatic low-hops and 60% bitterness due to CO_2-extract, has had the best flavor and aromatic qualities. Beer in which extract and aromatic hops was used in a proportion of 40:60% was not much different. Polyphenols and beta-fraction of aromatic low-hops hops positively influence the coarse bitterness of the CO_2-extract, softening and smoothing it, making the common bitterness of the beer balanced. Also, when we use these proportions, a maximum decrease in the index of high molecular weight polypeptides is observed, which predicts a high colloidal persistence of beer. When we use in brewing only a CO_2-extract, it is impossible to obtain beer with high taste qualities. However, an excessive amount of hoppy polyphenols leads to an astringent taste in beer.

Conclusions. Aromatic hop with a low alpha-acid content can be used in brewing as a polyphenol additive in combination with a CO_2-extract, taking into account the quantitative content and qualitative composition of hop products and adhering to a certain technology of making beer.

Introduction

Substances that are different in nature and chemical structure, which are part of the hops, give the beer a typical bitter taste, a characteristic specific flavor and cause many other important biotechnological properties. Hops compounds are effective agents for the deposition of high nitrogen substances from wort, involved in lighting and foaming, and exhibit bactericidal and preservative effect on the final product, increasing stability of beer in it storage [1-3].

Previous studies of national and foreign scientists [4-6] have found that beer made from hops of certain breeding varieties vary greatly in nature of bitterness, flavor and aroma. It's due with features of biochemical composition of bitter substances, polyphenolic compounds and essential oil of bitter and aromatic hop varieties. A different ratio of the components of these compounds has different effects on taste and aroma of beer [3, 5, 7-11]. Nowadays a significant part of hop with low content alpha acid is grown. Ukraine isn't an exception. The majority of hops plantation in Ukraine now occupied by traditional fine aromatic varieties for example: Clone 18, Zlato Polissya, Slovyanka, Natsionalniy. Due to difficult arid climatic conditions of recent years, that did not contribute to the synthesis of bitter substances, a significant part of hops have alpha acid content 3-4 %.

It is worth noting that regional as well as powerful breweries in Ukraine in their technology use a significant part of granulated hops. But when wort is hopping by granules containing only the AA 3-5 %, to a brewing machine is brought significant weight of hop, while there are significant losses of wort. Therefore, it was necessary to develop methods of increasing increase the content of alpha acids in granules by physical means, one of which is production of pellets type 45, which relate to preparations enriched of hop [1, 12]. This method includes additional processing of cones by cold air at a temperature of -35 ^{o}C, in which lupulin grains are getting more rigid and less resinous, which makes it possible to separate them from the petals of hop cones sifting about three times [1, 12]. Thanks to the separation of lupulin from hop cones and adding it in certain proportions to grinding hops, bitter substances content increased twice. Weight of enriched hop pellets is granulated and we get the granules of type 45. Due to the fact that it's impossible to separate lupulin from hop cones completely, there remains a certain amount of bitter substances. Therefore, there is a problem of using waste of subtly aromatic hops remaining in the manufacture of pellets type 45. Such hops, according to current standards, by the content of alpha acids is considered unusual and is not entitled to be used for direct hopping of wort, although all other indicators it meets standards.

Also in brewing along with granules is used CO_2-extracts of hops. Long-term studies show [3, 5, 11–12] that using only CO_2-extracts of hop can't get a beer with excellent taste. This is due to the fact that these extracts are mainly made from bitter hop varieties. Also, CO_2-extracts, unlike hops, doesn't contain the polyphenols of hop (PF).

Polyphenolic hop compounds contribute to protein precipitation and the formation of complex protein-polyphenolic complexes during boiling, thereby precipitating at the boil, thereby brightening the wort, and thereby preventing bitter hop substances from oxidation and loss. They are antioxidants and increase the restorative capacity of beer, affect the stability of taste. But high-molecular polyphenols with prolonged boiling cause an unpleasant astringent taste in beer. Extractable polyphenolic substances of hops affect the taste and quality of beer not independently, but in combination with bitter substances of hops, proteins and amino acids.

Salach and other researchers, analyzing the quality of hops, depending on its content of polyphenols, noted that in the Czech varieties content of polyphenols is significantly

higher than the varieties of hops other countries. Thus, the content of polyphenols in the Czech hops varieties Zhatetskyy, featuring the highest quality of 5,2–5,9%, while in the US - less than 2.6%. They considered high content of polyphenols in hops Zhatetskyy its advantage over other varieties. Nowadays scientists also claim that the best quality beer made from hops, containing about 5% of polyphenols [9,10].

Therefore, the selection of hops and products of its processing to produce beer with great bitterness and quality is an issue relevant to the Brewers Association of America [8] European brewers [4] and Ukrainian beer producers [5].

The aim of the research was to examine the features of using in brewing CO_2-extract of hops and low-alpha acids, which may be waste in the production of pellets type 45 and inventing ways of using and rational using of its valuable substances.

Materials and methods

It was used the international modern physicochemical methods of the analysis of bitter substances of hops and hop preparations and products of their transformation in the brewing process: high performance liquid chromatography, spectrophotometry, and also methods of monitoring, harmonised with the methods of the European Brewery Convention [2, 9, 10].

Methods of researches of qualitative indicators of hops and CO_2-extract

Subtly aromatic hop varieties with a low content of bitter substances were investigated. The weight of average sample for identification and biochemical studies was not less than 0.5 kg of dry hops. Alpha acids in hops were determined by conductometric EMU 7.4 [2, 13, 14]. Bitter substances of hops and the extract extracted with an organic solvent – methanol. The ratio between the weight of hop cones and extractant was 1:10. The number of α- and β-acids was determined by high performance liquid chromatography. Chromatography was performed using a liquid chromatograph Ultimate 3000 UV with the detector at 35 °C. The column 100 x 2.1 mm was used, which was filled with sorbent Pinacle DV C18 3 MK. A solution of methanol water and acetone in the ratio 38:24:38 was used as the mobile phase. International standard-a standard ICF-3 was used for the quantitative determination of the components of the bitter substances. Total polyphenolic compounds in hops were determined by the method of Folin [2].

Method of preparation samples of beer in the mini-brewery

Experimental brewing of the tested samples were carried out in the laboratory and mini-brewery of the Institute, with a capacity of 100 liters of beer per cycle, which rather adequately simulates the conditions of the real brewing industry.

In the experimental boiling preparation and filtration of the mash was performed according to the adopted at this production technology. The wort was prepared from 100% barley malt and CO_2-extract. Extract was contributed at the beginning of hopping. After the complete set, the wort was boiled for 30 min. Then in wort in each case made the experiment pawned represented hop varieties in two installments: 85% are pawned at the beginning of hopping, 15% are pawned 15 min before the end of the hopping. Duration of boiling of wort with hops was continued about 90 minutes.

Methods of researches of quality indicators of wort and beer

Bitterness of wort that is formed in the process of it boiling with the hops, as a result of extraction and isomerization of bitter substances of hops, was measured on a spectrophotometer according to the method of EMU 8.8 (International method MI). The method is based on measuring optical density of iso octane extract obtained in the extraction of bitter substances acidified hopped beer wort isooctane (2,2,4- three methyl pentane) spectrophotometer at wavelength 275 nm against isooctane. We counted quantity of bitterness, which is expressed in international units of bitterness - one EMU by index of optical density.

In the beer content of polyphenolic compounds and anthocyanins were determined on a spectrophotometer according to the EBC method 9.11 (International method MI). [4]. Antotsianoheny were determined by the method of Harris and Rikkets [14]. This method is based on the transformation of Antotsianogens in anthocyanidins upon heating with acid. Antotsianogens are completely adsorbed on the adsorbent and polyamide sorbent is dissolved in a mixture of butanol - HCl. Red pigments, anthocyanins and anthocyanidins are converted into colored form when they are heated. The intensity of color, which is determined on a spectrophotometer under the wavelength of 350 nm, determines the content of anthocyanidins.

In the prepared beer and wort was controlled the size of fractions of high polypeptides. In developing the method came from the ratio of ingredients, the method adopted in determining the fraction Lundin and Shroderhayma [15] A faction in determining macromolecular proteins.

A fraction was determined by tannin parameter that is using photoelectric by the green optical filter in the cell with the working face width of 10 mm.

Quantitative dependence of macromolecular polypeptides of fractions A content (mg / 100 ml) expressed by the equation:

$$T = -0,045 + 0,0276 \cdot A,$$

where A – A faction of content, mg / 100 ml;

T – index of tannin (optical density).

Colloidal stability of prepared beer predicted and evaluated by the "degree of ammonium sulfate precipitation" by method proposed by Basarjova, based on identifying substances that are precipitated saturated solution of ammonium sulphate using turbidimeter [16].

Preliminary, according to the formazine suspensions of known turbidity (from 0.5 to 12 units of EMU), calibration curves are constructed. In a row of tubes add 10 ml of beer, freed from carbon dioxide, and add a saturated solution of ammonium sulfate in increasing quantities. In the control, to the row of tubes with 10 ml of beer, the same amount of water is added. The turbidity at the nephelometer is measured at a wavelength of 670 nm. The measurements are carried out 15 minutes after the addition of ammonium sulfate, and the solution is transferred to the cuvette 2 minutes before the expiration of 15 minutes so that the solution in the cuvette is settled. Measurements are done against control.

Saturated ammonium sulfate solution is prepared so that at a temperature of 20 ° C in 100 ml of the solution there were 43 g of anhydrous ammonium sulfate, and after settling the solution for 48 hours, undissolved ammonium sulfate crystals remained on the bottom of the flask.

Results of discussion

There was conducted a series of experiments in brewing beer to study the effect of hop polyphenols of low-ash hop on quality indicators wort and beer, where near CO_2-extracts was currently used hops.

Characteristics of hops shown in the Table 1.

Table 1

Characteristics of hops

Hops	Contents, %			Weight of hops for hopping, g/dm^3
	Alpha-acids	Polyphenolic compounds	Antotsianogens	
Hop	1,2	7,2	5,6	4,132
CO_2 -extract	52,9	-	-	0,151

As you can see from the table, content of bitter substances in CO_2-extract is quite high and amounted to 52.9%, so its mass for hopping of wort is insignificant compared with hops (0.151 g/dm^3 for CO_2-extract and 4.132 g/dm^3 for hops). While currently hop holds 7.2% polyphenolic compounds, which does not have a CO_2-extract.

The weight of hop and extract that was introduced to the hopping for each variant of experiment, weight of hop polyphenols (PF) which were made to the wort, and also value of bitterness wort, content of total polyphenols, anthocyanogens (AG) and macromolecular polypeptides are shown in the Table 2.

Table 2

Influence of correlation of CO_2-extract and aromatic low-ash hop the on quality indicators of hopped wort

№ of sample	Was made, %		Weight of hop products, g/dm^3		Polyphenols of hop that were made mg/dm^3	Value of bitterness wort, for EMS	Content	
	CO_2-extract	Hop	CO_2-extract	Hop			polyphenols, mg/dm^3	fraction A for Lundin, mg/100 ml
1	100	-	0,1510	-	-	32,0	131,4	21,0
2	80	20	0,1208	0,826	52,3	33,5	143,6	20,7
3	60	40	0,0906	1,653	104,7	35,3	160,4	17,9
4	40	60	0,0604	2,480	157,1	37,6	188,8	14,5
5	20	80	0,0302	3,306	209,5	40,1	219,1	13,7
6	-	100	0	4,132	261,8	43,0	255,5	13,6

With an increase in the amount of hops introduced with each variant of the experiment, the amount of both the polyphenols introduced into the wort and those defined in the wort increases. It should be noted that hops polyphenols interact more intensely with wort proteins with the formation of insoluble complexes, which positively affects the colloidal resistance of beer. Proanthocyanidins are the most active compounds in the formation of polyphenolic-protein complexes. Therefore, if there are more of them in the hop preparations, much more scrap is formed when the wort is hopped and it is better illuminated. This is observed in our studies when hopping wort only carbon dioxide extract, extract and low-hops in different proportions and one low-hops hop. It was noted that in the 6th variant, in comparison with 2, the amount of hops hopped into the wort increased 5 times, although the actual amount in hop wort in version 6 increased only 1.8 times. The remaining polyphenols, obviously, precipitated with the formation of polyphenolic-polypeptide complexes. This assumption is confirmed by the fact that in the case of hopping of wort with an extract only in the absence of polyphenols, scrap hops are formed little, slightly more is formed in the second variant. We noted that in the third and fourth variants, the amount of sediment increased significantly. Most of all he was in the 5th and sixth versions. But in these cases there were also the largest wort losses with this.

Our assumption is also confirmed by the data in the table, which indicate that from 1 to 6, the high molecular weight polypeptide decreases, and this decrease is 35.2%.

Influence of correlation of beer quality which was made according to this variant and biochemical characteristic of beer are made in Table 3.

Table 3

Influence of correlation CO_2-extract and aromatic low-ash hops on beer quality indicators

№ of variant	Value of beer bitter, for EMS	Content in beer, mg/dm^3		Index of polymerization	Fraction A for Lundin, mg/100 ml	Degree of deposition $(NH_4)_2SO_4$, ml/10 ml
		PF	AA			
1	20,0	120,1	29,3	4,1	16,0	1,0
2	21,0	132,3	33,1	4,0	15,4	1,1
3	22,5	146,2	38,5	3,8	14,2	1,2
4	24,3	163,1	46,6	3,5	12,8	1,6
5	26,0	183,2	57,3	3,2	12,2	1,7
6	28,0	208,6	72,0	2,9	11,9	1,7

The table shows that increasing the dose of low-ash hop increases bitterness of wort and beer. This increase is due to the participation in its creation not only of alpha acids extract and hop and β-fractions of low-ash hops.

There is an increase of made polyphenols in wort and identified them in wort and beer. It should be noted that polyphenols of hope are more polymerized than malt phenols. And thus the rate of polymerization index in the manufacture of beer significantly increased from 2.9 to 4.1 with increase in the proportion of carbon dioxide hop extract. They also have more intensive interaction with wort proteins with creation of insoluble complexes that have a positive effect on the colloidal stability of beer.

Proantotsianidiny is most active compounds relative to the formation of polyphenol-protein complexes. Therefore, in case of a more hop preparations produced significantly more scrap at ohmelinni must and it is better illuminated. This is observed in our study with

only carbon dioxide hopping wort extract, hops extract and low-ash in different ratios and one low-ash hops. It produces a little hop scrap in case of hopping of wort only with extract without polyphenol, a little more than it produced in the second variant. We have seen that the 3 and 4th variants was significantly increased the amount of sediment. Most of it was 5 or 6th variants. But in these versions were the largest loss wort.

With increasing doses of hops low-ash reduced in the wort and beer of high rate increases the degree of polypeptides and proteins deposition saturated solution of ammonium sulfate that predicts high colloidal stability of beer.

The results of the tasting evaluation of the best by taste and aromatic qualities was beer produced using 40% low-ash bitterness of hops and 60% of bitterness due to CO_2-extract, and conversely. Compounds of low-ash hop positively affect the crude extract bitterness, softening and smoothing it, making a total bitter beer balanced.

Beer brewed only with CO_2-extract had rough, naked and residual bitterness. The reason for the poor quality of bitterness is bitter hop sorts, of which are produced CO_2-extracts and their lack of polyphenolic compounds. Beer at the stage of maturation doesn't illuminate. Was remained a significant number of high polypeptides due to lack of hop PF in the wort and it caused distraction. Moreover, an excess of high-protein, remaining in wort interacts with bitter substances of hops and reduces the extent of their use. Also complexes of bitter substances with proteins give beer a characteristic of unpleasant residual bitterness.

Quality bitter of beer was improved which along with CO_2-extract used 20% bitterness of low-ash hops.

5th and especially 6th version of beer, which used only low-ash for hopping had little astringent taste character for excessive amounts of hop polyphenols.

Obtained results testify that the formation of a full taste involved not only the bitter substances, but polyphenols, but not alone, but in conjunction with bitter substances, proteins and other specific compounds hops and wort.

Analysis of experimental brewing beer conducted by us show that polyphenols of low-ash aromatic hops contribute to the removal from the wart by coagulation macromolecular polypeptides to form complex systems, as a result we get higher colloidal stability of beer and the increased reliance on bitter substances by 15–20 %. Polyphenols of low-ash aromatic hops positively affect for gross bitterness CO_2- extract, softening and smoothing it, making a total bitter beer balanced.

Thus, low-ash hops in brewing can be used as an polyphenolic additive combined by extracts, processed it into pellets, which will cost significantly lower compared to conventional hop granules.

Technical and economic analysis shows that the use of polyphenol supplements low-ash aromatic hops in combination with CO_2-extracts in optimal conditions not only increases the quality of beer, as well as an effective means for the prevention of colloidal turbidity without using of stabilizing agents, reduces its costs and improves competitiveness.

Conclusions

1. Experimentally proved that the formation of flavor and aroma of beer mutually dependent for complex bitter core, essential and phenolic compounds hop.
2. Aroma of hop with a low content of alpha acids can be used in brewing as polyphenol supplement, if it was converted into granules and meets standards for all other indicators.

3. When we used in brewing only CO_2-extract is not possible to get a beer with high taste. It should be used in combination with aromatic or with aromatic low-ash hops, considering the quantitative and qualitative composition hops and following certain technology of beer.

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Effect of meat product with onion skin extract on metabolic profile in SHR

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Abstract

Introduction. Searching for the new product compositions is important for metabolic disorders correction. Onion contains flavonoid quercetin with antioxidant and cardioprotective effect.

Materials and methods. Meat product with an onion skin extract or quercetin at equal dose 2,25 mg of quercetin daily was used for animals feeding. Six–month-old spontaneous hypertensive rats (SHR) with fructose overload in drinking water (25%) were used to promote metabolic disorders. After 3 months of feeding glucose was measured in arterial blood by glucose sensors based on amperometric measurement. Plasma lipid profile was determined by an enzymatic colorimetric reaction.

Results and discussion. Blood glucose in SHR without diet interventions (group II) was 59% higher than in control (8.84±0.3 mmol/l vs 5.56±0.86 mmol/l, $P<0.01$). Fructose overload in SHR (group III) increased glucose level on 5% (9.3±0.4 mmol/l, $P>0.05$ compared to SHR of group II drinking tap water). Quercetin added to the meat product did not influence glucose concentration in SHR on fructose overload (group IV) – 9.2±0.8 mmol/l, $P>0.05$ compared to SHR of groups II and III. In SHR on fructose overload receiving meat product with onion skin extract (group V) blood glucose tended to decrease – 8.0±1.0 mmol/l, $P>0.05$ compared to SHR of group III.

Total cholesterol tended to increase in SHR of group II compared to control (1.36±0.10 vs 1.22±0.05 mmol/l, $P>0.05$). In SHR of group III was significantly higher than in control (1.45±0.09 mmol/l, $P=0.03$) but did not differ from SHR drinking tap water (1.45±0.09 vs 1.36±0.10, $P>0.05$). In groups IV and V total cholesterol was also significantly higher than in control (1.52±0.07 and 1.57±0.09 vs 1.22±0.05 mmol/l, $P=0.006$ and $P=0.005$, respectively).

The rise of total cholesterol observed in the SHR of groups IV and V was due to the increase of high-density lipoprotein (HDL) cholesterol because non-HDL-cholesterol did not change in them. In SHR supplemented by meat product with onion skin extract there was a significant increase in HDL-cholesterol compared to SHR of group II (1.25±0.09 vs 1.02±0.05, $P = 0.03$). An increase in HDL cholesterol was also observed in SHR receiving meat product containing purified quercetin powder compared to SHR of group II (1.23±0.08 vs 1.02±0.05, $P = 0.02$).

Conclusions. Supplementation with the meat product containing onion skin extract to SHR with fructose overload has a positive effect on blood glucose. The increase of HDL-cholesterol in SHR with fructose overload reflects anti-atherogenic effect of the developed meat product.

Introduction

Nowadays cardiovascular diseases (CVD) remains the important problem for health care service all over the world. CVD are the leading cause of death globally, most occurred in low and middle income countries [1]. High prevalence of CVD is supported by rising amount of people with metabolic syndrome, consisting of obesity, arterial hypertension, lipid and glucose disorders. According to WHO, CVD prevalence can be decreased by the influence on diet and body weight among others factors [1]. So nutrition researches and food industry need to search for the new product compositions to prevent and correct metabolic disorders.

The most important and widely cultivated vegetable

is onion *(Allium cepa L.)*. The onion world manufacture is about 55 billion ton per year *(Tina et al., 2016; Radga et al., 2016)*. This vegetable contains flavonoids with antioxidant and cardioprotective effect. Of particular interest is yellow onion – the most spread cultured onion in Ukraine.

At that, yellow onion contains the highest total amount of flavonoids among the other onion varieties tested [2]. According to the researchers, flavonoids of this culture have high content of quercetin (40000 mg/kg) [3].

Quercetin (3,3′,4′,5,7-pentahydroxyflavone) is a potent antioxidant, known for his anti-inflammatory activity. This flavonoid possess wide range of positive effects, including neuroprotective, cardioprotective and even life-span extending effects [4]. Quercetin protects blood vessels from the damaging effects of oxidative stress, especially from lipid peroxidation, decreases blood pressure, leads to lowering of LDL cholesterol and causes cardioprotective effect. Results from human randomized controlled trials showed that flavonol consumption, especially quercetin, improved biomarkers of CVD risk [5]. Dietary supplementation with quercetin significantly reduced systolic blood pressure in overweight subjects with a high CVD risk and decreased plasma oxidised LDL concentrations that reflects cardioprotective effect of flavonoid [6]. According to meta-analyses quercetin supplementation was associated with a positive effect on blood lipid profile. It was observed in small but significant decrease in total cholesterol, LDL cholesterol and triacylglycerol and significant increase in HDL cholesterol [5].

Animal studies have demonstrated as the anti-inflammatory effect of quercetin as its possibility to modify blood lipid profile [7-9]. Quercetin was able to reduce liver injury in the mice model of diet-induced steatohepatitis. Noteworthy, steatosis and steatohepatitis is common liver injury in patients with metabolic syndrome. Given orally at dose 50 mg/kg daily quercetin markedly suppressed lipoperoxidation in liver tissue, decreased profibrotic and proinflammatory gene pathways in mice with steatohepatitis compared to control group. According to investigators, attenuation of proinflammatory and profibrotic pathways was due to anti-inflammatory effect of flavonoid [7]. It is known that liver function plays the key role in lipid homeostasis. Supplementation with quercetin to a commercial chow (0.08% of the diet) influenced lipid profile in leptin receptor-deficient db/db mice, which has metabolic disorders associated with metabolic syndrome and type 2 diabetes. In this experiment quercetin decreased plasma total cholesterol and increased HDL-cholesterol compared with the control [8].

Different animal models are known for studying metabolic syndrome. One of them – spontaneously hypertensive rats (SHR) with genetic predisposition to high blood pressure and insulin resistance. This rat strain was chosen because arterial hypertension is prevalent CVD in Ukraine and is one of key components of metabolic syndrome. To provoke metabolic disorders in animals carbohydrate or fat overload is usually used [10–12]. We

choose carbohydrate overload, according to modern nutritional pattern of Ukrainian people with metabolic syndrome. The aim of our studying was to investigate the metabolic profile in SHR kept at high-fructose diet under the supplementation with meat product containing onion skin extract, rich source of quercetin.

Materials and methods

Investigated materials

A meat product with onion skin extract, a meat product with purified quercetin powder, six–month-old rats with genetically determined hypertension under fructose overload, blood glucose and lipid profile.

Description of the methods and facilities

Preparation of onion skin extract for meat product. For animal feeding meat product with onion skin extract was used. The onion skin extract for the meat product was prepared in this way: electro-activated water was bringing to its boiling, weighted onion peel was added to boiling water in amount of 4 % and was boiled for 10 min and filtered. Earlier the prepared onion skin extract was investigated and its quercetin content was determined [18].

The obtained extract was evaporated to 10 times smaller volume and was added to the meat product. Experimental animals received 1 gram of meat product with added 1,5 ml of the onion skin extract containing 2,25 mg (0,00225 g) of quercetin per rat daily during three months. In the prepared meat product the quercetin content was equal to 0,2% (or 7,5 mg of quercetin per kg of rat body mass). Feeding these products to rats was performed orally.

Animals and experimental diet. For studying quercetin influence on metabolic profile we used male SHR. This rat strain reveals genetic predisposition to metabolic disorders and is one of proposed animal model for metabolic syndrome among others. As control were taken male Wistar rats. Six–month-old rats were included in experiment. Animals were housed at vivarium standard conditions 5–6 rats in a cage at 22–24°C and maintained on a standard laboratory rat chow *ad libitum*.

Fructose overload in drinking water was used to promote metabolic disorders. Fructose overload in experimental animals is associated with increased body mass, insulin resistance, glucose and lipid metabolism disorders [10, 13-14]. High-fructose diet is also used in SHR to develop metabolic syndrome [10, 15].

Rats were divided into 4 groups (5–6 rats per group). The first, control group (I) – Wistar rats kept on the standard laboratory chow plus drinking tap water. The second (II) – SHR kept on standard laboratory chow plus drinking tap water. The third (III) – SHR kept on standard laboratory chow plus 25% fructose solution in drinking water [13]. The fourth (IV) – SHR received meat product with pure 96% quercetin powder added (Merk, Germany) and 25% fructose solution in drinking water. The fifth (V) – SHR received meat product with onion skin extract added and 25% fructose solution in drinking water. All series lasted for 3 months.

Sampling procedures. Animals were sacrificing by decapitation at the end of the treatment after an overnight fasting and blood samples were immediately collected. Blood

samples were centrifuged at 1,500g for 15 min to acquire plasma. Plasma samples were stored at –70°C for further analysis.

Blood glucose. After sacrificing the rats glucose was measured in arterial blood by using glucose sensors which worked on the basis of amperometric measurement after enzymatic glucose oxidation (Accu-Chek Active, Roche, Germany) [16].

Lipid concentration in the plasma. Plasma triglycerides, total cholesterol, HDL-cholesterol level were estimated using a commercially available test kit (Biosystems, Spain) with an automated analyzer of an enzymatic colorimetric reaction Avtolab 18 (Mannhein Boehringer, Germany) [17].

For total cholesterol measurement reagents and plasma were distributed on labeled test tubes, mixed thoroughly and incubated for 5 minutes at 37 ºC. The absorbance of the standard and sample were measured by automated analyzer at 500 nm against the blank. After that total cholesterol concentration was calculated.

For triglycerides measurement reagents and plasma were distributed on labeled test tubes. The content of the tubes was thoroughly mixed and incubated at 37° C for 5 minutes. The absorbance of the standard and sample were measured by automated analyzer at 500 nm against the blank and triglycerides concentration was calculated.

For HDL cholesterol measurement reagents and plasma were distributed on centrifuge tubes, mixed thoroughly and left for 10 minutes. After that tubes were centrifuged at 4000 r.p.m. for 10 minutes. The supernatant was collected. The reagent, sample supernatant, standard and distilled water were distributed on labeled test tubes, mixed thoroughly and incubated for 10 minutes at 37 ºC. The absorbance of the standard and sample were measured by automated analyzer at 500 nm against the blank. After that HDL cholesterol concentration was calculated using sample dilution factor.

Non-HDL cholesterol was calculated by formula: non-HDL cholesterol = total cholesterol – HDL cholesterol.

Statistical analysis. Data presented as means and standard errors of the means. The analysis was performed with the use of Statistica 6.0 software. The t-test for unpaired samples was used for group comparisons. The results were considered significant with a P value of less than 0.05.

Results and discussion

Arterial blood glucose in SHR of group II was 59% higher than in control (8.84±0.3 mmol/l versus 5.56±0.86 mmol/l, $P<0.01$; Figure 1). Fructose overload in drinking water increased glucose level on 5% in group III (9.3±0.4 mmol/l, $P>0.05$ compared to group II). Quercetin added to the meat product (group IV) did not influence glucose concentration in rats with fructose overload – 9.2±0.8 mmol/l, $P>0.05$ compared to group II and group III. Blood glucose in group V at the onion skin extract was 8.0±1.0 mmol/l, $P>0.05$ compared to groups II – IV.

However supplementation with the meat product containing onion skin extract to rats tended to decrease glucose level – in group V it was 14% lower compared to SHR of group III, receiving standard chow and 25% fructose solution in drinking water. This corresponds

to study by V. Brüll et al., who found quercetin from onion skin extract did not decrease glucose level in subjects with metabolic syndrome and hypertension [20].

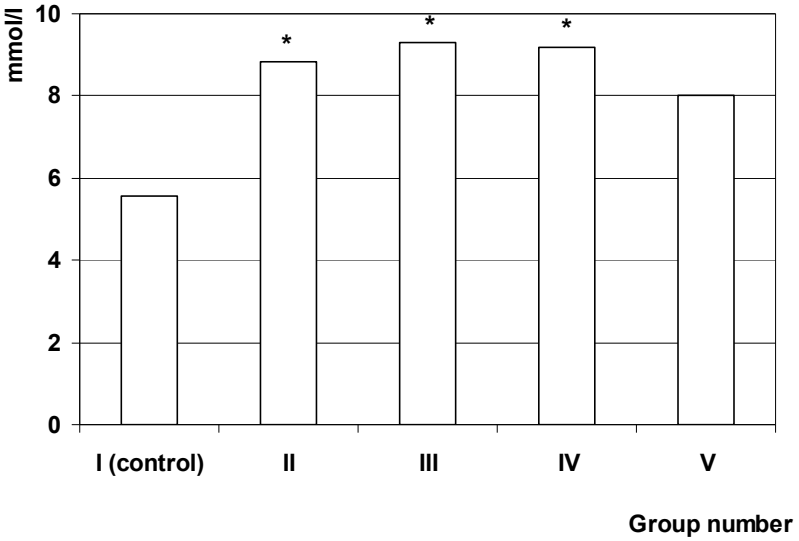

Figure 1. Blood glucose level in rats with the different diet interventions
*** – significant difference versus control, P<0.05**

On the other hand, fructose overload as 10% solution in drinking water for two months in Wistar rats caused the rise of blood glucose [14]. SHR fed with commercial chocolate bars for 12 weeks also revealed elevated glucose level compared to standard chow. These rats have increased body weight due to caloric exceed. Also they showed higher insulin and C-peptide level [12]. It is noteworthy that we had initially high glucose in the rats with genetically determined hypertension. In these conditions dietary intervention with fructose and the meat product may do not cause obvious changes in glucose metabolism. So we did not receive an additional significant rise of blood glucose over initial level under the fructose overload.

Comparing two rat strains, M. Oron-Herman et al. showed that sucrose supplementation for 7 weeks failed to rise markedly glucose level in SHR. Authors noted that SHR strain has initially impaired glucose tolerance and represents metabolic syndrome. So it is hard to cause in them metabolic disorders progression to diet interventions compared to other rat strain without hypertension. However sucrose overload caused further elevation of blood pressure in SHR [11].

Weight gain in all groups did not differ during and at the end the study. This corresponds to study by M. Oron-Herman et al., in which sucrose supplementation failed to cause an obesity [11]. A. Zemančíková and J. Török also did not find an increase in body weight of Wistar rats drinking 10% fructose solution for 8 weeks in spite of plasma glucose rise [14].

Results of total cholesterol, triglycerides, HDL-cholesterol and non-HDL-cholesterol are presented in the Table 1.

Table 1

Lipid profile in rats with the different diet interventions

	I Control n=6	II SHR n=5	III SHR + fructose overload n=6	IV SHR + fructose overload + quercetin n=5	IV SHR + fructose overload + onion skin extract n=6
Total cholesterol, mmol/l	1.22±0.05	1.36±0.10	1.45±0.09*	1.52±0.07*	1.57±0.09*
Triglycerides, mmol/l	0.64±0.03	0.64±0.06	0.65±0.05	0.66±0.10	0.65±0.07
HDL-cholesterol, mmol/l	0.93±0.03	1.02±0.05	1.09±0.05*	1.23±0.08*&	1.25±0.09*&
Non-HDL-cholesterol, mmol/l	0.29±0.05	0.34±0.05	0.36±0.10	0.29±0.03	0.38±0.05

* – significant difference versus control, P<0.05;
& – significant difference versus SHR (II group).

Total cholesterol tended to increase in SHR of group II compared to control (P>0.05). In SHR with fructose overload it was also significantly higher than in control Wistar rats (P=0.03) but do not differ from SHR drinking tap water. Our results are in accordance with study by M. Oron-Herman et al. Earlier they found slightly elevated total cholesterol in SHR fed either standard laboratory chow or sucrose without any difference between groups [11]. In groups IV and V total cholesterol was also significantly higher than in control (P=0.006 and P=0.005, respectively). The rise of total cholesterol observed in the different SHR groups was due to the increase of HDL-cholesterol because non-HDL-cholesterol did not change in them. HDL-cholesterol was increased in all groups with fructose overload compared to control Wistar rats. In SHR on fructose overload and receiving meat product with quercetin HDL-cholesterol was greater elevated compared to SHR drinking tap water (P=0.02). The same increase was observed for group receiving the meat product with onion skin extract compared to SHR of group II (P=0.03). Noteworthy, the SHR strain has a genetic background of insulin resistance which usually is characterized by low HDL-cholestrol [20]. The rise of HDL-cholesterol is positive phenomenon because of its antiatherogenic effect. In this case we can see similar effect of purified quercetin powder and onion skin extract added to the meat product.

Triglycerides did not differ in all experimental groups and control. M. Oron-Herman et al. also showed that triglycerides did not change in SHR under sucrose supplementation [11]. In contrary, J. Török et al. received increased triglycerides in Wistar rats and SHR drinking water containing 10 % fructose for two month [15].

In above mentioned animal studies of carbohydrates overload for developing of metabolic syndrome different lipid profile results can be in part explained by rat strain, type of carbohydrates used and experiment design [12].

Literature data conserning the quercetin effect on lipid profile are a little bit contradictory. In human studies quercetin supplementation did not influence lipid profile in the subjects with metabolic syndrome and pre-hypertension or stage I hypertension despite

of lowering of blood pressure in patients with hypertension. Authors did not find significant differences between quercetin supplemented group and placebo group in serum total cholesterol, LDL-cholesterol, HDL-cholesterol and tryacilglycerol levels [19]. In study by S. Egert et al. the decrease of oxidized LDL-cholesterol consentration was shown, but serum HDL-cholesterol and LDL-cholesterol levels remained unchanged [6]. Consistent with the our findings, increased HDL-cholesterol was also reported by K.H. Lee et al. in healthy male smokers supplemented with quercetine from onion peel [21].

Thus, our data indicate that dietary intervention with the onion skin extract rich in quercetin at dose 7,5 mg/kg may have positive influence on glucose and lipid profile.

Furthermore, our data showed non toxic effect of suggested meet supplement with onion skin extract that might be introduced for the development of new food product with hypoglycemic properties and modulating lipid metabolism. Further studies are needed to investigate the effect of supplementation with the meat product containing onion skin extract on more wide range of metabolic risk factors.

Conclusions

1. Supplementation with the meat product containing onion skin extract to SHR at dose 2,25 mg (0,00225 g) of quercetin daily is safe.
2. Supplementation with the meat product containing onion skin extract tended to decrease glucose level in SHR on fructose overload
3. There was a positive effect of the meat product containing either purified quercetin powder or onion skin extract on HDL-cholesterol in SHR with fructose overload. Rise of HDL-cholesterol reflects better anti-atherogenic effect of the developed meat product.

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Study of technological factors impact on the viscosity of "Wheat starch-Tween 20 (E432)" system

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Abstract

Introduction. The purpose of this article is to study the impact of technological factors (temperature, sugar, citric acid) on the model system "Wheat starch-Surfactant", which is the basic foundation for the realization of mousses technology using wheat starch.

Materials and methods. The viscosity of the model systems "Wheat starch-Tween 20 (E432)" with white sugar and citric acid under the temperature influence was measured on a rotary viscometer of VPN-0.2 type.

Results and discussion. The literature contains enough information about the progress of gelatinization process of different types of starches and the impact of various factors, including surfactants, acids, salts, sugar and others on it, however data about the impact of these substances on "Wheat starch-Tween 20 (E432)" system are absent.

Understanding changes in the properties of "Wheat starch-Tween 20 (E432)" system under the influence of various technological factors will allow to create the scientific base for the implementation of technology of new products with foamy structure.

The studies confirmed the feasibility of using Tween 20 (E432) with wheat starch as structure-maker of system, which will provide the necessary viscosity at the expense of dynamical phase transitions at heat treatment. The presence of Tween 20 (E432) in the system enhances the starch gelatinization temperature and decreases the viscosity values at the beginning of the process, providing conditions for foaming.

Adding of white sugar and citric acid inhibits the viscosity growth in the temperature range of 60–65 °C, the further temperature increase promotes the increase of indicators.

Thus, "Wheat starch-Tween 20 (E432)" model system rational parameters that will provide the optimal viscosity, which is necessary to obtain high indicators of the foaming capacity during whipping, are Tween 20 (E432) concentration – 0.25 %, wheat starch concentration – 6–12 %, white sugar concentration – 10.0 %, whipping temperature – 60–65 °C. These options will allow to obtain mousses using wheat starch and Tween 20 (E432) with new consumer characteristics by the realization of functional properties of wheat starch and surfactant.

Conclusions. The rational parameters of heat treatment of model systems using wheat starch and Tween 20 (E432) in order to provide the lowest viscosity indicators that will promote the maximal foaming capacity and will allow to realize the mousses technology were defined and substantiated.

Introduction

Modern food production conditions increasingly require from manufacturers to improve the technology of food production and to refine consumer characteristics and dictate trends of new technologies development to the scientists.

The monitoring of the food market shows that the most popular among consumers are sweet dishes, which are dispersed systems containing respectively at least two phases – dispersed phase and dispersion medium.

The most common representatives of this group are sweet dishes with gel- (jelly-) like and foamy (mousses, sambucas, creams, souffles) structures that are multicomponent mixed dispersed systems i.e. both foam and emulsion or emulsion and suspension with the possible priority of one of system types.

It is known that for foamy structure obtaining usually poultry eggs or gelatin is used, while starch in the composition of desserts serves as a thickener. The most often used are the starches whose properties are changed by various factors (pregelatinized, cold-swelling et al.), that promotes to more rapid progress of technological processes and formation of food systems with predetermined viscosity characteristics. In the scientific literature there is no information about the starches using in recipes of sweet dishes with foamy structure.

In view of analytical researches and innovative idea of the new products we have defined the innovative strategy of mousses technology development, which is to regulate the dynamic phase transitions of native wheat starch together with surfactant, as which Tween 20 (polyoxyethylene (20) sorbitan monolaurate, E432) was elected [1].

At the first stage of the technology implementation we obtained a model system "Wheat starch-Tween 20 (E432)", which was characterized by high levels of foaming ability (FA) at 60 °C, but thermodynamically unstable in time. In order to stabilize the foam system it is proposed its further heating up to 85±2 °C, that will result in gelatinization of the rest of starch achieving the effect of concentration stabilization of the foam by injection of additional heat and mechanical energy [2].

It is known [3] that the structure of disperse systems is determined by:

– properties of the dispersed phase particles;
– properties of dispersion medium;
– interaction between the particles of the dispersed phase and the dispersion medium;
– interaction of the dispersed phase particles with each other.

The properties of the dispersed phase and dispersion medium and their interaction together characterize inherent for food products structural-mechanical properties, one of which is viscosity.

Viscosity is the body's ability to resist relative displacement of its layers. For non-Newtonian (abnormally viscous) fluids, the viscosity is variable value that depends on shear stress and velocity gradient.

Published data indicate that many scientists devoted their researches to studying of behavior of different types of native starches, such as changes in viscosity depending on the processing temperature and the presence of other components in system such as surfactants, sugar, acid, salt and others.

It is known that the presence of chemical substances affects the nature of gelatinization. Some salts are capable to destruct the hydrogen bonds, what promotes the gelatinization start (Leanch, Lindqvist) [4, 5], while others inhibit it and act as salting-out agents (Ganz, Lindqvist) [5]. Sugar is known as a substance that is capable to slow down the gelatinization process by inhibiting of the starch granules swelling in water systems (D'Appolonia, Bean and Yamazaki, Savage and Osman, Wootton and Bamunuarachchi)

[5]; some lipids form complexes with amylose, thereby changing the gelatinization nature (Collison and Elton, Osman, Ito, Ghiasi) [5].

Other researchers note that adsorbing on the surface of the starch granules surfactants can reduce the viscosity and the swelling ability [6, 7]. Azizi and Rao [8] studied the effect of such surfactants as sodium stearoyl-2-laktylat (SSL, anionic surfactant, HLB=10–12), diacetyl tartaric acid esters of monoglycerides (DATEM, anionic surfactant, HLB=8–10), glycerol monostearate (GMS, nonionic surfactant, HLB=3–4), distilled glycerol monostearate (DGMS, nonionic surfactant, HLB=3–4) and noted that the injection of these surfactants increases the gelatinization temperature and decreases the peak viscosity, but its growth was noticed during cooling especially for SSL.

Lehrman [9, 10] indicates that the interaction between starch and surfactant depends on the surfactant adsorption on the surface of the starch granules. His further research showed that surfactants form insoluble compounds with amylose. Some surfactants form complexes with amylose and influence on the process of starch gelatinization. Krog [10], who noticed the ability of some emulsifiers to form complexes with amylose, found that distilled monoglycerides (DMG) have the best ability to form complexes among nonionic surfactants; sodium stearoyl laktylat (SSL) and calcium stearoyl laktylat were the best among ionic. These differences turned out to be associated with the length of hydrocarbon chains, the number of hydrocarbon chains in molecules and the structure of hydrophilic residues. Krog and Nybo-Jensen [9-11] showed that the ability of monoglycerides to form complexes with amylose depends on the physical form of surfactant.

It is known that the addition of surfactant reduces maximal viscosity with the increasing of initial and maximal gelatinization temperature. For sucrose esters [12] such behavior is explained by the formation of a combination of emulsifier-starch by the interaction of hydrophilic groups that form hydrogen bonds. Esters also can penetrate inside the amylose spiral structure and unite in supramolecular structures with hydrophobic bonds, reducing the hollow amylose structure. As a result the dissolution rate of starch increases and viscosity decreases. Thus results of many researches show that different in character surfactants differently interact and affect the starch during the heat treatment.

Sugar is one of the main components of desserts recipes, which affects the viscosity of starch suspensions during heat treatment [13, 14]. Fasihuddin and Williams studied the effect of sugar on sago starch and found that it increases the gelatinization temperature and the starch swelling increases to 25.0 % in the presence of sugar. Al-Malah, Azzam and Abu-Jdail determined a similar pattern for wheat starch at the presence of glucose to 6.0 %. Thus the addition of sugar to starch suspensions promotes the increase of temperature of viscosity growth start (initial gelatinization temperature), increasing the maximal system viscosity.

The basis for many sweet dishes is fruit raw material, which contains organic acids (citric, malic, lactic, etc.) in its composition. Also organic acids are specially added as an acidity regulator, antimicrobial, aromatic or preserving substances [15]. Despite the importance and prevalence of the interaction between organic acids and starch, information about them is limited. Most researches are devoted to the study of the process of starch hydrolysis under the influence of acids at high temperatures.

Summing up the above we can say that in the literature there is information about the impact of certain surfactants, acids, salts, sugars on the different kinds of native starches, but there is no data about the effect of these substances on "Wheat starch-surfactant (E432)" system. Since the scientific substantiation of mousses technology using Tween 20 (E432) as a foaming agent and wheat starch as structurant oversees the understanding of changes in functional and technological properties of starch during the technological

process, the investigation of influence of different technological factors on the aforementioned model system will allow to create a scientific basis for new products technology implementation.

Materials and methods

The research materials were such model systems:
– Tween 20 (E432) and wheat starch aqueous solutions;
– Tween 20 (E432), wheat starch and white sugar aqueous solutions;
– Tween 20 (E432), wheat starch and citric acid aqueous solutions;
– Tween 20 (E432), wheat starch, white sugar and citric acid aqueous solutions, that were obtained by the combination of components with distilled water.

Determination of the effective viscosity was carried out on a rotary viscometer of VPN-0.2 type [16]. Electric structural scheme of viscometer is shown on Figure 1.

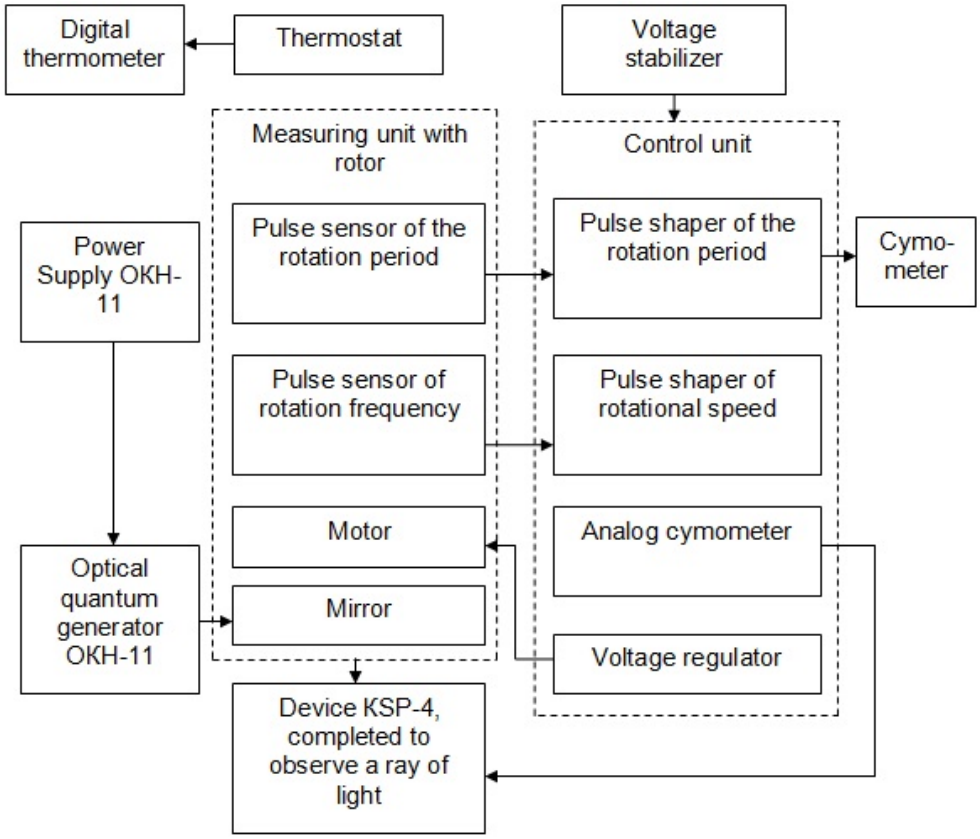

Figure 1. Electric structural scheme of viscometer VPN-0.2M

For the determination of the effective viscosity samples were prepared as follows: at the temperature 20 °C the components of the model system and distilled water were put together and heated with constant stirring in a water bath to 60 °C. Heated sample was transferred to the measuring unit of VPN-0.2, which was previously set in a thermostat at 60 °C, and left for (5–7)·60 seconds to restore the temperature then measurements were performed. After the reading of results the temperature in the thermostat was increased at 5 °C and after reaching the set temperature the device values were read again. Heating was carried out with stirring.

For measurements at VPN-0.2 the prepared sample was loaded into a measuring unit ($50 \cdot 10^{-6}$ m^3). Gradually increasing the voltage by a handle "Setting the voltage" rotation period was picked so that the viscosity values for samples were calculated at the same values of shear rate. For the fixed voltage value five values of the rotation period were read, excluding serious mistakes the average was found. For the obtained values of the rotation period voltage values in volts were noted and its average was found.

Dynamic or effective viscosity (η, Pa·s) was determined by the formula 1:

$$\eta = k \cdot U \cdot T \cdot A \quad (1)$$

where k – constant of measuring unit, Pa/V;

U – voltage, V;

T – rotation period, s;

A – measuring unit shape coefficient.

The shear rate ($\dot{\gamma}$, s^{-1}) was determined by the formula 2:

$$\dot{\gamma} = \frac{1}{T \cdot A} \quad (2)$$

To compare the viscosity of two or more samples the viscosity with the same shear rate in the field of minimal viscosity of the destroyed structure that was 320 s^{-1} was compared.

Results and discussion

Within the framework of innovative idea realization the aim of the study was to determine the influence of white sugar and citric acid as mousses recipe components on wheat starch in the presence of Tween 20 (E432) with heating (at temperatures above 60 °C). Wheat starch concentration in model systems was 8.0 %.

Firstly the impact of Tween 20 (E432) concentration at the viscosity of wheat starch suspension at different processing temperatures was determined (Figure 2). It is known from the literature sources that gelatinization temperature of wheat starch lays within the range 60 °C (initial)...80 °C (final), and the pasteurization temperature, which provides microbiological purity and stability is 90±2 °C, so exactly in this temperature range studies were carried out.

It can be seen from Figure 2 that the presence of chosen surfactant in the system reduces viscosity values of starch suspension in 2–2.7 times for a system containing Tween 20 (E432) at 0.3 % concentration and slows the beginning of viscosity growth at the temperature range 60–70 °C, i.e increases the wheat starch gelatinization temperature.

Since the viscosity of starch systems did not differ with adding Tween 20 (E432) at concentrations of 0.2 % and 0.3 % at the temperatures 60–70 °C, and at 90 °C the difference was only $0.14 \cdot 10^{-2}$ Pa·s, so for further studies 0.25% Tween 20 (E432) was elected as a working concentration.

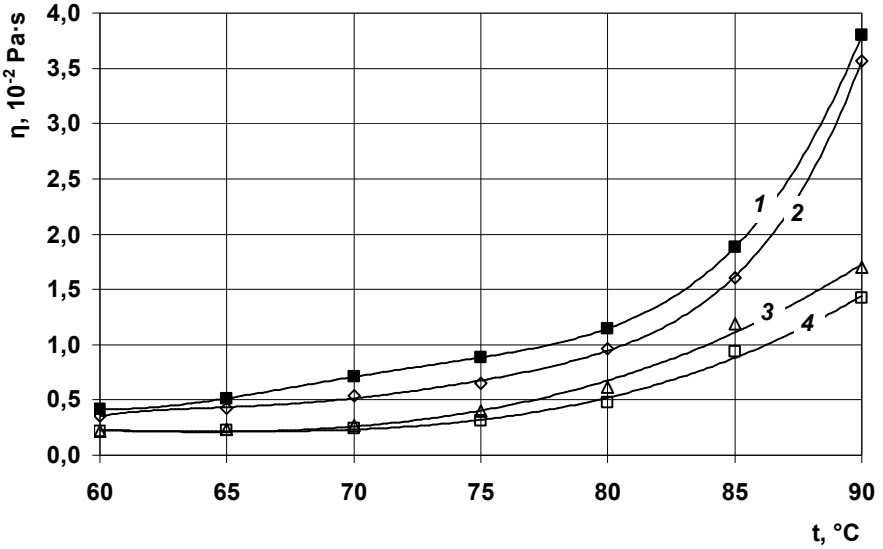

Figure 2. Changes of the effective viscosity of wheat starch suspensions depending on the treatment temperature at the concentration of Tween 20 (E432): *1*■ – 0; *2*◊ – 0.1; *3*Δ – 0.2; *4*□ – 0.3

In order to adapt the chosen model system to real technological conditions of production of sweet dishes, the influence of white sugar and citric acid on the viscosity values of "Wheat starch-Tween 20 (E432)" model system was studied.

Literature data indicate that sugar concentration in sweet dishes varies from 5.0 to 20.0 %, that provides good consumer characteristics. Known, that sugar has the structure-forming ability based on the property of sucrose solution to change system viscosity gradually at the temperature changes, while not altering the phase state.

With adding white sugar to "Wheat starch-Tween 20 (E432)" model system in the temperature range 65–70 °C viscosity increase was observed in 2–2.3 times in the presence of 5.0–10.0 % of sugar content and 3.4 times in the presence of 20.0% of sugar content (Figure 3). Viscosity values were $(0.23–0.3) \cdot 10^{-2}$ Pa·s at 65 °C and $(0.52–0.59) \cdot 10^{-2}$ Pa·s and $0.87 \cdot 10^{-2}$ Pa·s at 70 °C respectively. It should be noted that a further viscosity increase was observed at temperatures of 85...90 °C.

The obtained results (Figure 3) indicate that established by scientists patterns of the impact of sugar on the starch suspension at the heat treatment, as gelatinization temperature increase and maximal viscosity increase are also characteristic for the "Wheat starch-Tween 20 (E432)" system. For sugar content 20.0% the largest values of effective viscosity were observed ranging from 66 °C (at 70 °C the viscosity was $0.87 \cdot 10^{-2}$ Pa·s, and at 90 °C – $2.4 \cdot 10^{-2}$ Pa·s, whereas the system's viscosity without sugar was $0.26 \cdot 10^{-2}$ and $1.6 \cdot 10^{-2}$ Pa·s respectively). Obviously, at the gelatinization beginning sucrose delays the starch grains swelling in aqueous suspension by the increased dry matter content, what inhibits the beginning of viscosity growth at the temperature range 60...65 °C.

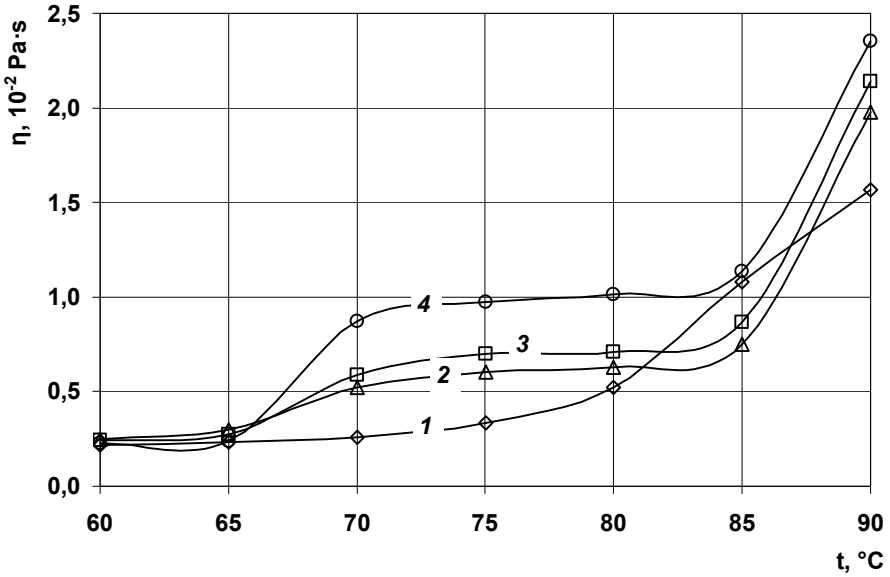

Figure 3. Changes of the effective viscosity of "Wheat starch – Tween 20 (E432)" model systems depending on the treatment temperature at the white sugar concentrations, %: *1*◊ – 0; *2*Δ – 5.0; *3*□ – 10.0; *4*○ – 20.0

Based on the viscosity values and organoleptic characteristics of new products the most appropriate concentration of white sugar in the system was chosen 10.0 %.

Thus in the desserts recipes fruit or vegetable raw material, which is characterized by certain pH, is used, we have modeled a food system in which the properties of the raw material were performed by citric acid.

The citric acid content was varied in the range of 0–1.0 %, which was elected in recalculation of pH of fruit raw material which is provided in the mousses recipe composition. The results of the citric acid impact on the viscosity of "Wheat starch-Tween 20 (E432)" model system are represented in Figure 4.

The results of determination of the effective viscosity of "Wheat starch-Tween 20 (E432)" model systems in the presence of citric acid showed a slight increase in values that was observed at the temperature 65±2 °C. So at 70 °C values have doubled, maintaining this trend to 85±2 °C. At the temperature 90 °C the largest viscosity characterizes model system with a 0.5 % concentration of acid, value of which amounted $5.1 \cdot 10^{-2}$ Pa·s, while the viscosity of a system without acid was $1.6 \cdot 10^{-2}$ Pa·s.

For the detection of joint influence of white sugar and citric acid on model systems the viscosity values at 10.0 % of white sugar and 0–1.0 % of citric acid content were determined (Figure 5).

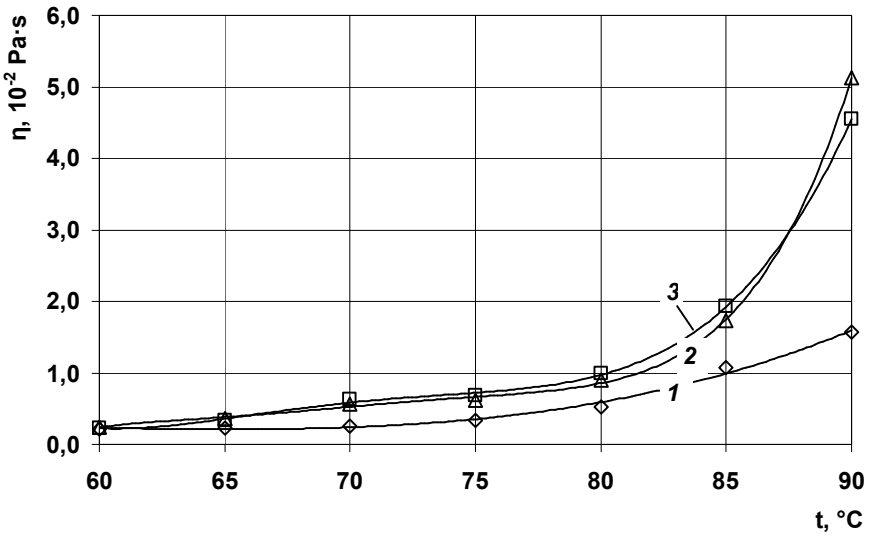

Figure 4. Changes of the effective viscosity of "Wheat starch – Tween 20 (E432)" model systems depending on the treatment temperature at the concentration of citric acid, %: *1*◊ – 0; *2*Δ – 0.5; *3*□ – 1.0

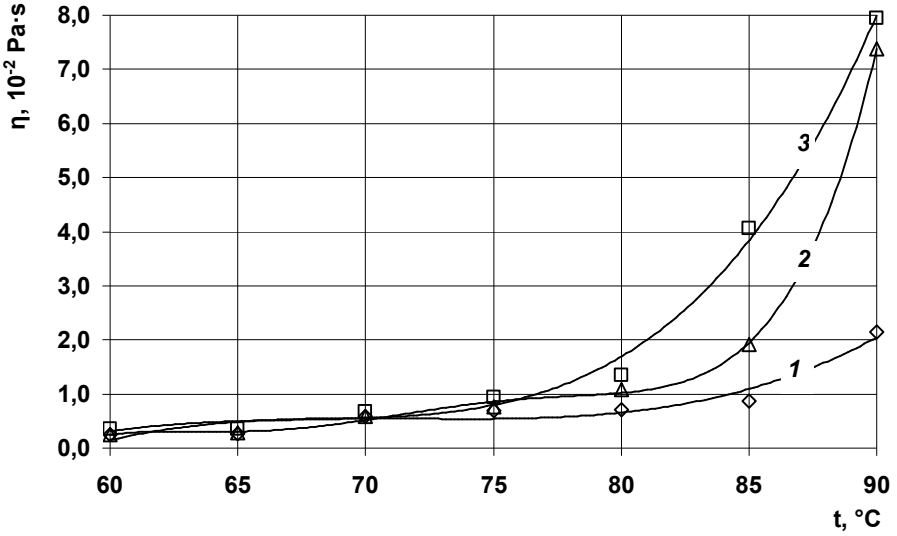

Figure 5. Changes of the effective viscosity of "Wheat starch – Tween 20 (E432) – white sugar" model systems depending on the treatment temperature at the concentration of citric acid, %: *1*◊ – 0; *2*Δ – 0.5; *3*○ – 1.0

The Figure 5 shows that the presence of citric acid in "Wheat starch-Tween 20 (E432)-white sugar" model system promotes the viscosity values increase beginning from 70 °C, and at 90 °C they are $7.4 \cdot 10^{-2}$ and $7.9 \cdot 10^{-2}$ Pa·s for systems containing 0.5 and 1.0 % of

citric acid respectively, whereas the viscosity of systems without acid is $2.1 \cdot 10^{-2}$ Pa·s. The viscosity values of the investigated systems in the temperature range 60–70 °C almost does not depend on the content of citric acid and are at the level of values of "Wheat starch-Tween 20 (E432)" model system, that contains 10.0 % of sugar ($\approx 0.3 \cdot 10^{-2}$ Pa·s).

Conclusions

The obtained results testify that the presence of surfactant in "Wheat starch-Tween 20 (E432)" model system under the temperature impact promotes the decrease of the viscosity values of the system compared to starch suspension that doesn't contain E432.

We can assume that at the time of the addition of Tween 20 (E432) to the starch suspension its distribution on the surface of wheat starch grains (adsorption) takes place, which conduces to impeding of the water penetration to the starch grains and the decrease of viscosity. That is, the inhibition of swelling of starch grains in water systems occurs, that results in a shift of the initial gelatinization temperature toward larger values.

It should be noted that the presence of sugar and citric acid in a model system promotes the increase of the viscosity values that does not contradict scientific literature data. The important point is practically constant viscosity values in the temperature range 60–70 °C, that allows to implement an innovative idea.

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Substantiation of the conditions of obtaining porous carbon materials from pyrolyzed wood wastes by chemical activation of H_3PO_4

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Abstract

Introduction. The purpose of this publication is to search for alternative materials – food industry wastes; valuation of it's use in the production of porous carbon materials (PCM) for use in water treatment systems.

Materials and methods. Pyrolyzed wood waste (PWW) of the meat processing industry as raw material for the production of sorbents. Chemical activation of PWW by orthophosphoric acid. Using the adsorption-desorption methods of nitrogen, the porous structure was determined at 77 K; mesopore distribution by size and mesopore's volume – by *BJH*-method; distribution of micropores by size – using *QSDFT*-method; volume of micropores – by Dubinin-Radushkevich method; subnanopor's volume – by *QSDFT*-method.

Results and discussion. The microporous structure has the following characteristics: pore diameters are in the range of D_{mi}=0,60-2,5 nm, mostly represented by pores with a diameter of 0,87; 1,56 nm; volume of micropores – V_{mi}=0,091 cm^3/g; differential pore volume dV_{mi}/dD=(0,021-0,166)·10^{-2} cm^3/g; micropores are about 49% of the total pore volume. According to the breakdown of micropores by size we can identify the range of values of D_{mi}=0,5-2,5 nm with two peaks: at ~ 0,9 nm and at ~ 1,6 nm. Mesoporous structure has the following characteristics: pore diameters are in the range of D_{me}=3,3-50,0 nm, most represented pores are with a diameter of 3,69 nm; mesopore's volume varies in the range of V_{me}=0,005-0,049 cm^3/g; pore surface area is S_{me}=5,7-28,0 m^2/g; differential pore volume: dV_{me}/dD=(0,06-2,58)·10^{-4} cm^3/g; differential pore area: dS_{me}/dD=(0,001-0,305) m^2/g; fraction of mesopores in the total pore volume is 3-26%. Curves of pore's differential volume and differential area of pore's surface at the interval of D=15,3-50,0 nm are located at the static area. Maximum located at the area of the smaller pore's diameter at the differential pore volume dV_{me}/dD=2,58·10^{-4} cm^3/g is observed at the point of 3,69 nm at the interval D=2,5-15,3 nm. The most number of mesopores located at the range of D=2,5-15,3 nm. The cited data shows that the proposed method allows to get PCM with a high output of 87,6%. The obtained PCM has a low rate of specific surface are S_{BET}=257,0 m^2/g and pore space. Total pore volume is V_{Σ}=0,187 cm^3/g.

Conclusion. An energy-saving method is proposed for the production of PCM from secondary «renewable» resources – PWW, for use in water treatment systems.

Introduction

Today it is known that organic matter of carbon-containing material consists of carbon (96,0%), hydrogen (1,0–2,5%), nitrogen (0,3–1,5%), sulfur (0,0–1,0%).

The PCM is made of materials that forms a solid carbon residue [1-8]. These matherials areas follows: wood – 36%, coal – 28%, brown coal – 14%, peat – 10% coconut shell – 10% organic materials and waste – 2% (Figure 1) [1].

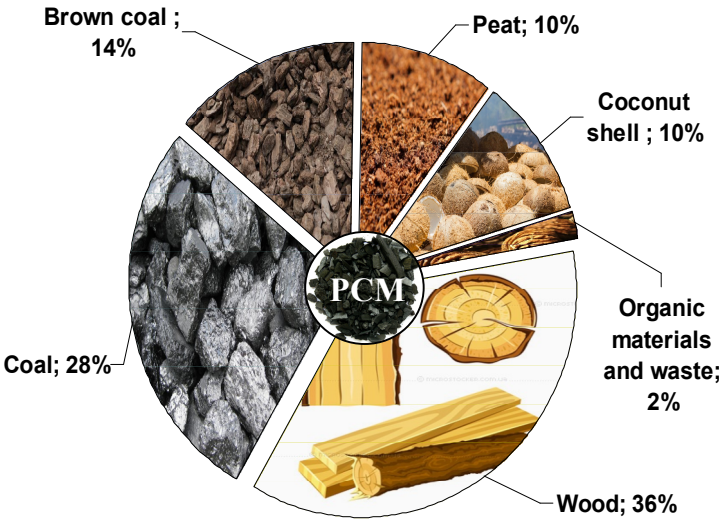

Figure 1. PCM receiving characteristics

Only 2% of organic material and waste are used to produce PCM [1]. Therefore, there is urgent need for an alternative materials. The search for these materials should involve existing technologies of food industry. Wastes of these industries can be used to produce adsorbents [1–22].

Today are known two ways of getting PCM – with the chemical [1–6, 9, 12, 13, 15, 16, 19, 21, 22, 24, 26, 27] and physical activation [1, 15, 17, 21, 27]. Benefits of chemical activation are: one-step process; low activation temperature; short activation time; large output; developed surface; controlled microporosity is well developed [26]. The chemical activation involves usage of activating agent ($ZnCl_2$ [4], H_3PO_4 [2, 3, 9, 12, 16], NaOH [26], KOH [24, 26], et al.), administered by impregnation, followed by carbonization of raw materials in the atmosphere or inert gases and activation [27].

Today are known many ways of receiving of PCM (Yorgun, Yildiz, 2015; Kumar, Jena, 2017; Kucherenko et al, 2010; Lillo-Rodenas, 2003) [2, 4, 24, 26], such as (Pat. 61059 Ukraine): grinding carbon-containing material with $(1–2)\cdot10^{-3}$ m, mixing with KOH in solid form in a weight ratio – 1:0,5–1:1, carbonization and activation at mode heatstroke at T=873–1073 K, cleaning with water and drying.

This method of receiving of PCM (Pat. 61059 Ukraine) has the following disadvantages: raw materials grinding has a high energy consumption; the small size of raw materials' fractions – it became charcoaled after carbonization and activation and evaporates with the gaseous components; high temperature carbonization and activation of PCM; activation in a heatstroke mode causes tearing of the structure and reduction of PCM shares; low rate of PCM release.

The most promising raw material for PCM – PWW is formed by pyrolysis of wood chips

(Kuzmin, Shendrik, 2016) [1]. This includes: the stage of grinding materials is absent due to the use of wood chips of PCM witht the size of lxbxh=(6x12x3)·10^{-3} m; PCM fractional increases up to 3,6·10^{-3}>d≥1,0·10^{-3} m; temperature reduction of charcoal carbonization and activation up to T=773–973 K; absence of heat stroke of activation due to carbonization at non-isothermal heating and isothermal heating at activation; output increase of PCM ratio.

One of the promising activating agents is orthophosphoric acid (Yorgun, Yildiz, 2015; Kwiatkowski et al, 2017; Ould-Idriss et al, 2011; Mahmood et al, 2017; Kumar, Jena, 2017) [2, 3, 9, 12, 16] with mass part (MP) H_3PO_4≥85%, which is added to the carbonaceous material and can withstand up to full impregnation, allowing acid to interact with organic and mineral components, with the formation of water-soluble substances washed with PCM [2, 3, 16]. During the interaction of organic acid and component of PWW produced are oxygen function and sulfate formed pore space. Thus, the use of H_3PO_4 allows to receive PCM with a low charcoal [9, 12].

Variation of MP activating agent in relation to PWW can affect the surface pores factor, yield ratio of PCM, the volume of wastewater [23, 25, 28–34].

A mixture of raw material/agent during carbonization and activation undergoing non-isothermal heating up to the activation temperature during the subsequent isothermal aging. In the scope of PWW is the formation of thermal degradation of products of low organic matter of PWW and PWW products of chemical reactions with acid takes place. Their output forms the spatial framework of PWW within. This leads to the formation of micropores and subnanopor and, consequently, increases the specific surface area and pore volume of the total. This improves adsorption characteristics PCM (Shendrik et al, 2003; Kucherenko et al, 2010; Zubkova, 2011) [23–25]. Fractional composition determined by PCM through MP residue on sieves with holes with a diameter of 3,6 mm, 1,0 mm and pallet.

It has been proved that PWW is an alternative carbon-containing raw material for PCM (Kuzmin, Shendrik, 2016) [1].

The aim of this work is the search for alternative materials of available technology of food industry. The wastes of which can be used for a production of PCM.

Materials and methods

Conditions for PCM production are presented at Table 1.

Obtained PWW is dried in the open air (T_1=293–298 K; W_1=67–82%; v_1=1–2 m/s) during τ_1=(336–504)·60^2 s, followed by more drying at T_2=373–383 K up to air-dry state with humidity of W_2=4–8%.

An orthophosphoric acid with MP of H_3PO_4 – 85% used as an activating agent for impregnating PWW/acid in mass ratio (MR) 1:0,5–1:1. The received mixture withstands for τ_2=(18–24)·60^2 s at T_3=291–295 K and PWW dried to receive a constant weight of MP moisture W_3=4–8% at T_4=373–383 K. Activation carried out in a stream of argon with a volumetric flow – Q_1≤5,6·10^{-7} m^3/s with drying bubbling after 96% in sulfuric acid under non-isothermal heating 0,07 deg./s upto activation temperature T_5=773–973 K and isothermal aging for τ_3=1·60^2 s at temperature activation and non-isothermal cooling – 0,1 deg./s in a stream of argon to a temperature T_6 = 323 K.

The received PCM cleaned from activating agent with a usage of water for τ_4=300–600 s and dried at a temperature T_7=373–383 K up to level of humidity W_4=4–8% with the rate of release of PCM Y_1=80–90%, followed by fractioning with the help of MP residue on sieves with holes: d≥3,6·10^{-3} m – MP≤2,5%; 3,6·10^{-3}>d≥1,0·10^{-3} m – MP≥95,5%; d<1,0·10^{-3} m – MP≤2,0% with the following selection of working faction on a sieve with holes 3,6·10^{-3}> d≥1,0·10^{-3}.

Table 1

Terms of PCM

Symbol	Characteristic	Experimental data	Rationed data
T_1	The temperature drying in the open air, K	295	293–298
W_1	Relative humidity,%	74	67-82
v_1	Air traffic speed, m/s	1,5	1–2
τ_1	PCM drying time outdoors, s	$336 \cdot 60^2$	$(336\text{-}504) \cdot 60^2$
T_2	The temperature drying in the drying cabinet, K	373	373–383
W_2	MP moisture PWW,%	6,58	4–8
	MP N_3PO_4,%	85	85
	MR PWW/acid, kg/kg	1:1	1:0,5–1:1
τ_2	Time withstand PWW with acid, s	$24 \cdot 60^2$	$(18\text{-}24) \cdot 60^2$
T_3	PWW holding temperature acid, K	294	291–295
T_4	Drying temperature, K	381	373–383
W_3	MP moisture PWW,%	6,02	4–8
Q_1	The volumetric flow of argon, m^3/s	$5{,}6 \cdot 10^{-7}$	$\leq 5{,}6 \cdot 10^{-7}$
	Non-isothermal heating, deg./s	0,07	≤0,07
	MP sulfuric acid,%	96	96
T_5	Activation temperature, K	773	773–973
τ_3	The time of activation, s	$1 \cdot 60^2$	$1 \cdot 60^2$
	Non-isothermal cooling, deg./s	0,1	≤0,1
T_6	The final temperature after cooling PCM, K	323	≤323
τ_4	Time cleaning PCM from activating agent, s	600	300–600
T_7	The temperature drying in the drying cabinet, K	378	373–383
W_4	MP moisture PCM,%	4,92	4–8
Y_1	PCM yield ratio,%	87,6	80–90
	MP remnant of PCM (%) in the sieve with holes, m: $d \geq 3{,}6 \cdot 10^{-3}$ $3{,}6 \cdot 10^{-3} > d \geq 1{,}0 \cdot 10^{-3}$ $d < 1{,}0 \cdot 10^{-3}$	 57,6 26,8 15,6	 MP≤2,5 MP≥95,5 MP≤2,0

Figure 2 shows the stages of PCM production; Figure 3 – general scheme of PCM obtaining according to experimental data from Table 1.

Figure 2. Stage receiving PCM:
a – technological chips of oak large (6x12x3)·10^{-3} m; b – PWW with MP moisture W=43,01%;
c – PWW after drying of moisture MP W=6,58%; d – PCM to fractionation;
e – PCM after fractionation of d≥3,6·10^{-3} m; f – PCM after fractionation of 3,6·10^{-3}>d≥1,0·10^{-3} m;
g – PCM after fractionation of d<1,0·10^{-3} m

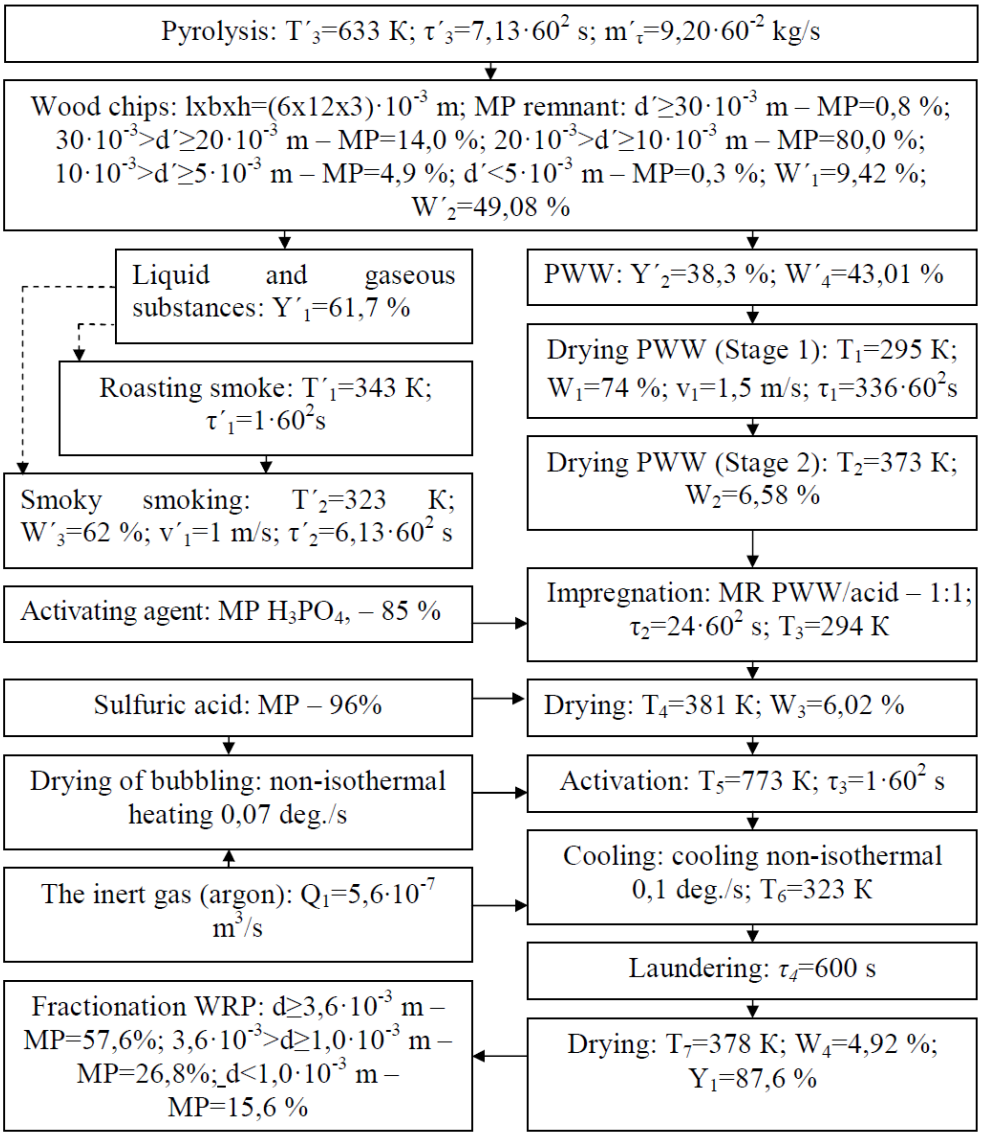

Figure 3. The general scheme of PCM receiving as per experimental data

PWW dried for $\tau_1=336\cdot60^2$ s outdoors (T_1=295 K; W_1=74%; v_1=1,5 m/s), followed by drying at the drying cabinet at T_2=373 K to air-dry state with MP moisture – W_2=6,58%. Phosphoric acid with MP H_3PO_4 – 85% injected by impregnation of PWW – H_3PO_4 and kept for $\tau_2=24\cdot60^2$ s at temperature T_3=294 K and dried up to a moisture obtained at MP PWW W_3=6,02% at T_4=381 K. The volume of solution has been choosed to create MR PWW/acid – 1:1 kg/kg. Activation was performed in a vertical cylindrical tubular reactor made of steel, with thickness of 3 mm, diameter of cylinder – 0,15 m, height – 0,3 m.

The reactor was purged with argon volumetric flow of Q_1=5,6·10^{-7} m^3/s, drained bubbling through concentrated sulfuric acid (96%). The heating of reactor's furnace has been switched on after 0,17·60^2 s after the start of argon input. The temperature mode of process included a period of non-isothermal heating (0,07 deg./s) up to an activation temperature, isothermal holding at this temperature for τ_3=1·60^2 s and rapid cooling in a stream of argon cooled at non-isothermal 0,1 deg./s to T_6=323 K. The activation temperature was T_5=773 K when activated via H_3PO_4.

Samples of PCM activating agent washed with distilled water for τ_4=600 s and dried at T_7=378 K to humidity W_4=4,92% of the rate of release of PCM Y_1=87,6%. Fractionation PCM remnant of MP conducted on sieves with holes: $d\geq3{,}6\cdot10^{-3}$ – MP=57,6%; $3{,}6\cdot10^{-3}>d\geq1{,}0\cdot10^{-3}$ – MP=26,8%; $d<1{,}0\cdot10^{-3}$ (pallet) – MP=15,6% with the following collection of working fractions on sieves of 3,6 mm and 1,00 mm MP – 84,4%.

Results and discussions

Characteristics of porous structure was determined on a basis of isotherms adsorption-desorption of nitrogen at T=77 K in the range of relative pressure P/P$_0$=0,00-1,00 (device Quantachrome Autosorb 6B) (Figure 4).

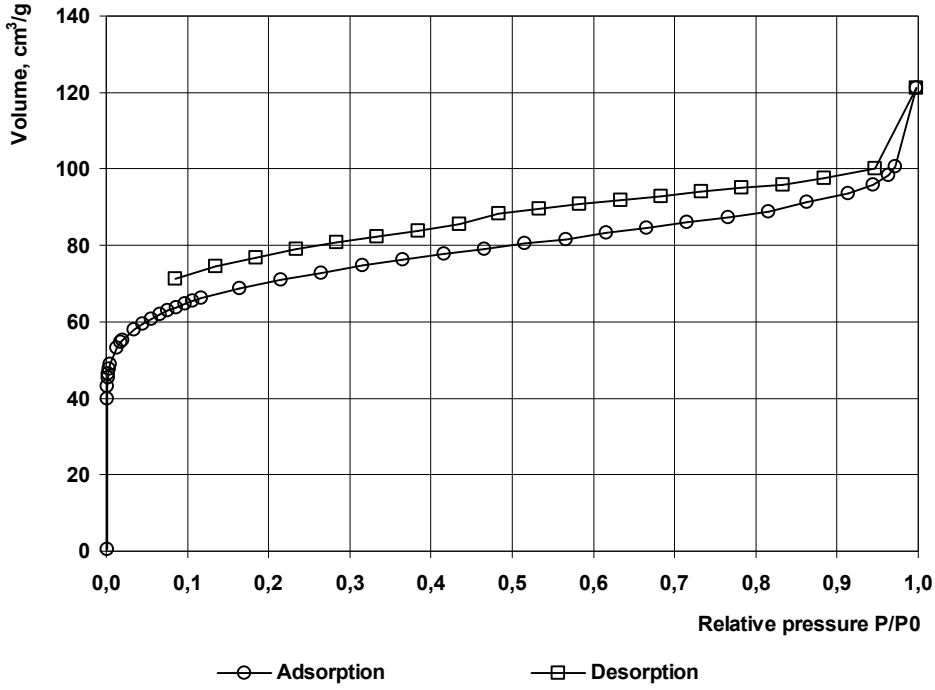

Figure 4. Isotherms of adsorption-desorption of nitrogen at PCM at T=77 K

The obtained isotherms of type II – according to Brunauer S. classification [28], per multimolecular adsorption. Sorption hysteresis loop approaching the point of relative pressure P/P_0=0,4, indicating a predominance of micropores of meso- and macropores.

Figure 5 shows the distribution of micropores by the size of sample.

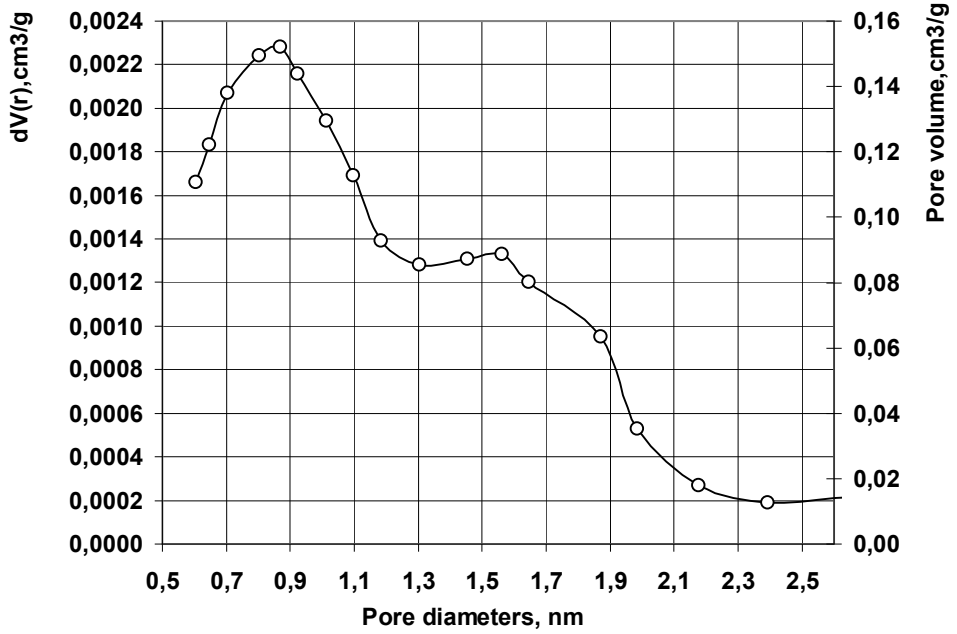

Figure 5. Distribution of micropores in size of the sample PCM – (pore diameter dependence of the differential pore volume) by QSDFT-method

Table 2 presents the results of a study by *BJH*-method mesopores' size distribution. Figures 6–10 shows the distribution of mesopores (*BJH*-method) the size of the sample and the corresponding volumes accumulated in these pores.

The microporous structure has the following characteristics: pore diameters are in the range of D_{mi}=0,60–2,5 nm, mostly represented with pores with a diameter of 0,87; 1,56 nm; volume of micropores – V_{mi}=0,091 cm^3/g; differential pore volume dV_{mi}/dD=(0,021–0,166)·10^{-2} cm^3/g; micropores fraction of the total pore volume is 49%.

As per allocation of micropores by size areas of values (Figure 5) D_{mi}=0,5–2,5 nm with two peaks: at ~ 0,9 nm and at ~ 1,6 nm can be identified.

Mesoporous structure has the following characteristics: pore diameters are in the range of D_{me}=3,3–50,0 nm, most represented pores with a diameter of 3,69 nm; mesopore volume varies in the range of V_{me}=0,005–0,049 cm^3/g; pore surface area – S_{me}=5,7–28,0 m^2/g; differential pore volume dV_{me}/dD=(0,06–2,58)·10^{-4} cm^3/g; differential pore area dS_{me}/dD=(0,001–0,305) m^2/g; fraction of mesopores in the total pore volume is 3–26% (Figure 6–10).

Curves of pore differential volume and pore differential surface area at the interval of D=15,3-50,0 nm are in the static area. Maximum located in a smaller diameter pores at the pore's differential volume dV_{me}/dD=2,58·10^{-4} cm^3/g at the point of 3,69 nm at the interval D=2,5-15,3 nm is observed. The most number of mesopores located at a range of D=2,5–15,3 nm.

Table 2

Distribution of mesopores' size by BJH-method

Pore diameter, nm	Pore volume, cm^3/g	Pore differential volume, cm^3/g	Pore surface area, m^2/g	Pore differential area, m^2/g	dV(logr), cm^3/g	dS(logr), cm^3/g
3,30	0,005	0,0002510	5,73	0,304640	0,095	115,47
3,69	0,011	0,0002578	12,47	0,284850	0,108	118,59
4,14	0,016	0,0002060	17,21	0,210570	0,093	94,78
4,68	0,019	0,0001022	19,79	0,090060	0,054	46,98
5,36	0,021	0,0000731	21,81	0,056194	0,044	33,62
6,21	0,024	0,0000541	23,46	0,035971	0,038	24,87
7,33	0,026	0,0000402	24,84	0,022830	0,033	18,45
8,86	0,029	0,0000255	25,85	0,012418	0,025	11,71
11,24	0,031	0,0000168	26,69	0,006473	0,021	7,71
15,35	0,034	0,0000092	27,38	0,002531	0,017	4,18
27,94	0,048	0,0000061	28,01	0,001335	0,021	2,72
416,58	0,072	0,0000009	28,45	0,000008	0,025	0,24

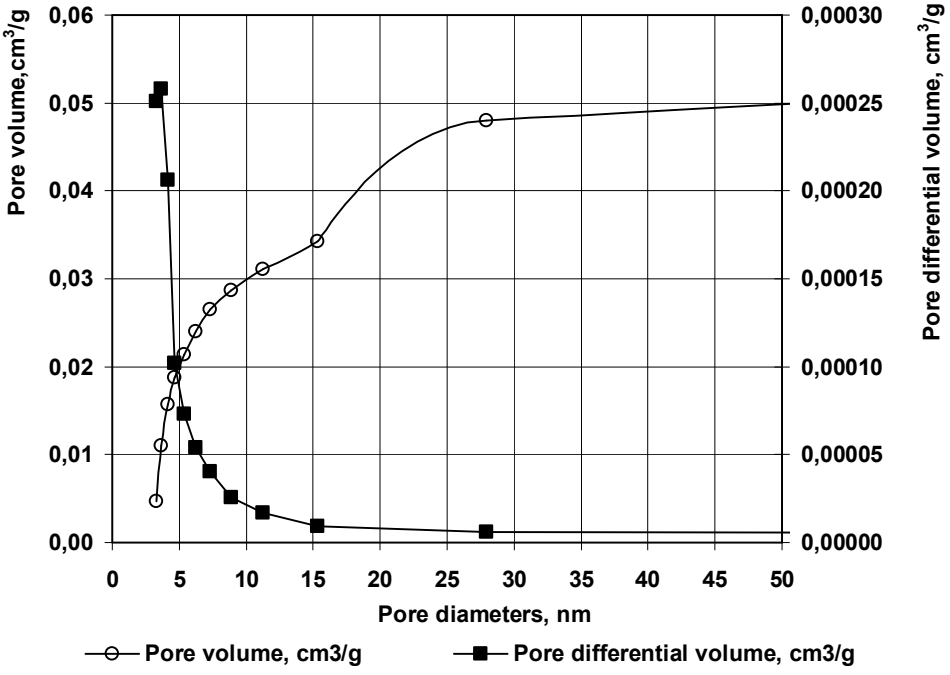

Figure 6. Distribution of mesopores by size of the sample PCM – (pore diameter dependence of pore volume and pore volume differential) by BJH-method

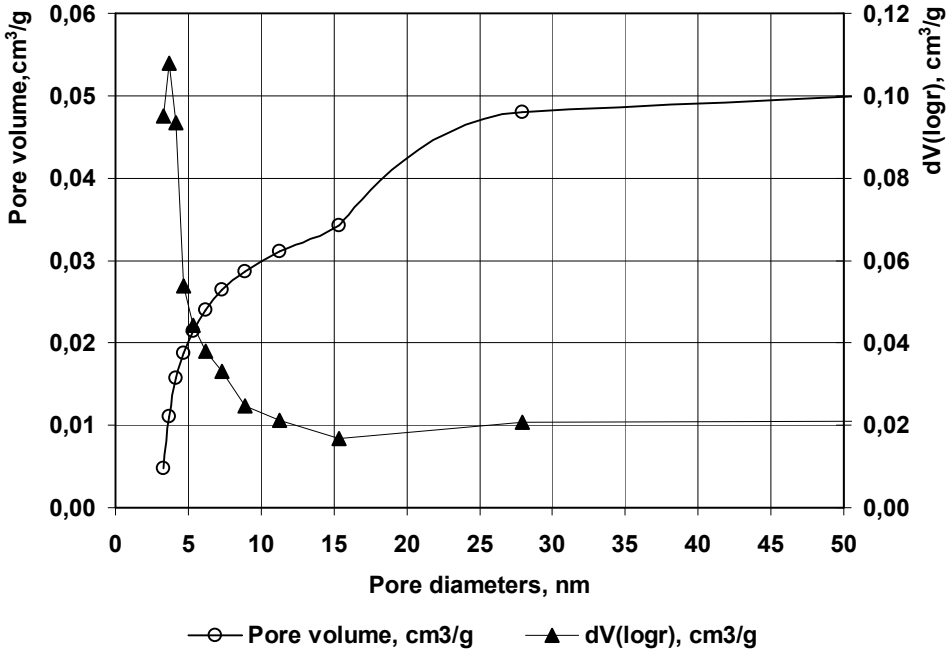

Figure 7. Distribution of mesopores by size of the sample PCM – (dependence pore diameter of pores and volume dV(logr)) by BJH-method

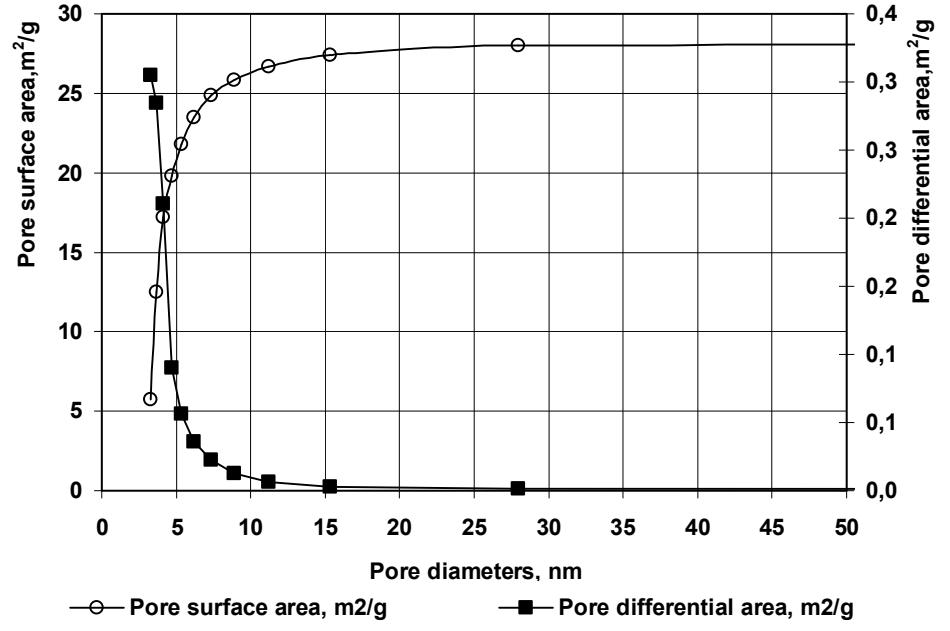

Figure 8. Distribution of mesopores by size of the sample PCM – (pore diameter dependence of surface area and pore surface area differential) by BJH-method

It was measured characteristics of PCM: Y – yield ratio of PCM (%); S_{BET} – pore surface area (m^2/g); V_{Σ} – pore total volume (cm^3/g); V_{ma} – macropore volume (cm^3/g); V_{me} – mesopore volume (cm^3/g); V_{mi} – micropores volume (cm^3/g).

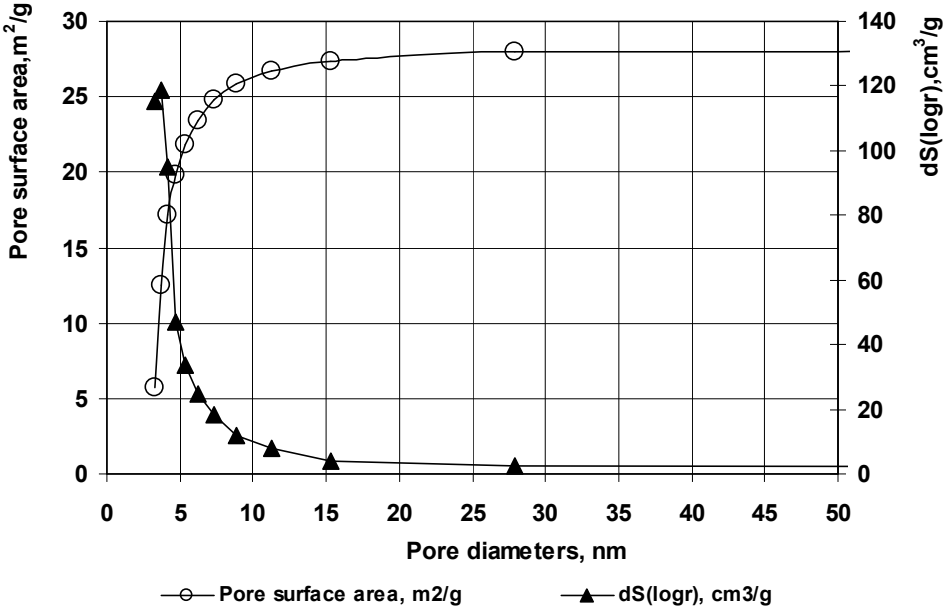

Figure 9. Distribution mesopores the size of the sample PCM – (pore diameter dependence of surface area and pore dS(logr)) by the BJH-method

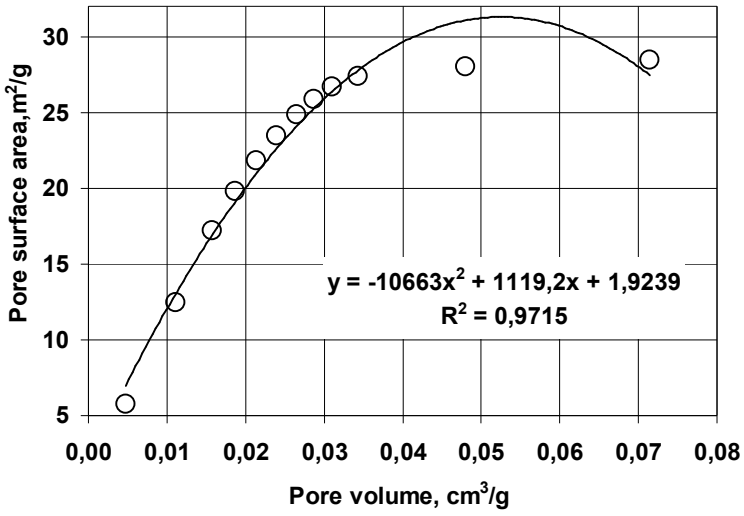

Figure 10. Distribution of mesopores by size of the sample PCM – (pore volume of pore surface area) by the BJH-method

Terms of PCM and its characteristics are shown at Table 3.

Table 3

Terms of PCM and its characteristics

Characteristic	Method PCM (Pat. 61059 Ukraine)		Method of PCM experimental data	
Type of raw	lignite		PWW	
The temperature activation, K	873		773	
Activating agent	*KOH*		H_3PO_4	
MR raw/agent, kg/kg	1:1		1:1	
Y,%	40,0		87,6	
S_{BET}, m^2/g	980,0		257,0	
V_Σ, cm^3/g	0,500	100%	0,187	100%
V_{ma}, cm^3/g	0,040	8%	0,047	25%
V_{me}, cm^3/g	0,220	44%	0,049	26%
V_{mi}, cm^3/g	0,240	48%	0,091	49%

Conclusions

An energy-saving method is proposed for the production of PCM from secondary «renewable» resources – PWW.

The data show that the proposed method allows to get PCM with high yield of 87,6% compared to the method of obtaining of PCM (Pat. 61059 Ukraine) – 40,0%. The PCM has a low proportion surface S_{BET}=257,0 m^2/g with respect to PCM (Pat. 61059 Ukraine) S_{BET}=980,0 m^2/g and pore space – total pore volume V_Σ=0,187 cm^3/g to V_Σ=0,500 cm^3/g. Moreover, the ratio of micropores to the total volume of the two options for 49% and 48% is unchanged, and the ratio of macropores in the experimental sample (25%), increased in relation to the prototype (8%), and the ratio of mesopores in the experimental sample (26%) reduced relative to the prototype (44%).

It can be concluded that the proposed method production of PCM from PWW, produced when smoking foods, with further carbonization at non-isothermal heating and activation at low temperature to 773–973 K in the presence H_3PO_4, lets to sorbents with a high exit rate (yield) of 80–90% and fractional composition particle size 1,0-3,6 mm (more 84%). These PCM can used in water treatment systems for water cleaning from solids, residual chlorine, organic compounds and odor and taste.

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Determination of structure and morphology of the cyclodextrins-iodine complexes

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Abstract

Introduction. The objective of these investigations is to study surface morphology of inclusion complexes between α- and β-cyclodextrins and molecular iodine as well as determine chemical stoichiometric ratio between these components in the formed complexes.

Materials and methods. The host-guest complexes between α- and β-cyclodextrins and iodine were synthesized according to the procedures, given in literature sources.. Morphology of the surface of the samples has investigated by use of scanning electronic microscope JSM-6700F (JEOL, Japan). The platinum layer with 10 nm in depth was preliminary placed on the samples. The samples were mounted on SEM and irradiated with beam of electrons at 15 kV and probe current 0,65 nA.

Results and discussion. The scanning electronic microscopy (SEM) has been used in order to investigate morphology and structural features of the obtained complexes. This method has widely used in macromolecules analysis. It allows precise determination of elemental content in the samples. The results of iodine content in inclusion compounds with α- and β-cyclodextrins obtained from SEM and iodimetrical titration methods are almost similar. It has found, that iodine content in β-CD-I_2 complex within the range 16,7-16,9 %, whereas α-CD-I_2 consisted 18,0–19,9% of active iodine. Some differences were found in respect to the iodine content in α-CD-I_2, obtained by two methods may related to the high water absorption on the complex surface result in the drop of iodine content on the surface. Experimental data of iodine content in the inclusion complexes suggested that α- and β-cyclodextrins react with KI_3 resulted in the host guest complex formation with the chemical stoichiometric ratio value of 1:1. Analysis of surface morphology of the cyclodextrin-iodine samples obtained from high resolution SEM method revealed about coarse crystalline structures formation, which is nontypical for organic polymeric compounds. Comparative studies have revealed, that cyclodextrin: iodine ratio in the obtained complexes is 1:1. It has been confirmed that one molecule of cyclodextrin bound one molecule of iodine, forming host-guest complex.

Conclusions. The complex β-cyclodextrin-I_2 was loss 9 % of active iodine at the prolonged storage during 1 year at 4 °C. It was shown, that iodine content in the α-CD-I_2 and β-CD-I_2 can be estimated with use of relatively simple and quick method of iodimetric titration, which is being important property of these complexes for their further application in food technologies.

Introduction

Cyclodextrins (CDs) are the cyclic oligosaccharides, composed from residues of α–D–glucopyranoses, made during starch transformation by specific enzymes, for example *Bacillus macerans*. Cyclodextrins belonging to ring molecules, which due to rigid glycosidic bonds between glucopyranose units have a toroidal form. The most widely used CDs are so called α-, β- and γ-cyclodextrin, which consisted six, seven and eight glucose units, respectively. Unique properties of cyclodextrins related to their ability of inclusion complexes formation in which non-polar guest molecule substitute water molecules from internal cavity of the host molecule which is leading to the complex formation [1,2]. The most common chemical stoichiometric ratio between cyclodextrins and guest molecules is 1:1 [1,3].

These complexes have been widely used in food technologies, particularly in oil-soluble compounds protection sensible to the oxygen, light and high temperatures action as well as improvement of vitamins solubility; taste and aroma stabilization of essential oils, undesirable compounds removal, lipophilic compounds solubilization, as photostabilization of light sensitive compounds, catalytic activity retention, protection from enzymatic deterioration, unnecessary taste and aroma suppression, controlled release of some food components e.t.c. CDs themselves can be recognized as non-digestible oligosaccharides and, thus, their consumption can improve beneficial microflora in gastrointestinal tract.

We have earlier synthesized host-guest complex between β-cyclodextrin and molecular iodine and applied this compounds as a food additive in boiled sausages formulation [4,5]. This compound can be considered as a promising iodophor, which able to increase iodine status of humans. According with experimental data, regular consumption of these boiled sausages by adult individuals resulted in significant improvement of their iodine status. The sensory and microbiological characteristics of the boiled sausages made with CD-I_2 inclusion and standard samples were similar so that this complex has no negative impact on quality of the boiled sausages [4,6].

X-ray analysis suggests that iodine and cyclodextrins form linear polymer chain in which one molecule of CD can bind more than one iodine molecule [7]. At the same time, however, other authors indicated that CD and iodine react with the complex formation, in which one molecule of β-cyclodextrin quench one molecule of iodine [8]. This inconsistency in iodine content of CD-iodine complexes is substantial obstacle that complicates wide application of CD-iodine complexes in food technologies and confuses rapid iodine determination

The objective of these investigations is to study surface morphology of inclusion complexes between α- and β-cyclodextrins and molecular iodine as well as determine chemical stoichiometric ratio between these components in the formed complexes.

Materials and methods

Materials

I_2, α- and β-cyclodextrin, DMF, KI were offered from Sigma-Aldrich. Unless specific notifications, all the chemicals were analytical reagent grade without further purification.

Synthesis of β-cyclodextrin-I_2 complex.

Synthesis of β-CD/I_2 complex was done according to synthesis procedure, described by Wang and co-authors [8]. 3,8 g of KI and 0,38 g of I_2 (1,5 mM) were dissolved in 15 ml of distilled water during 10 minutes resulted in KI_3 formation. Further, this solution was dropped into 10 ml β-cyclodextrin solution (223 mg, 0,5 mM) in 50 ml conical flask. The mixture was stirred during 5 h at 25 °C and then retained 10 h at 4 °C in order to fully encapsulate iodine in β-CD. After storage, brown crystals of β-CD/I_2 were filtered and washed KI solution in order to remove I_2 molecules from the filter cake and distilled water which aid to get rid from both KI and β-CD. The final product was dried at vacuum during 4 h at 40 °C. The total preparative yield was 93 %.

Iodine content in the complex was determined by iodimetrical titration, described by Wang and co-authors [8]. Sample of α- or β-CD/I_2 (0,2 g) was weighed precisely, when placed in the 10 ml flask and 4 ml of DMF was added and stirred until complete dissolution. When 140 ml of deionized water was added and titred by $Na_2S_2O_3$ standard solution (0,01 M). Titration was continued until the solution turned out light yellow and added 3 ml starch-iodine indicator and keep on titrating until solution became colorless. Titration procedure was repeated thrice. The iodine content was calculated by formula:

$$I(\%) = 0{,}1269 \times C(Na_2S_2O_3) \times V(Na_2S_2O_3) \times 100/m$$

The iodine content in the complex was 16,9±0,1 %, which corresponds equimolecular ratio of β-CD and I_2 in the complex. Moreover, we determined melting point of β-CD/I_2 in capillary tube, which was 76 °C. This value is in agreement with the data obtained by Wang and co-auth [8].

α-CD/I_2 complex has synthesized by the same manner, taking to account that α-cyclodextrin more soluble in aqueous solution than β-CD. The total preparative yield was 94,5 %.

Methods

The scanning electronic microscopy (SEM) has been used in order to investigate morphology and structural features of the obtained complexes. This method has widely used in determination of macromolecules analysis. It allows precise determination of elemental content in the samples [9].

Morphology of the surface of the samples has investigated by use of scanning electronic microscope JSM-6700F (JEOL, Japan). The samples were applied on metal slab, and preliminary were coated with platinum layer with 10 nm in dept. The samples were mounted on SEM and irradiated with beam of electrons at 15 kV and probe current 0,65 nA.

Results and discussion

The experimental data of iodine content in the complexes, obtained by several methods was given in the table 1. According with these data molecular iodine is interacting with α- or β-CD resulted in the host-guest complex formation with the ratio1:1.

These results are not agreed with the known X-ray diffraction assays, which indicates, that β-cyclodextrin form with iodine inclusion complex β-CD-I_7^-, whereas interaction between α-cyclodextrin and iodine resulted with complex formation with total formula α-CD-I_5^- [6]. The authors suggested that polyiodide chain consists of discrete I_7^- units, which can be formulated as $I_2 \cdot I_3^- \cdot I_2$. These units are shaped into Z-like structures. Furthermore, in

the α-CD-I_5^- complex, α-CD molecules are stacked together to form columns similar to nanotubes, and I_5^- ions are located in the columns and nearly linerly arranged in the direction of columns [10].

Table 1

Iodine content (%) in cyclodextrin-iodine complexes

Complex	SEM	Titration
α-CD-I_2	18,0±0,2	19,9±0,1
β-CD-I_2	16,82±0,4	16,9±0,1
β-CD-I_2 (1 year storage)	15,42±0,3	14,9±0,1

As it can be seen from the table 1, the results of iodine content in inclusion compounds with α- and β-cyclodextrins obtained from SEM and iodimetrical titration methods are almost similar. These evidences indicates both high reproducibility of complexes synthesis procedure and precision of iodimetric titration method. However, some differences are found in respect to the iodine content in α-CD-I_2, obtained by two methods may related to the high water absorption on the complex surface result in the drop of iodine content on the surface. Surprisingly, the data of iodine content in the samples obtained from iodimetric titration is close to the theoretically estimated on the basis of individual atomic weight. Thus, experimental data of iodine content in the inclusion complexes suggested that α- and β-cyclodextrins react with KI_3 resulted in the host guest complex formation with the chemical stoichiometric ratio value of 1:1. Interesting, that storage for 1 year at 4 °C, indicates that β-CD-I_2 inclusion complex has lost a small amount of iodine, which can be simply and accurately determined by iodimetric titration method (Table 1). Thus, the complex has remained relatively stable during prolonged storage.

Table 2

Oxygen content (%) in cyclodextrin-iodine complexes

Complex	Experimental	Theoretical
α-CD-I_2	30,9±0,5	36,3
β-CD-I_2	39,52±0,6	38,1
β-CD-I_2 (1 year storage)	38,7±0,5	38,1

The oxygen content in the samples of CDs and their complexes with iodine was derived with the help of SEM method. As it can be seen from the table 2, these data close to those theoretically calculated taking to account masses of the individual atoms constituting the bonds in the molecules (table 2). It is known, that SEM method usually is not able to give reliable data for mass content of atoms with relatively low atomic weight, like oxygen or carbon. This was observed for the carbon content in the samples, whereas SEM method provides good result for oxygen content in the samples. These findings are also indicated

that iodine with the α- or β-CD will form 1:1 complex. Potassium is also present in the complexes, mainly due to KI application at the complexes synthesis. The potassium content in the samples varies within the range 0,8-1,48 % which is also confirmed stoichiometric ratio of the complexes.

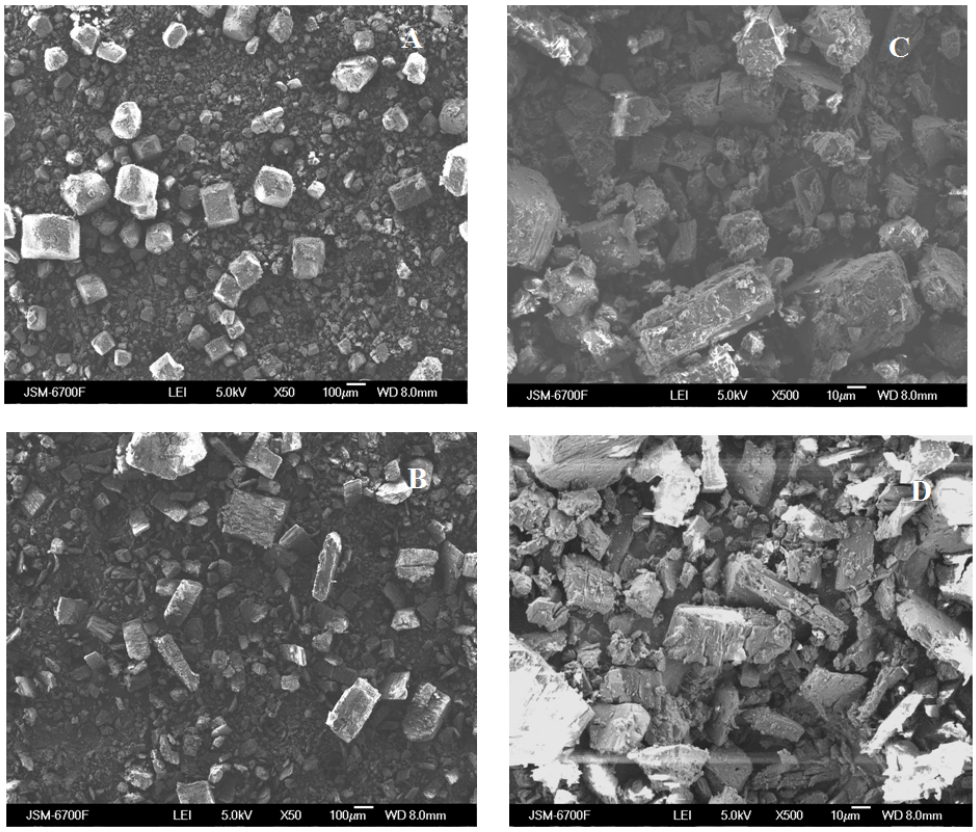

Figure 1. Scanning electronic microphotographs of the surfaces of α-CD (A) and β-CD (B) Left, 50×magnification; α-CD (C) and β-CD (D) Right, 500×magnification

The changes in particle morphology that occurred during CDs synthesis are indicated in the SEM study. The SEM microphotographs of α- and β-CD shown in Figure 1. These images observation indicates the presence of some not fully transformed starch granules in a very small amount. It is confirmed high level of starch transformation into CDs. As illustrated in Figure2, CDs complexes with iodine existed in needle like crystals, whereas α- and β-CD was observed as irregular "shrinked" crystals.

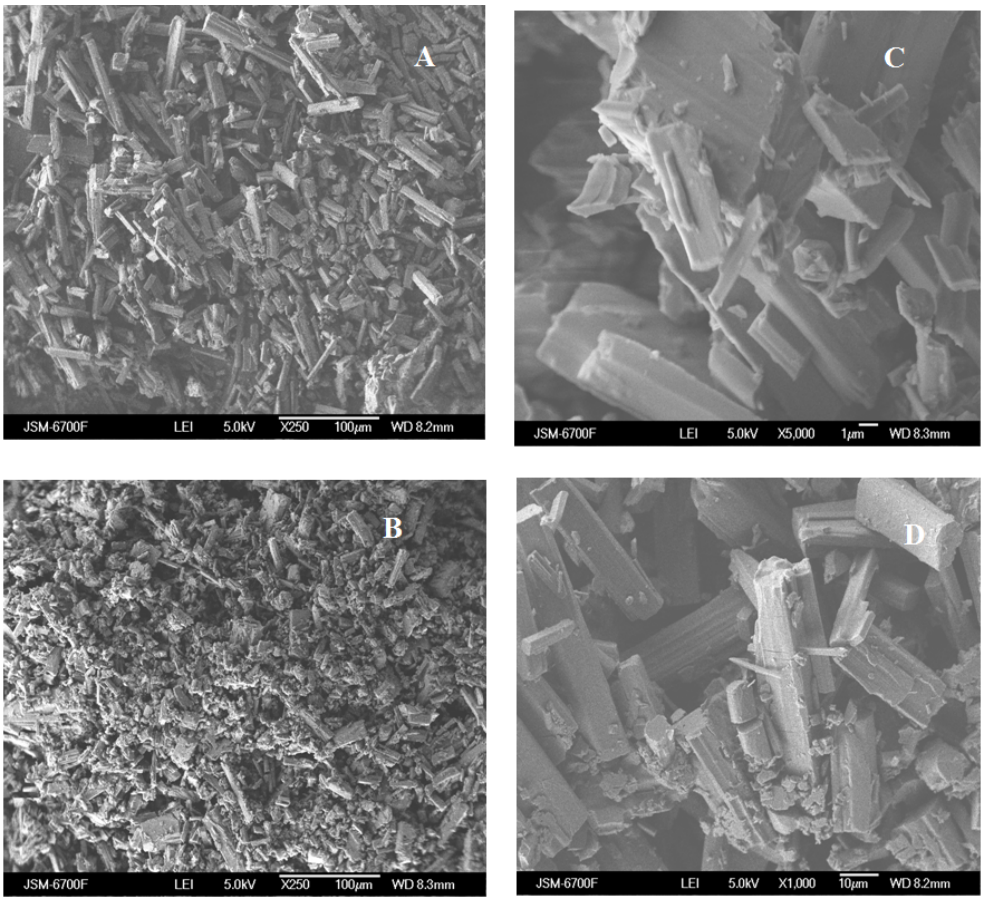

Figure 2. Scanning electronic microphotographs of the surfaces of α-CD-I_2 (A) and β-CD-I_2 (B) Left, 250×magnification; α-CD-I_2 (C) and β-CD-I_2 (D) Right, 5000×magnification

The changes in particle morphology that occurred during CDs synthesis are indicated in the SEM study (Figures 1 and 2). The SEM microphotographs of α- and β-CD complexes with iodine are almost similar as shown in Figure 2. It is appeared, that during synthesis, original morphology of CDs almost fully disappeared and needle shaped crystals with regular size were present.

The SEM microphotographs of CDs are similar to those obtained by Ikotun and coauth [11]. Analysis of surface morphology of the cyclodextrin-iodine samples obtained from high resolution SEM method revealed about coarse crystalline structures formation, which is nontypical for organic polymeric compounds.

The mentioned above disparity between literature data and our experimental results related to the iodine content in CD-I_2 inclusion complexes can be explained by intense washing of synthesized crystals by KI aqueous solution. This is obviously resulted in polyiodide chain disruption and incapsulated extrinsic molecular iodine washing out. In the

other words, one molecule of α- or β-CD was binding a one molecule of iodine during synthesis.

Probably, at the initial stage of complex formation, iodine molecule bind to the molecule of cyclodextrin give rise to inclusion complex formation with stoichiometric ratio 1:1. Further, additional complexation may occur as a result of iodine interaction with the 1:1 complex.

Conclusions

Thus, comparative studies have revealed, that cyclodextrin: iodine ratio in the obtained complexes is 1:1. Reproducibility of procedure of CD-I_2 synthesis has confirmed. These complexes remain stable during storage for 1 year and lost approximately only 9 % of iodine. It has shown, that iodine content in the α-CD-I_2 and β-CD-I_2 can be estimated with use of relatively simple and quick method of iodimetric titration, which is being important property of these complexes for their further application in food technologies.

Acknowledgements
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Antimicrobial activity of *Lactobacillus plantarum* strains against Salmonella pathogens

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Abstract

Introduction. Lactic acid bacteria produce various compounds such as organic acids, diacetyl, hydrogen peroxide and bacteriocin during lactic fermentations. All of these can antagonize the growth of some spoilage and pathogenic bacteria in foods.

Materials and methods. To determine the antimicrobial activity of *Lactobacillus plantarum* D1 and *Lactobacillus plantarum* D2 against *Salmonella* sp. and *Salmonella abony* ATCC 6017, the method of co-culturing was applied. The study was conducted under static conditions at 37±1 ºC for 72 hours, taking samples at 0, 12, 24, 36, 48, 60 and 72 h and monitoring the changes in the titratable acidity and the concentration of viable cells of both the pathogens and the *Lactobacillus plantarum* strains.

Results and discussion. In the single-strain cultivation of each *Lactobacillus plantarum* strain and each *Salmonella* strain high concentration of viable cells were achieved by the 24th hour and it was maintained by the end of the culturing. In the co-culturing of each *Lactobacillus plantarum* strain and each *Salmonella* strain, the *Lactobacillus* strain was not significantly influenced by the presence of any of the *Salmonella* strains. But the number of viable cells of the pathogens was greatly reduced, the reduction being strain-specific. In the co-culturing of each *Lactobacillus plantarum* strain and *Salmonella abony* ATCC 6017, the concentration of viable cells of the pathogen strain was reduced by the 60th h. In the co-culturing of each *Lactobacillus plantarum* strain and *Salmonella* sp., the concentration of viable cells of the pathogen strain was reduced by the 72th h. The observed antimicrobial activity was due to a great extent to the acidification of the medium because of the production and accumulation of lactic and other oraganic acids.

Conclusions. The demonstrated antimicrobial activity is a prerequisite for further research on the probiotic potential of the two *Lactobacillus plantarum* strains for their inclusion in the composition of probiotic preparations and starters for probiotic functional foods.

Introduction

Lactic acid bacteria play an important role in food fermentation processes. Raw foods such as milk, fruits, vegetables or meat are often preserved by lactic acid fermentation. These organisms produce various compounds such as organic acids, diacetyl, hydrogen peroxide and bacteriocin during lactic fermentations. All of these can antagonize the growth of some spoilage and pathogenic bacteria in foods [1, 2].

Most of the probiotic lactobacilli in human foods are supplied in highly concentrated forms containing more than 10^{10} cfu/cm^3. The ability of *Lactobacillus* strains to adhere to the mucosal surfaces of the intestine and the subsequent long or short term colonization has long been one of the most commonly encountered criteria for the selection of probiotic strains [3, 4, 5].

Enteric disorders are one of the most important problems in the food industry, with salmonellosis and colibacillosis regarded as the major bacterial diseases occurring in human. *Salmonella* and *Escherichia coli* infections range from severe acute disease to mild infections of a chronic nature [6].

The purpose of the present work was to study the antimicrobial activity of *Lactobacillus plantarum* D1 and *Lactobacillus plantarum* D2 against the Gram-positive pathogenic microorganisms *Salmonella* sp. (clinical isolate) and *Salmonella abony* ATCC 6017, that cause toxicoses and toxicoinfections.

Materials and methods

1. Microorganisms

Lactobacillus plantarum D1 and *Lactobacillus plantarum* D2, isolated from salad dressings;

test pathogenic microorganisms *Salmonella* sp. (clinical isolate) and *Salmonella abony* ATCC 6017.

2. Media

2.1. MRS – broth medium

Composition (g/dm^3): peptone from casein – 10; yeast extract – 4; meat extract – 8; glucose – 20; K_2HPO_4 – 2; sodium acetate – 5; diammonium citrate – 2; $MgSO_4$ – 0.2; $MnSO_4$ – 0.04; Tween 80-1 cm^3/dm^3; pH = 6.5. Sterilization – 15 minutes at 118 ºC.

2.2. LAPTg10 – agar medium

Composition (g/dm^3): peptone – 15; yeast extract – 10; tryptone – 10; glucose – 10; Tween 80-1 cm^3/dm^3, agar – 15. pH=6.6 – 6.8. Sterilization – 20 minutes at 121 ºC.

2.3. LBG – agar medium

Composition (g/dm^3): tryptone – 10; yeast extract – 5; NaCl – 10; glucose – 10; agar – 15; pH = 7,5. Sterilization – 20 minutes at 121 °C.

3. Determination of the antimicrobial activity against pathogenic microorganisms – by co-culturing

To determine the antimicrobial activity of the studied lactobacilli strains against the two pathogens a 48 hour cultural suspension of each *Lactobacillus plantarum* strain was used. Separate cultivation of the two *Lactobacillus plantarum* and the two *Salmonella* strains as well as co-culturing of each of the two *Lactobacillus plantarum* strains and each *Salmonella* strain included in the study were conducted. For the examination of the co-culturing, 0.5 cm^3 of the suspension of the *Lactobacillus plantarum* strain, 0.5 cm^3 of the

suspension of the *Salmonella* strain and 9 cm^3 of culture medium (MRS-broth medium) were mixed. In the control of each *Lactobacillus plantarum* strain and in the control of each pathogen, 9.5 cm^3 of the MRS-broth medium were mixed with 0.5 cm^3 of the suspension of the *Lactobacillus plantarum* strain or of the suspension of the *Salmonella* strain, respectively. The study was conducted under static conditions in a thermostat at 37±1ºC for 72 hours, taking samples at 0, 12, 24, 36, 48, 60 and 72 h and monitoring the changes in the titratable acidity and the concentration of viable cells of both the pathogens and the *Lactobacillus plantarum* strains. The determination of the number of viable cells was done by the spread plate method on LAPTg10-agar (for the enumeration of lactobacilli), on LBG-agar (for the enumeration of pathogens). The titratable acidity was determined according to a standard protocol [7].

Results and discussion

In the study of the antimicrobial activity of the two *Lactobacillus plantarum* against the two *Salmonella* strains by the method of co-culturing, the dynamics of the change in the number of viable cells of both the lactobacilli and the pathogens and in the titratable acidity were monitored (Fig. 1, Fig. 2, Fig. 3, Fig. 4, Fig. 5, Fig. 6, Fig. 7 and Fig. 8).

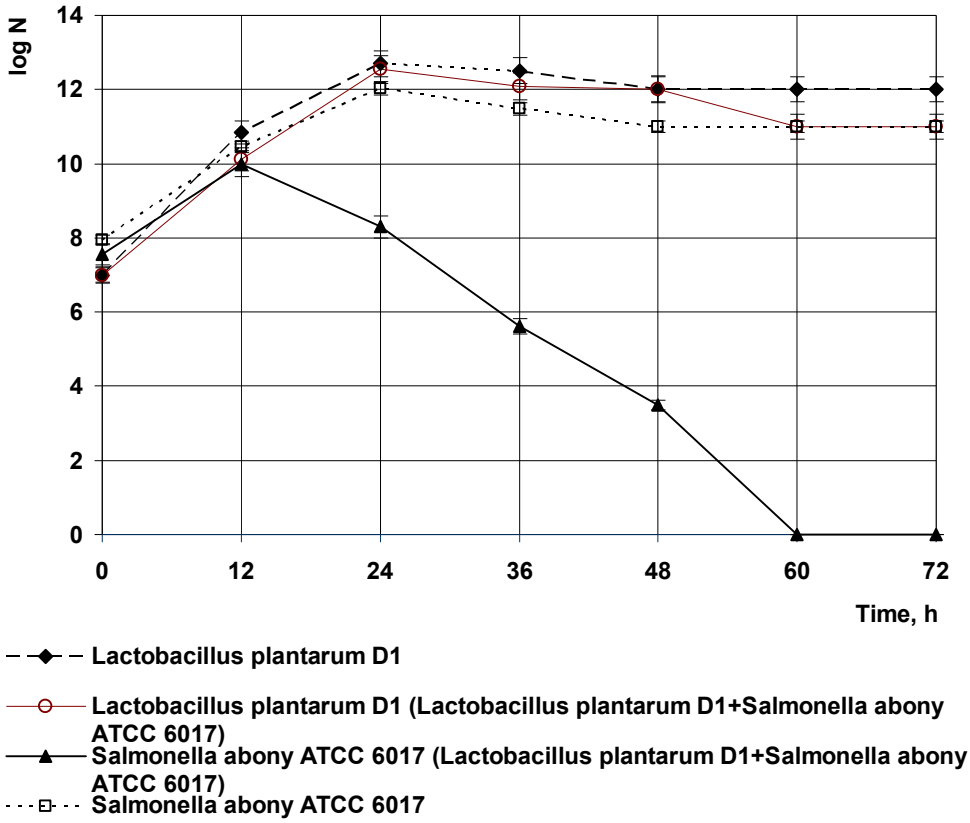

Figure 1. Changes in the number of viable calls of *Lactobacillus plantarum* D1 and *Salmonella abony* ATCC 6017 in single-strain culturing and in a mixed population at 37±1 °C

In the single-strain cultivation of each *Lactobacillus plantarum* strain and each *Salmonella* strain high concentration of viable cells were achieved by the 24th hour and it was maintained by the end of the culturing. In the co-culturing of each *Lactobacillus plantarum* strain and each *Salmonella* strain, the *Lactobacillus* strain was not significantly influenced by the presence of any of the *Salmonella* strains. But the number of viable cells of the pathogens was greatly reduced, the reduction being strain-specific. The obtained results were commesurable with the observations described in [9].

The *Lactobacillus plantarum* and *Salmonella* strains entered the stationary growth phase at the 24th h, reaching maximum concentration of viable cells – above 10^{12}cfu/cm^3 (Fig. 1, Fig. 2, Fig. 5 and Fig. 6). Meanwhile the titratable acidity of the medium in the culturing of both the two strains of lactobacilli reached 140°T (Fig. 3, Fig. 4, Fig. 7 and Fig. 8). A similar trend was established in the single-strain culture of the two *Salmonella* strains. Therefore, *Salmonella* sp. Entered the stationary growth phase at the 12th h, while *Salmonella abony* ATCC 6017 entered it at the 24th h, reaching concentrations of viable cells about 10^{12}cfu/cm^3 (Fig. 1, Fig. 2, Fig. 5 and Fig. 6).

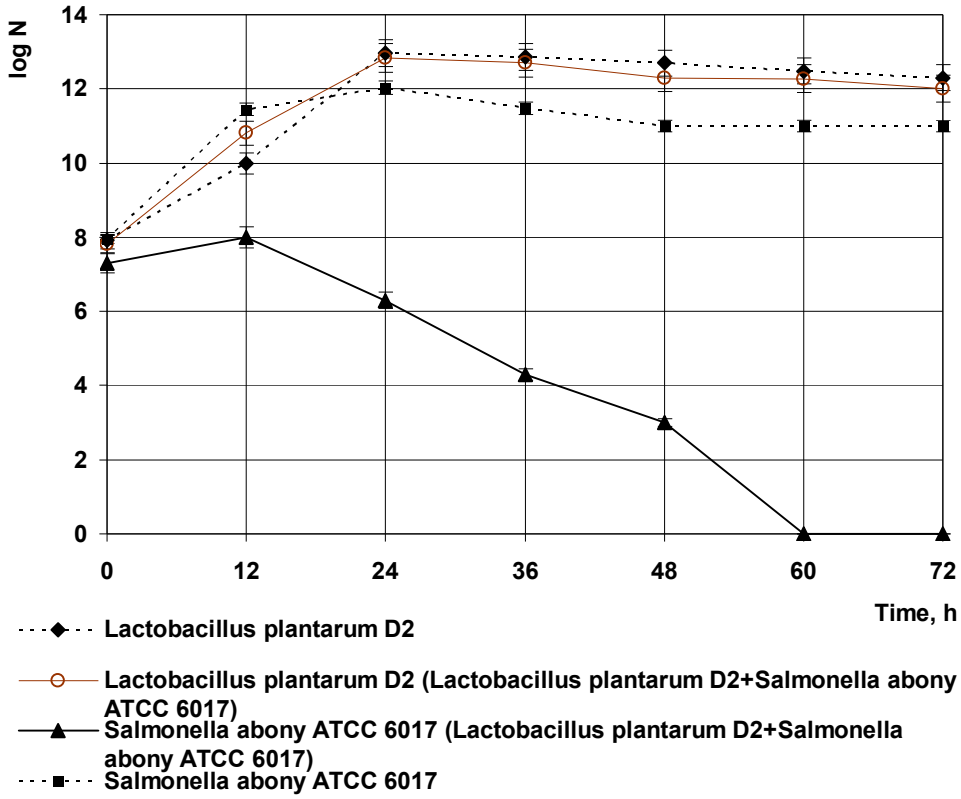

Figure 2. Changes in the number of viable calls of *Lactobacillus plantarum* D2 and *Salmonella abony* ATCC 6017 in single-strain culturing and in a mixed population at 37±1 °C.

In the co-culturing of each *Lactobacillus plantarum* strain and *Salmonella abony* ATCC 6017, the concentration of viable cells of the pathogen strain was reduced by the 60th h (Fig. 3 and Fig. 4).

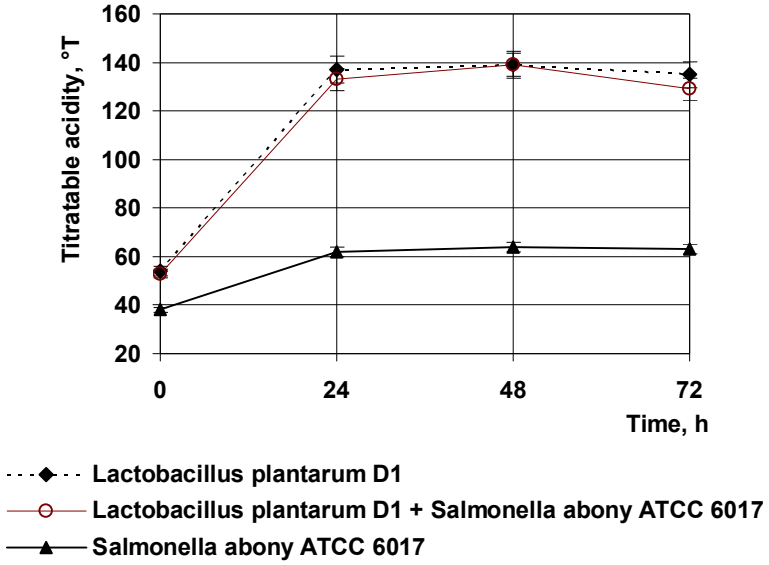

Figure 3. Changes in the titratable acidity of the medium in single-strain culturing and in a mixed population of *Lactobacillus plantarum* D1 and *Salmonella abony* ATCC 6017 at 37±1 °C.

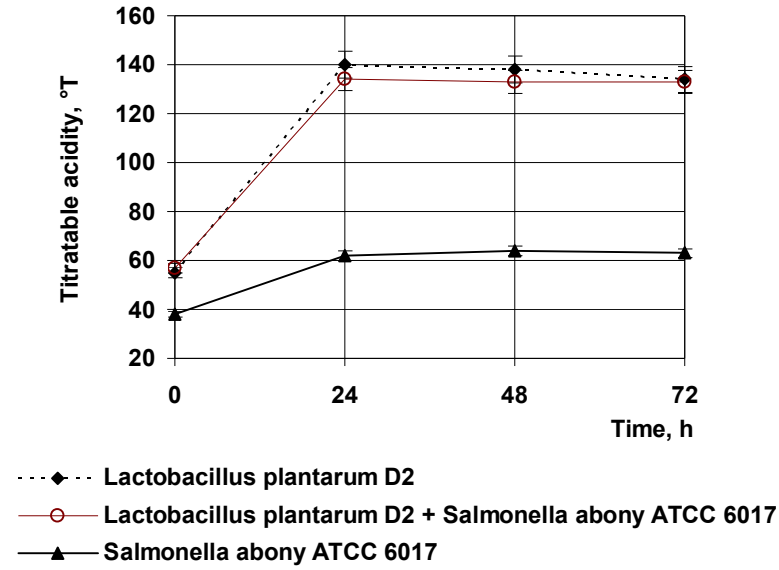

Figure 4. Changes in the titratable acidity of the medium in single-strain culturing and in a mixed population of *Lactobacillus plantarum* D2 and *Salmonella abony* ATCC 6017 at 37±1 °C

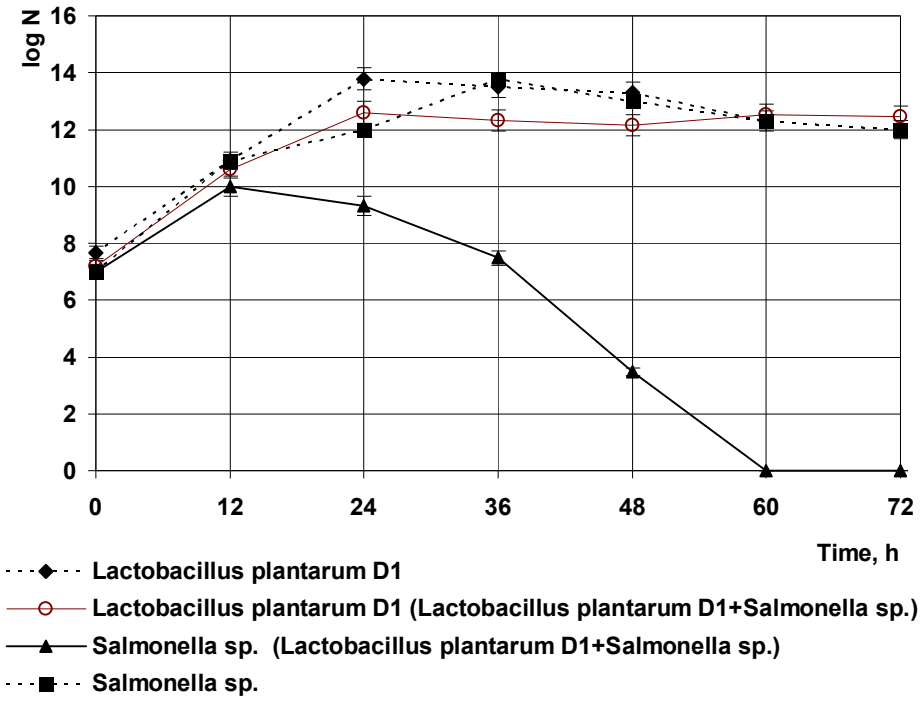

Figure 5. Changes in the number of viable calls of *Lactobacillus plantarum* D1 and *Salmonella* sp. In single-strain culturing and in a mixed population at 37±1 °C.

In the co-culturing of each *Lactobacillus plantarum* strain and *Salmonella* sp., the concentration of viable cells of the pathogen strain was reduced by the 72th h (Fig. 7 and Fig. 8). The two *Salmonella* strains differed in their growth characteristics. In the co-culturing of the two *Salmonella* strains with each of the two *Lactobacillus plantarum* strains, a slight increase in the number of living cells was observed, but it had different behavior depending on the very *Lactobacillus plantarum* strain.

The observed antimicrobial activity of the two *Lactobacillus plantarum* strains included in the present study was due to the production and accumulation of lactic and other organic acids. According to Helander et al. [8], *L. plantarum* produces a variety of low molecular mass compounds including acids, alcohols, carbon dioxide, diacetyl, hydrogen peroxide and other metabolites. Many of these metabolites have a broad activity spectrum against other species, and their production is largely affected by the food matrix itself. [6].

The *L. plantarum* strains isolated from salad dressings reduced the amount of viable cells of the two Salmonella strains in a mixed population (*Lactobacillus plantarum* and *Salmonella* strain) in the present in vitro study. The obtained results confirm the research by Denkova R. et al., 2013 [9]. But *Lactobacillus plantarum* D1 and *Lactobacillus plantarum* D2 reduced the number of living cells of *Salmonella abony* NTCC 6017 by the 60th h, while *Lactobacillus plantarum* X2 (isolated from spontaneously fermented sourdough) could not do so even by the 72nd h. On the other hand, *Lactobacillus plantarum* F3 (isolated from spontaneously fermented sourdough) and *Lactobacillus plantarum* LBRZ12 reduced the

Salmonella abony NTCC 6017 living cells by the 60th h, in compliance with the results reported in the present manuscript. Hence, *Lactobacillus plantarum* D1 and *Lactobacillus plantarum* D2 possess higher antimicrobial activity against *Salmonella abony* NTCC 6017 than *Lactobacillus plantarum* X2 [9]. *Lactobacillus plantarum* F3 (isolated from spontaneously fermented sourdough) managed to supress all *Salmonella* sp. (clinical isolate) cells by the 72nd h, which is in compliance with the obtained results for the same pathogen in its co-culturing with *Lactobacillus plantarum* D1 and *Lactobacillus plantarum* D2. But *Lactobacillus plantarum* X2 and *Lactobacillus plantarum* LBRZ12 demonstrated lower antimicrobial activity against *Salmonella* sp. (clinical isolate) – the number of viable pathogen cells by the 72nd h was 10^3cfu/cm^3 [9]. After additional research on the probiotic properties of the two *Lactobacillus plantarum* strains, they can be included in the composition of probiotic preparations and starters for functional probiotic foods and beverages. This in turn would ensure the microbiological safety of the foods and beverages. Moreover, upon intake the high concentration of viable cells of lactobacilli will provide the necessary beneficial flora to maintain the balance in the gastrointestinal tract and perform its inherent preventive role.

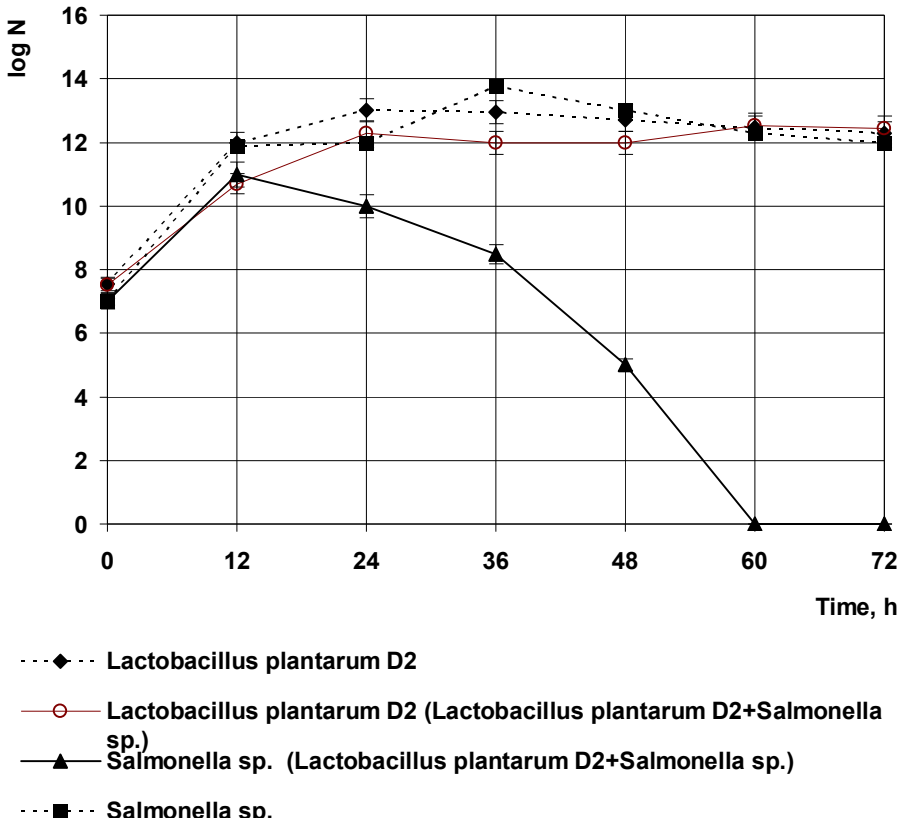

Figure 6. Changes in the number of viable calls of *Lactobacillus plantarum* D2 and *Salmonella* sp. In single-strain culturing and in a mixed population at 37±1°C.

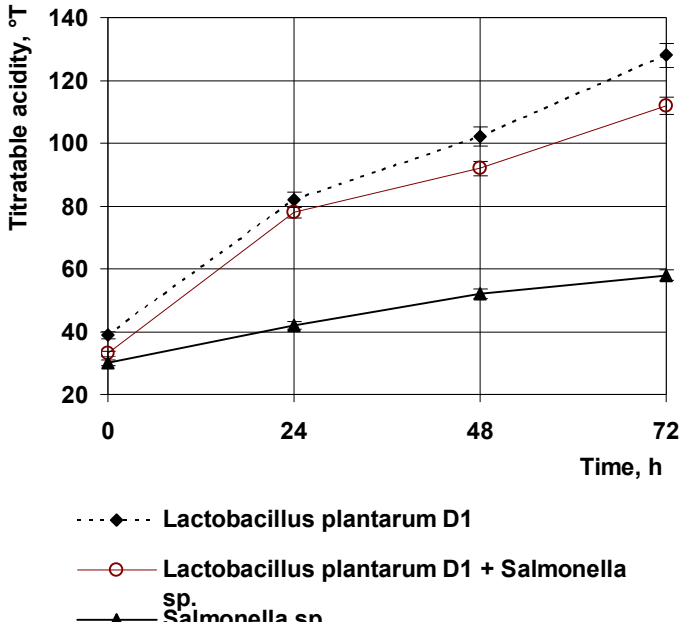

Figure 7. Changes in the titratable acidity of the medium in single-strain culturing and in a mixed population of *Lactobacillus plantarum* D1 and *Salmonella* sp. at 37±1 °C.

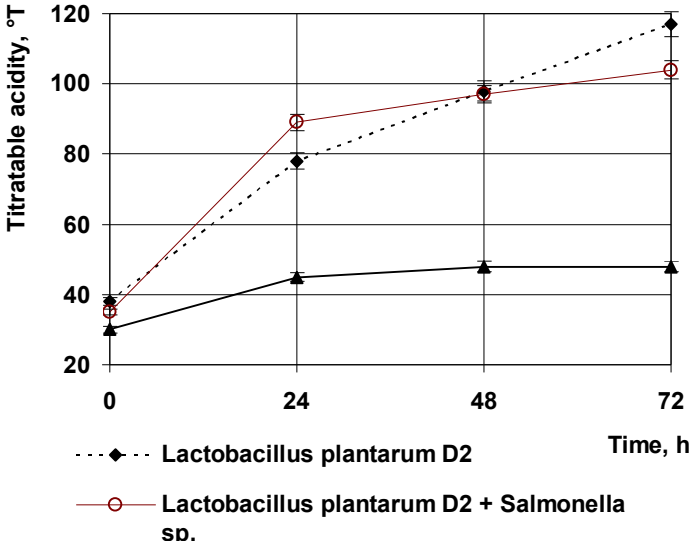

Figure 8. Changes in the titratable acidity of the medium in single-strain culturing and in a mixed population of *Lactobacillus plantarum* D2 and *Salmonella* sp. At 37±1°C.

Conclusion

Lactobacillus plantarum D1 and *Lactobacillus plantarum* D2 maintained high concentrations of viable cells in single-strain culturing and in co-culture at a temperature of 37±1°C. Both *Lactobacillus plantarum* strains inhibited significantly the growth of the two *Salmonella* pathogens. The observed antimicrobial activity was due to a great extent to the acidification of the medium because of the production and accumulation of lactic and other oraganic acids. The demonstrated antimicrobial activity is a prerequisite for further research on the probiotic potential of the two *Lactobacillus plantarum* strains for their inclusion in the composition of probiotic preparations and starters for probiotic functional foods.

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Osmotic pressure in the fermentation media technologies

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Abstract

Introduction. It was conducted the research for creating the physical and mathematical formalization of the changes in the chemical composition of the environment, its energy potential and osmotic pressures.

Materials and methods of a research is defined on the basis of the purposes and problems of theoretical searches, excluded need of physical materials' usage, and as the basis of researches were used the known regularities of anaerobic processes of fermentation and phenomenological reasons with approaching to the provisions of thermodynamics.

Result and discussion. It is considered the use of biochemical activity of microorganisms in the fermentative productions in which input supply streams are transformed with destructive influences and formation of substances with various molecular masses. Such processes can be considered self-flowing and irreversible that means the presence of entropy losses in the form of thermal energy. At the same time the destructive influences accompanied by formation of substances with a smaller molecular masses that leads to increase of osmotic pressure in cultural environments. Critical value achievement of the last ones stops the further biochemical transformations with the achievement of bacteriostatic and even fatal outcome on microflora. Energy ensuring of these processes is reached due to the chemical energy of high-molecular connections of input material streams.

Transition from solutions with accurately designated structure to environments of food and microbiological industries means the essential complication during osmotic pressure determining. It is explained, firstly, by continuous dynamics of change in environments' structure and, secondly, the presence of set of substances of transition processes. It is offered to use in the determination of osmotic pressure of the superposition principle. The basis for such position is well-known information that all transformations and synthesis of intermediate substances happen at the level of endogenous processes in yeast cells. Also, it is noted the efficiency of process organization of biological system functioning from constancy of environments' indicators with taking into account the external influences and the importance of the directions of osmotic molecular diffusion. Colligative properties of solutions in cultural environments change in proportion to the molality of the dissolved substance.

Conclusion. The osmotic pressure of the substances' solutions, which are formed as a result of chemical and biochemical reactions are proportional to the equalizing coefficients in the corresponding equations, and changes of osmotic pressure before and after the chemical and biochemical reactions are defined by changes of the number of molecular structures, which are formed.

Introduction

Biochemical activity of microorganisms is used in technologies, related to production of bread, milk products, wine, alcohol, vinegar, pickled or marinated vegetables, beer, amino acid, enzyme preparations, antibiotics, dietary proteins, etc [1, 12, 14]. The incoming supply streams with their organically structure are transformed upon destructive influence of microorganisms to their components with formation of substances with different and, often, smaller molecular mass [2, 8, 10]. In such cases an increasing of osmotic pressure of solutions, in which those changes are in process, are expected [8, 10, 13].

Microbiological provision, that is required for transformation behavior of a material flow, can result in critical values of transformations, whereby the microorganisms of the environment cause bacteriostatic effects. An example for this is a fermentation of sugar-containing substances with alcohol accumulation in the brew of 10–12%, and the yeasts have to be extracted from the beer after fermentation.

Modern technical possibilities allow to guaranteed reach the bacteriostatic conditions in separate processes, but the special conditions of the following processes can neutralize them, for example, because of microbial flora of packing materials, package, environment [1]. Upon such conditions, when selecting a technology, such methods, upon which the environments themselves or final products ensure an "aseptically protection" shall prevail, for example, by high osmotic pressures (molasses, juice concentrates, beer must, honey). Thereat, the important role belongs to possibilities of non-stop control of osmotic pressures.

*Research objective***.** In connection with mentioned above, the physical and mathematical formalization of definitions of the osmotic pressures is specified.

Materials and methods

The object of researchs is the technology of anaerobic fermentation. It were researched the parameters of culture medium, the influences and interaction of physical and chemical factors in the biochemical synthesis of ethanol.

As the basis of researches were used the known regularities of anaerobic processes of fermentation and phenomenological reasons with approaching to the provisions of thermodynamics [8, 10].

The physical and mathematical formalization of definitions of the osmotic pressures in the fermentation media technologies was determined basing on detailed analysis of physical and chemical principles and effects of osmotic pressure of environments colligative properties [1–14].

For calculating of the values of the osmotic pressure it was used the principle of superposition, the laws of Gay-Lussac [4, 9], equivalent weights and Van't Hoff [6, 7, 11], taking into account the fact that the nature of the osmotic pressure is defined by the formations at the molecular level.

As the basis for studying of effects on biological objects it was used the experience of solutions estimates taking into account the the concept of the systems stationary state [1, 2, 4, 8, 10, 16, 18].

Result and discussion

Transition from environments with defined components and concentrations of dry substances (DS) to the food technologies environment means an essential increasing of difficulty level in definition of osmotic pressures. Even in cases of clear definition of concentrations and molecular masses of incoming flow and final result of their transformation, this questions remains open, taking into account the fact that the transition itself is accompanied by synthesis and presence of transitional processes substances. It's obvious, that in such cases the principle of superposition would be useful, but only upon conditions of known chemical and concentric composition. However, in modern circumstances and upon absence of corresponding analyzers, this question remains open.

For appraisal of degree of complexity of solution of task of definition of osmotic pressure values lets consider the example of technology, in which the process of transition characteristics is clearly represented. Such example can be a wine champagnization process in its classical presentation, that consists of following stages:

- preparing of the mass-production mixture by mixing of blended wine materials with mass-production liqueur, sand sugar;
- mixing of the mass-production mixture with a blend of pure culture yeast with fining materials;
- packaging of the mass-production mixture and sealing of bottles with corks and metal brackets;
- lining of the bottles in piles in the horizontal for secondary fermentation at a temperature of 10-15 ^{o}C and 3-year maturation;
- re-laying of bottles and blending of environments for finishing of biochemical changes processes.

Corresponding to demands of microbiological provision, there are from 5 to 50 billions of yeast cells, that equals the level under 20m^2 of square of mass exchange of cells with the environment.

The biochemical process of wine maturation divides to 4 periods:

1. Active fermentation, multiplication and increasing of biomass (up to 15 days);
2. Death of cells and transition of ferments and biologically active substances to the environment of the bottle (up to 100 days);
3. Active evolvement of fermentation processes (up to 350 days);
4. Inactivation of the ferments and fading of all biochemical process.

From the perspective of interests of definition of dynamic of osmotic processes, a special meaning has the transition in the substances transformation. The main components of osmotic pressures at starting of the process are represented by occurrence of sugar and alcohol. Hereby the concentration of the sugar is calculated in such a way as to possibly receive a final concentration of CO_2 in the wine at a rate of 10 g/l. The osmotic pressure of the dissolved sugar is accompanied by the osmotic pressure of the ethyl alcohol. Results of the biochemical transformation are represented by a correlation

$$\frac{C_6H_{12}O_6}{180} = \frac{2C_2H_5OH}{92} + \frac{2CO_2}{88} \quad (1)$$

that is accompanied with masses proportion.

It follows that for obtaining of concentration of carbon dioxide in the wine at the rate of 10 g/l, it's necessary to brew the glucose in an amount of

$$m_{gl} = \frac{180 \cdot 10}{88} = 20,45 \text{ g}$$

Thereat, amount of the synthesized alcohol will make

$$m_{CO_2} = \frac{20,45 \cdot 88}{180} = 10 \text{ g}$$

Considering that the abovementioned masses of alcohol and glucose relate to 1 l of wine, it means that the concentration of alcohol will increase by 1,045%. With that, the mass of carbon dioxide will make:

$$m_{CO_2} = \frac{20,45 \cdot 88}{180} = 10 \text{ g.}$$

Let's define the volumes of liquid phases that correspond to the solution in proportion 1 g/mole of the substance:

1 l – 20,45 g of glucose V – 180 g	1 l – 10,45 g C_2H_5OH V – 146 g	1 l – 10 g of CO_2 V – 44 g
$V_{gl} = \frac{180}{20,45} = 8,8$ л	$V_{alk} = \frac{46}{10,45} = 4,4$ л	$V_{CO_2} = \frac{44}{10} = 4,4$ l

With rate of temperature T=293 K the osmotic pressure of the glucose at starting of the process equals:

$$P_{\text{osm.gl.}} = \frac{RT}{V} = \frac{8,3144 \cdot 10^3 \cdot 293 \cdot 10^{-6}}{8,8} = 0,27683 \text{ MPa.}$$

Osmotic pressures of synthesized C_2H_5OH and carbon dioxide, respectively:

$$P_{\text{osm.alk.}} = \frac{RT}{V} = \frac{8,3144 \cdot 10^3 \cdot 293 \cdot 10^{-6}}{4,4} = 0,553663 \text{ Mpa}$$

$$P_{\text{osm.}CO_2} = \frac{RT}{V} = \frac{8,3144 \cdot 10^3 \cdot 293 \cdot 10^{-6}}{4,4} = 0,553663 \text{ Mpa}$$

Cumulative change of osmotic pressures of the substances in proportion

$$\frac{P_{\text{osm.alk.}} + P_{\text{osm}CO_2}}{P_{\text{osm.gl.}}} = \frac{0,553663 + 0,553663}{0,27683} = 4$$

means a possibility to formulate the following rule on basis of the principles of equivalence of mass and Van't Hoff law:

> *"Osmotic pressure of solution of substances, that interact in chemical or biochemical reactions, are directly proportional to the comparative coefficients in the corresponding formulas".*

With that, it's possible to arrive at an other conclusion when evaluating results corresponding to changes of the osmotic pressure and quantity of molecules of solutes. This is because every molecule of glucose transforms to two molecules of alcohol and two molecules of carbon dioxide. It results to the other conclusion that relates to generalization of physical background of osmotic pressure phenomenon:

> *"Changes of osmotic pressures are directly proportional to the changes of quantities of molecular structures in solutions"*

In other words, the nature of osmotic pressures is defined by formations at molecular levels.

The mentioned estimated changes of the osmotic pressures, that display champagnization processes, shall be considered at the level of the first approximation, because an unaccounted potential of molecular structures, connected with destruction of the yeast cells, evolvement of fermentation processes with a following inactivation of the ferments, takes place. It's obvious that those final occurrences of the champagnization increase the level of the osmotic pressure in the system. But theoretical possibilities, related to this additional quantity of molecular structures are practically exhausted, so further steps to the definition of the osmotic pressures have to be connected with experimental measurements.

The ground for those is the experience of the study of characteristics of the solutions at the different levels of values. Such study, in the first place, is targeted at an evaluation of their impact on biological objects. The totality of such values defines an estimated functional level of the organism, which is supported due to the activity of complexes of systems, that are responsible for performing of different functions. Corresponding to the homeostasis conception, a biological object can remain in the balanced condition only upon condition that every subsystem in its composition also is in balanced condition. Effectivity of processes of organization and functioning of living systems depends on the state of the interior environment, that has to be constantly supported with a glance to the exterior impact. For example, the key factor for the system "environment – microorganisms" during its existence is a proportion of osmotic pressures of the cultural environment $P_{osm.env.}$ and the cell cytoplasm $P_{osm.s}$. If the formula $P_{osm.env.} > P_{osm.s}$ is accomplished, the osmotic and molecular diffusion will be trended from the cell to the environment. In cases of rehydration of the primary product, direction of the osmotic and molecular diffusion changes to the opposite one, that corresponds with special aspects and laws of thermodynamic of biological processes. The special aspect of the latter is the irreversibility, and the balanced condition of the cell is unsuitable, cause in such a case flowing of directed processes will be impossible, except accidental variations from the balanced condition. For this very reason thermodynamics of biological processes operates with concept of *stationary state* of a system. In the stationary states the values don't change in course of time, but can differ in various parts of the system. In other words, in such systems there are

value gradients, which are constantly supported. It's possible only due to inflow of an energy or substance from outside.

In the human organism a system that is responsible for processes of absorbing, allocation and excretion of water and salts and supporting of osmotic pressure of the liquids of the interior environment is the osmoregulation system. It's main controlled value is total concentration of the osmotic active substances, that is supported with especially high accuracy. The executive organs, that are responsible for supporting of the osmotic pressures of the blood plasma (285±10), saliva (100–200), gastric juice (130–340), bile (280–300), urine (50–1550 mmol/kg H_2O) are kidneys, sudoriferous glands, digestive tract [19, 20].

The molality of solutions is defined by the proportion of amount of solution to mass of the dissolvent, and therefore, as distinct from the molality (proportion of amount of solution to the volume of the dissolvent) the molality of the solution does not changes with change of temperature. Simultaneous, variety of colors of substances in solutions points at necessarily of reference to the superposition principle of definition of osmotic pressures. With that, colligative traits of molality of solutions point at possibilities of usage of different technologies for definition of osmotic pressures. Four features from the colligative group are usually considered together and relate to the following phenomena:

1. Decreasing of pressure of a dissolvent spirit:

$$\Delta P_{spirit} = K_{spirit} m, \tag{2}$$

where K_{spirit} is a constant of the spirit pressure; m – molality.

2. Increasing of boiling temperature of solutions:

$$\Delta T_{boil} = Em, \tag{3}$$

where E is an ebullioscopic constant;

3. Decreasing of freezing temperatures of solutions:

$$\Delta T_{freeze} = Km, \tag{4}$$

where K is a cryoscopic constant.

4. Osmotic pressures

$$\Delta P_{osm} = K_{osm} m, \tag{5}$$

where K_{osm} is a constant of the osmotic pressure.

As is clear from the abovementioned generalization, the specified features of substances are changing proportionally to the molality of solution. With that, those features do not depend on the nature and chemical composition of the solution, and every unit of the mentioned colligative characteristics can be measured, and on the basis of its values the other are calculated using the known formulas.

Conclusion

The analysis of special aspects of flowing of the material transformations in the anaerobic brew processes made on the basis of Gay-Lussac law allows to notice the following using the phenomenological considerations:

1. Summation of osmotic pressures of solutions of different substances shall be appropriately defined using the superposition principle.

2. Osmotic pressures of solutions of substances, that arise as a result of chemical and biochemical reactions, are proportional to the comparative coefficients of the corresponding formulas.

3. Changes of osmotic pressures before and after flowing of chemical and biochemical reactions are characterized by changes of quantity of molecular structures that are building up.

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Change of physical and chemical parameters of the liquid binary systems by alternating impulses of pressure

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Abstract

Introduction. It were conducted the researches with a purpose to determine the impact of non-reagent method, namely alternating impulses of pressure on the parameters of water-ethanol mixtures in a wide range of concentrations.

Materials and methods. The methods of direct potentiometry (ionometry) were used for the researches. Experimental investigations of liquid samples were carried out with use laboratory measurement devices: pH-meter-millivoltmeter pH-150 M and oximeter EZODO PDO-408.

Results and discussion. At influence of alternating impulses of pressure in liquid binary systems such as water systems and water-ethanol mixtures occurs intensive deoxygenating, decrease in quantity of the dissolved oxygen in water and water-ethanol mixtures in comparison with the initial maintenance occurs practically on 50–55 %.

During researches increases pH of the distilled water on 13% have been established, thus the hydrogen potential of the water prepared on technology of the distillery has raised on 14–14,5%.

A value of redox potential in the course of processing by alternating impulses of pressure depending on processing time decreases on 20–60%.

The change of physical and chemical properties and parameters of water systems has been established at processing application high-frequency oscillation which it is possible to explain change of reactionary ability, owing to initiation of carrying over of a proton in associated liquids such as water, aliphatic alcohols, water-ethanol mixtures with different percentage of ethanol and formation of a grid of hydrogen bonds which in turn influences the structural organisation and a structure.

Conclusions. A water and water-ethanol mixtures treatment by nonchemical reagentless method in rotary-pulsating devices can greatly reduce the duration of the process of mixing mode, reduce power consumption, increase capacity and replace the batch process for the continuous mixing.

Introduction

Nowadays one of the important problems that are of interest to the scientific community is to develop innovative nonstandard products and technologies that meet modern international standards of quality and safety.

Actual to solve this problem is to use low-cost methods that require cost-effective investment and allowing the use of existing reserves to reduce specific energy consumption of existing equipment due to the intensification of technological processes.

The sustainable development of modern food enterprises and food processing plants is impossible without the introduction of high-tech and energy-efficient production processes.

During the realisation of the processes which associated with requirement of uniform mixing and distribution of different phases in a liquid basis of great value gets possibility of forecasting of reaction of such systems depending on a different sort of external periodic power or energy influences.

Water and alcohol is sufficient difficult associate systems, which are sensitive to the smallest amount power influences. Formation of water-alcoholic mixtures is the process of mixing of water and alcohol.

In pure clean water and in the diluted solutions there is a continuous three-dimensional grid of hydrogen bonds, it proves to be true many researches and mathematical experiments [1, 2].

Inevitability of research of the structural organization of water and liquid binary systems is caused by their unique properties, and also exclusive value in the live and lifeless nature, a science and the technician, modern technologies.

The founding of principles and conditions of formation of structure and intermolecular hydrogen bonds gives the opportunity to change purposefully character and speed of many physical and chemical processes which take place in such liquid associated systems. Besides, physical and chemical parameters and properties depend on structural transformations and bonds which can create between molecules, for example hydrogen bonds.

Liquid binary systems, specifically aqueous-alcoholic such as mixtures of water and aliphatic alcohol (ethanol, methanol etc.), are enough complicated objects for researches as belong to open systems, and can exchange with environment not only energy, but also substance. At the same time it is metastable, systems which have the certain structural organization and structure which properties and parameters depend on many factors which are insufficiently studied.

One of the ways to improve the quality and safety of products derived benefits have processing technology using a reagent-free non chemical methods, modes and different devices of physical impacts and influences, without the use of chemical materials and substances.

Analysis of scientific works

During the past decade, there has been considerable investigation of the many alternative technological methods of treatment liquids.

Non-reagent methods of water and liquid binary systems treatment include:

– Acoustic treatment: ultrasonic treatment, sound treatment;
– The electromagnetic pulse effect of the low-frequency field;
– Cavitation processing;

– Emitting treatment: ultraviolet, ionizing, infrared etc.
– Hydrodynamic effects.

In recent years researches and technologists have turned their attention to employment of power sound and ultrasound in processing.

Among available technologies, ultrasound technology has a significant potential to produce good-quality, healthful, delicious, and affordable convenience food products and different drinks [3]. The numerous applications of ultrasound, the approach are used in the field of water treatment. Ultrasonic treatment in a liquid leads to the acoustic cavitation phenomenon such as formation, growth, and collapse of bubbles (cavitation), accompanied by generation of local high temperature, pressure, and reactive radical species (°OH, °OOH) with thermal dissociation of water and oxygen [4].

Recently there has been considerable investigation of the electromagnetic pulse effect of the low-frequency field on water or on the behaviour of aqueous solutions. The physico-chemical properties and parameters of water, such as: oxidation-reduction potential, pH value, dissolved oxygen and act. may be tainted by the magnetic and electromagnetic fields. These changes depend on the field intensity and frequency. Although intensive research, the mechanisms by which electromagnetic fields act on water are still a controversial issue [5]. Extremely low frequency electromagnetic fields have significant and lasting effects on liquid water [6].

The majority of theories explain effect of magnetic processing of water magnetic field action on there is at water ions of salts which are exposed to polarisation and deformation [7]. As main and key parameters of devices for processing of water by a magnetic field intensity of a magnetic field, time of stay of water serve in an active zone of a magnetic field, frequency rate and periodicity of influence of a field on water, speed of a stream of water in the device [8].

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

Cavitation is the phenomena of the formation, growth and collapse of microbubbles or cavities occurring in extremely small interval of time (milliseconds) in a liquid [9]. Cavitation can be used as the working tool for the organisation of different technological processes, for example for: clarifications and processing's of surfaces, hashing of multiphase streams (a liquid - a liquid, gas - a liquid, firm particles - a liquid etc.), activation of chemical reactions, structuring and is final, in technologies of clarification and water disinfecting. In the conditions of cavitation hydroxyl (OH°) and hydrogen (H°) radicals would be formed by thermal dissociation of water and oxygen [10].

Emitting treatment: ultraviolet, ionizing, infrared is very perspective nowadays.

A number of alternative methods are commercially available for the removal of microbiological pollutants and some chemical contaminants from water sources. Conventionally, the ultraviolet spectrum is divided into three discrete sections:

– Ultraviolet A (320–400 nm);
– Ultraviolet B (280–320 nm);
– Ultraviolet C (less than 280 nm).

Exposure to ultraviolet light can result in the formation of a range of photoproducts whose distribution and relative yields depend on the wavelength and intensity of incident radiation.

Infrared treatment of water used for micro-organism inactivation and structural transformation by the infrared radiation. But infrared laser water treatment apparatus is limited, however, by the energy consumption and cost required activating water.

Photocatalysis has great potential as an alternative water treatment method due to possibility to remove by-product precursors. This process also ensures the public health safety of drinking water due to its ability to inactivate micro-organisms and to change physical and chemical parameters of water.

Photocatalytic processes are divided into:

– homogeneous photocatalytic oxidation, e.g. ultraviolet/hydrogen peroxide
– heterogeneous photocatalytic oxidation, such as ultraviolet/semiconductor photocatalysis [11].

Hydrodynamic effects occur at water and water binary systems and mixtures treatment by physical and mechanical methods.

The method of discrete-pulsed input of energy (DPIE) is one of physical methods which can influence on structural transformations in complex liquid systems on micro- and nano- level and gives possibility to initiate physical and chemical changes in these systems [12].

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

Spatial and time concentration of energy gives the possibility to receive the big capacity of pulse power action, to liberate internal energy of substance, to make active processes which occur at microlevel also.

The method of discrete-pulsed input of energy is divided into such effects and mechanisms:

– effects which associated with acceleration of movement of a continuous phase;
– influence of pressure of shift;
– cavitations mechanisms;
– the mechanism of explosive boiling;
– collective effects in assembly of vials;
– indignation of an interphase surface in gas-liquid bubbly medium.
– action of alternating impulses of pressure.

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

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

Search of new equipment and technological decisions are directed on increase of an overall performance of devices and an intensification of processes in environments which requires theoretical researches on studying of hydrodynamic conditions, modelling of processes in new devices.

The purpose of the research is to study the changes of physical and chemical parameters of liquid binary systems: water and water-ethanol mixtures using reagent-free method of treatment, such as the influence of alternating impulses of pressure.

Materials and methods

Materials

Water and water-ethanol mixtures in a wide range of concentration were used for experiments. Percentage of ethanol in mixtures was varied from 5 to 90%.

Experimental installation

This study was carried out in experimental form at the pilot unit. The main part of the pilot unit is a rotary pulsed apparatus in which liquids treat by alternating impulses of pressure [13].

Sample preparation

Water and water-ethanol mixtures were prepared using the method described by [14]. Water and ethanol of different types was used for mixing.

Water gave in to processing by alternating impulses of pressure before the technological process of receiving of mixtures. Water treatment and mixing process was spent in rotary pulse apparatus.

Liquid binary systems were passed through rotating coaxial cylinders with cuts on a surface and small clearances between them (which reach 100nm) instantly, that allowed to spend this process by continuous mode.

Methods

For the definition of physical and chemical parameters of liquid samples of binary systems which obtained during the experiment, standard methods described in special literature are used [15].

Study of quantity and quantitative changes of dissolved oxygen in water and water-ethanol mixtures of different concentration from 5 to 90% is carried out with use microprocessor-based device oximeter EZODO PDO-408 with remote electrode.

Determination of change of potential of hydrogen and redox potential of liquid samples of binary systems is carried out with use analogue pH-meter-millivoltmeter pH-150 M with electrodes.

For receiving valid data, liquid samples were analyzed not less than three times with the following statistical processing.

Results and discussion

For research of changes of chemical and physical parameters of liquid binary systems such as technological water following properties were investigated:

– potential of hydrogen (pH value);

– redox potential.

Influence of preliminary processing of water with application of method of discrete-pulsed input of energy for technology of receiving of water-ethanol mixtures was studied.

During processing of water and mixing of water and ethanol in the conditions of alternating impulses of pressure represented:

– ΔP = 370 kPa near an external surface of an internal rotor;
– ΔP = 240 kPa near an external surface stator;
– ΔP = 155 kPa near an internal surface stator;
– ΔP = 190 kPa near an internal surface of an external rotor.

Thus pressure of shift of a stream represented:

– 219,8 Pa (the first rotor);
– 235,5 Pa, (the second rotor)

Speeds of shift of a stream:

– $2{,}2 \times 10^5$ s^{-1} (the first rotor);
– $2{,}4 \times 10^5$ s^{-1} (the second rotor).

Linear speeds:

– 21,98 m/s (the first rotor);
– 23,58 m/s (the second rotor).

During water processing by alternating impulses of pressure the potential of hydrogen and reactionary ability of water varies. For carrying out of process of mixing of water and alcohol water gave in to treatment during special time from 30s to 300s.

The potential of hydrogen characterizes concentration of free ions of hydrogen in water and is one of the main working indicators of quality of water, in many respects defines character of chemical and biological processes which occur in water and water-ethanol mixtures. The change of pH value is shown in Table 1.

Table 1

Change of potential of hydrogen under the alternating impulses of pressure treatment in water

N	Potential of hydrogen, pH		Temterature, °C		Duration of treatment, s
	Before treatment	After treatment	Before treatment	After treatment	
1	6,12	6,59	17,0	17,3	30
2	6,09	6,60	16,3	16,9	60
3	6,10	6,69	17,9	18,5	90
4	6,09	6,75	18,0	19,2	120
5	6,05	6,99	18,2	18,7	150
6	6,13	7,18	17,5	18,3	180
7	6,06	7,31	18,1	19,0	210
8	6,12	7,48	17,9	18,8	240
9	6,12	7,79	17,4	18,3	270
10	6,10	7,99	18,0	18,9	300

During researches increases pH of the distilled water on 13 % have been established, thus the hydrogen potential of the water prepared on technology of the distillery has raised on 14-14,5%.

Treatment of liquid binary systems such as water in the conditions of alternating impulses of pressure allows changing physical parameters throughout long time (6 month).

Value of redox potential Eh and pH are interdependent.

A direct potentiometry concerns also redoximetry. It is a measurement standard and real redox potentials and balance constants redox reactions. The redox potential depends from activity of oxidized form of substance.

In scientific work the presented researches concerning change redox potential in binary water systems.

The change of redox potential of water in technological process of mixing during experimental treatment in rotary pulse apparatus is shown in Table 2.

Table 2

Change of redox potential during experimental water treatment by alternating impulses of pressure

N	Redox potential, mV		Temterature, °C		Duration of treatment, s
	Before treatment	After treatment	Before treatment	After treatment	
1	+260	+210	17,0	17,3	30
2	+264	+211	16,3	16,9	60
3	+268	+198	17,9	18,5	90
4	+270	+132	18,0	19,2	120
5	+258	+135	18,2	18,7	150
6	+258	+132	17,5	18,3	180
7	+270	+105	18,1	19,0	210
8	+273	+101	17,9	18,8	240
9	+258	+103	17,4	18,3	270
10	+271	+110	18,0	18,9	300

Results of researches are presented that redox potential of ware is value actable and at interaction with atmospheric air rises. In the isolated systems of increase occurs much more slowly.

A value of redox potential in the course of processing by alternating impulses of pressure depending on processing time decreases on 20-60%.

For research of changes of chemical and physical parameters of liquid binary systems following properties were investigated:

– quantity of dissolved oxygen;
– potential of hydrogen (pH value);
– redox potential.

The dissolved oxygen in water systems is in the form of molecules O_2. Concentration of the dissolved oxygen in water systems is integrated value which is defined by a parity of different modes of physical and chemical, hydrodynamic processes which occur in water systems and on border of division of phases «water system-atmosphere».

Absorption of oxygen from atmosphere occurs on a surface of water systems. Speed of this process raises with temperature decrease, with increase of pressure and mineralization decrease.

The quantity of the dissolved oxygen is the significant parameter at processing of liquid systems.

The quantity of the dissolved oxygen influences on speed of oxidation-reduction reactions. The smaller quantity of the dissolved oxygen in water-ethanol mixtures, there is more long their storage time. The change of quantity of dissolved oxygen by the alternating impulses of pressure treatment in water-ethanol mixtures is shown in Table 3.

Table 3

Change of quantity of dissolved oxygen by the alternating impulses of pressure treatment in water-ethanol mixtures

N	Quantity of dissolved oxygen, mg/l		Temterature, °C		Percentage of ethanol, %
	Before treatment	After treatment	Before treatment	After treatment	
1	11,1	5,6	14,0	14,3	5
2	10,9	5,5	14,3	14,4	10
3	10,8	5,8	14,3	14,5	15
4	10,2	5,1	14,7	14,7	20
5	10,4	5,8	14,5	14,7	25
6	10,1	5,3	14,7	14,9	30
7	10,2	5,3	14,4	14,5	35
8	10,1	5,2	14,6	14,9	40
9	10,9	6,0	14,2	14,6	45
10	10,8	5,9	14,3	14,7	50
11	11,0	5,5	14,2	14,4	55
12	10,1	5,5	14,6	15,0	60
13	10,2	5,5	14,5	14,9	65
14	10,8	5,4	14,3	14,7	70
15	11,5	6,3	14,6	15,1	75
16	11,7	5,9	14,7	15,2	80
17	10,9	5,5	14,3	14,9	85
18	10,5	5,3	14,5	15,2	90

Besides, it is established that at influence of alternating impulses of pressure in liquid binary systems such as water systems and water-ethanol mixtures occurs intensive deoxygenating, decrease in quantity of the dissolved oxygen in water and water-ethanol mixtures in comparison with the initial maintenance occurs practically on 50–55 %.

Owing to deoxygenating in aqueous-alcoholic mixes the quantity of harmful impurities, owing to decrease in reactionary ability of free radicals decreases. Such results confirm that carrying out of process of mixing in the conditions of alternating impulses of pressure is capable to slow down oxidizing reactions in water-ethanol mixtures. It is very important condition and it gives additional possibilities for producing of safe alcoholic beverages.

For technological process of receiving of alcoholic beverages and alcoholic products the great value has change of a pH value to initial value to processing.

Depending pH value on speed of course of chemical reactions can change.

The change of potential of hydrogen in conditions of the alternating impulses of pressure during mixing water and ethanol is shown in a Table 4.

Table 4

Change of potential of hydrogen in conditions of the alternating impulses of pressure in water-ethanol mixtures

N	Potential of hydrogen, pH		Temterature, ^{0}C		Percentage of ethanol, %
	Before treatment	After treatment	Before treatment	After treatment	
1	6,79	7,90	14,0	14,3	5
2	6,81	7,92	14,3	14,4	10
3	6,77	7,96	14,3	14,5	15
4	6,80	7,90	14,7	14,7	20
5	6,80	8,01	14,5	14,7	25
6	6,75	7,93	14,7	14,9	30
7	6,80	7,92	14,4	14,5	35
8	6,79	7,97	14,6	14,9	40
9	6,84	8,01	14,2	14,6	45
10	6,79	7,92	14,3	14,7	50
11	6,77	7,91	14,2	14,4	55
12	6,79	7,92	14,6	15,0	60
13	6,77	7,91	14,5	14,9	65
14	6,78	7,92	14,3	14,7	70
15	6,75	7,96	14,6	15,1	75
16	6,78	7,92	14,7	15,2	80
17	6,82	8,00	14,3	14,9	85
18	6,81	7,97	14,5	15,2	90

Application of alternating impulses of pressure in technology of receiving of alcoholic mixtures allows receiving the activated water with the certain physical properties and parameters, assured value of a pH.

As a result of the carried out researches change of physical and chemical properties and parameters of water systems has been established at processing application high-frequency oscillation which it is possible to explain change of reactionary ability, owing to initiation of carrying over of a proton in associated liquids such as water, aliphatic alcohols, water-ethanol mixtures with different percentage of ethanol and formation of a grid of hydrogen bonds which in turn influences the structural organisation and a structure.

The change of redox potential during mixing water and ethanol by alternating impulses of pressure is shown in a Table 5.

During carrying out of experimental investigations carrying out of researches of systems in which water for mixing have been realised was not exposed to activation, was exposed to activation, and processing of a mix which has been received by distillery technology in the tanks with a mixer without additional activation of water was carried out.

A value of redox potential in the course of processing by alternating impulses of pressure in water-ethanol mixtures depending on processing time.

Carrying out of process of mixing is direct in a continuous mode and water treatment before mixing process give possibility to decrease redox potential on 22–63%.

The general tendency to decrease redox which takes place during processing on an extent 120s has been noted. Figure1 after that there is not substantial increase redox.

Table 5

Change of redox popential during mixing water and ethanol by alternating impulses of pressure

N	Redox potential, mV		Temterature, ^{0}C		Percentage of ethanol, %
	Before treatment	After treatment	Before treatment	After treatment	
1	+115	+82	14,0	14,3	5
2	+120	+86	14,3	14,4	10
3	+121	+85	14,3	14,5	15
4	+119	+84	14,7	14,7	20
5	+120	+84	14,5	14,7	25
6	+115	+76	14,7	14,9	30
7	+117	+70	14,4	14,5	35
8	+118	+70	14,6	14,9	40
9	+117	+75	14,2	14,6	45
10	+120	+77	14,3	14,7	50
11	+121	+78	14,2	14,4	55
12	+122	+82	14,6	15,0	60
13	+119	+85	14,5	14,9	65
14	+120	+85	14,3	14,7	70
15	+121	+88	14,6	15,1	75
16	+117	+83	14,7	15,2	80
17	+115	+86	14,3	14,9	85
18	+116	+86	14,5	15,2	90

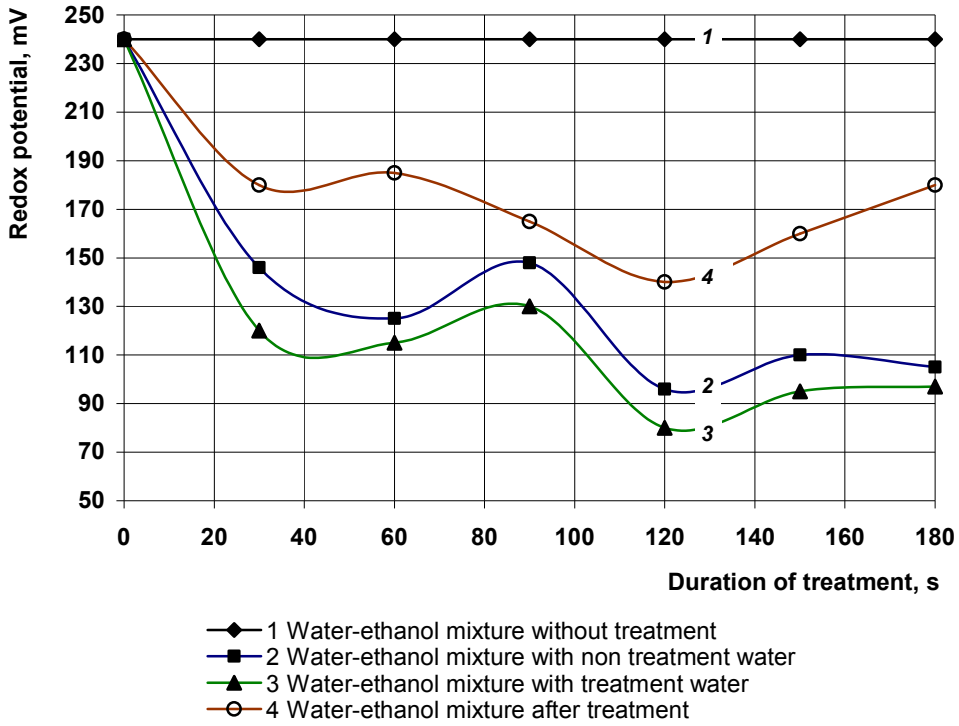

Figure 1. Profile changes redox during mixing process

The obtained data confirm, that the lowest level of redox was observed in water-ethanol mixtures which have been received with application of alternating impulses of pressure. Also it is necessary to pay attention that water in such mixtures gave in to processing in the conditions of alternating impulses of pressure. The general level of decrease redox in comparison with the initial makes 65%.

Conclusions

As a result of research, it was found that the water and water-ethanol mixtures treatment by nonchemical reagentless method of discrete-pulsed input of energy in rotary pulse devices can greatly reduce the duration of the process of mixing mode, reduce power consumption, increase capacity and replace the batch process for the continuous mixing.

Experimental and theoretical studies have shown that rotary pulse apparatus may be suitable for processing in food industry, where hydrodynamic effects are found to be an alternative to traditional mixing tanks.

A detailed analysis of experimental data showed that the use of alternating impulses of pressure in the preparation of water-ethanol mixtures in a wide range of concentration allows obtaining mixtures with improved physical and chemical parameters.

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Public opinion surveys of consumers for manner of labeling the food product in the Republic of Macedonia

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Abstract

Introduction. The consumer should be informed about the quality and characteristics of the food product that wants to buy, and that is possible only if the product is properly labeled. We conducted a study to examine the opinion of the consumers for the manner of labeling the food in Republic of Macedonia.

Materials and Methods. The review is realized with electronic surveys of 200 people from 13 different cities in Macedonia. Interviewees are divided into five groups according to age: under 19 years, 19–25 years, 26–32 years, 33–50 years and over 50 years.

Results and discussion. When choosing the right foodstuff majority of respondents, regardless of age read labels that marked products. Another problem emphasizes the use of many numbers and signs with unknown relevance to them, as well as "E" mark on the packaging. For all respondents, the shelf life of the product has more influence in selecting the products that they buy than the product cost. The energy value of the products and the content of salts in them, were not really important when choosing a product. All respondents agree that if the food product contains components that could endanger the human health, it should be properly labeled. Respondents believe that it would be better if the label by which the product is labeled, emphasize the intended customer group.

Conclusion. Consumers when choosing a food product they want to buy most often read the label with which the products are marked. For respondents of great importance is the existence on the product of an information for which group are those products intended to be spend. At the same time it is important to increase the awareness of the consumers about the importance of numbers, symbols and labels, which they meet on the labeling of food products.

Introduction

In the last decade Consumer's attitudes towards the nutritional aspect of the foods and proper eating habits are increasing rapidly. Therefore, consumers' are more concern about balance and healthier diet. Further they are becoming more demanding about nutritional information, safe and quality food [1]. Everyone's health depends very much on healthy eating, with a diet consistent with the nutritional needs of everyone [2]. Nutrition information on food labels is an important source of nutrition information but is typically underutilized by consumers [3].

Urbanization has led to a dramatic shift in the food con-sumption patterns around the world. It has increased the availability of unhealthy food, which contribute substantially as a risk factor to the pandemic of non-communicable diseases (NCDs) along with other life style related risk factors such as physical inactivity, consump-tion of alcohol and smoking. Though seen mostly duringadult life, diet-related NCDs result from unhealthy diet-ary practices acquired since childhood. Therefore,healthy eating behaviour should be established early in life as a strategy to prevent NCDs [4].

Label is the most important thing when you want to buy food. When deciding which foods to buy information to labels about nutrition and health it may not be clear to many consumers. What was the best choice for healthiest? The purpose of this study is to analyses consumer's understanding and used of nutrition labels from food products [5].

The labeling of food is an important information for consumers through which they can make their own choice of products depending on their health status, age, physical activity, religious beliefs. "Food" means any substance or product processed, partially processed or unprocessed and intended to or be expected to be consumed for human consumption [6].

Quality labels guarantee compliance not only with current standards, but also with additional quality criteria determined in a corresponding certification system [7].

Sadílek T., System of quality labels in the European Union, Ukrainian Food Journal. 2016. Volume 5. Issue 3, 579-587.

Food quality on the market depends of several factors that are found step by step from manufacturing flow to the development phases of the agro-foodstuffs status. Food labeling is a way of communication that characterizes the quality of the food elements. The information transfer from the label to the consumer is made after purchasing the food product, and usually consumers read the labels from the food products packaging only after they bought the product home [8].

Dumitru Mnerie, Liviu Gaceu, Oleksii Gubenia, Mark Shamtsyan, Adriana Birca, Gabriela Victoria Mnerie (2016), Comparative study on the evolution of the food labeling quality in some countries from the Black Sea region**,** *Journal of Hygienic Engineering and Design,* 14, pp. 60-65.

Obligations for marking which the producers and food distributors have, are regulated by the Law on Food Safety and bylaws arising from it. Mandatory requirements for labeling of food are given in the Rulebook on food labeling [9]. Additional requirements for tags that are defined depending on the category of food are prescribed by the regulations for specific security requirements or regulations for quality of certain foods / food product.

By the Agency for Food and Veterinary of Republic of Macedonia is made a guidance in order to provide guidelines to operators with food, about the way of presenting food information to consumers in accordance with the applicable rules in the European Union [10].

By applying the provisions of the Rulebook on labeling of the food:

- consumer receives all the necessary information's about the composition (listed in descending order according to the proportion of the ingredients in the final product), storage and use of food, expiration date, net weight or volume of the food and more;
- marking must be clearly visible, understandable and easy to read;
- allergens should always be clearly specified on the label;
- is not allowed food labeling which suggests the healing properties of the food;
- food operators may indicate additional data on the tag, if they are accurate and do not cause consumer deception;
- the food must be marked in Macedonian language, it can be marked in other languages as well, but only in addition to marking in Macedonian language [11]. Food operators, despite the data listed above, are obliged to mark the food with information which are determined in accordance with the specific requirements of certain types of food.

The obligation of the buyer is to read the marking before buying the product. If the consumer carefully read the labeling, one can find out more about the ingredients contained in the foodstuff that he wants to buy and thus decide whether the product meets his requirements.

With this paper we wanted to determine whether consumers in Macedonia are satisfied with the way of labeling the food products and what problems they face when choosing a food product that they want to buy.

Materials and methods

Consumer′s opinion is determined based on the answers given to the questions of a questionnaire, which was online. On some of the questions were offered several answers and for each answer respondents should answer "Yes" or "No" (Figure 2, 3, 5 and 6).

The survey was voluntary filled by 200 people from 13 different cities in R. Macedonia: Berovo (1), Bitola (4), Valandovo (1), Veles (102), Kichevo (1), Kumanovo (1), Makedonski brod (3), Prilep (3), Radovish (1), Sveti Nikole (2), Skopje (78), Tetovo (2) and Shtip (1). From the surveyed,63 were men (31.5%) and 137 women (68.5%). Respondents were divided into five groups according to age, under 19 years (8), from 19-25 years (71), from 26-32 years (61), 33-50 years of age (49) and over 50 years (11).

The obtained results of the survey were presented, analyzed and processed using the program Microsoft Excel from the program package Microsoft Office. Each question is specifically analyzed and discussed.

Results and discussion

The first analysis are based on the respondents who choose food products in the markets. From the determined answers it can be concluded that most of the respondents read the product labels and on basis of that they choose the product, indicating that the labeling of food products is important for consumers (Figure 1). "I read the labels of products" replied 40.85% of respondents aged between 19–25 years, 50.82% of respondents aged between 26–32 years, 42.83% of respondents aged between 33–50 years 27.27% of respondents aged over 50 years.

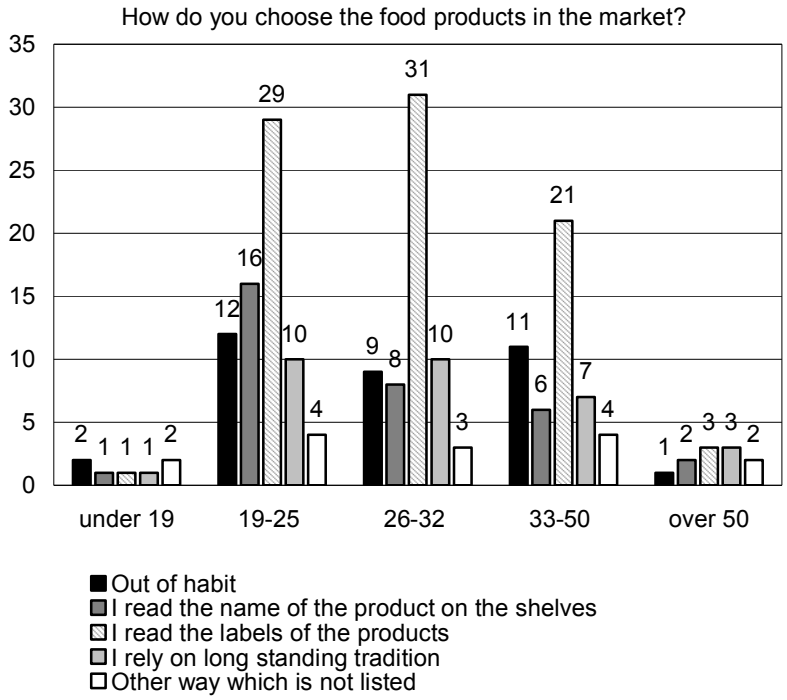

Figure 1. How do you choose the food products in the market?

Alibabić et al. (2012) investigate the extent to which these laws and the regulation are implemented, the results showed that consumers are mostly interested in the data concerning the turation of its shelf live, and 62% of consumers always chekerd this information [12]. Regarding the question: "Which of the listed difficulties do you meet?" it has been Offered a few answers and for each response respondents had to answers by "Yes" or "No". The Figure 2 shows the only the answer "Yes". From the graphics display it can be concluded that the respondents in the age group below 19 years have difficulties with the small fund, but it should not be ignored other difficulties. Persons from 19-25 years of age with most "Yes" answers stated for small fund and usage of many numbers and signs of unknown significance (with "Yes" replied 46 out of 71 respondents). The persons from 26-33 years and from 33 to 50 years reported to have major difficulties with the small fund (with "Yes" replied 44 out of 61 respondents and 42 out of 49 respondents, respectively). The persons over the age of 50, despite the very small fund and numerous figures and characters (with "Yes" answers replied 10 out of 11 respondents), have problems with the fact that "the information is vague and not readable" (with "Yes" replied 9 out of 11 respondents).

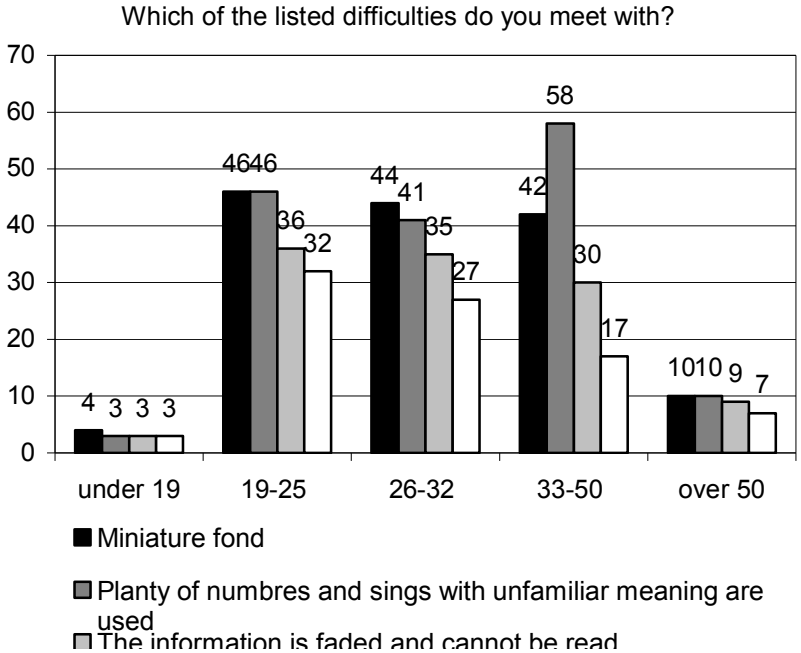

Figure 2. Which of the listed difficulties do you meet with?

Gracia A. and Tiziana de magistris (2016) measured the importance consumers attach to differend labeling schemes aviaible in the food market. The results show that people most preferred labeling shame was the PDO indication, EU organic logo and closely followed by the nutritional fact panel [13].

The answers "yes" to the question: "What information while reading the packaging is not clear even when reading easily?" are shown in Figure 3. Based on the presented results we can conclude that in all age groups, symbols and signs are what is at least understandable and clear. It can also be concluded that the designation "E" on the product packaging for most of the respondents is a problem, because they do not know the exact meaning of this mark. The Agency for Food and Veterinary of Republic of Macedonia has developed a brochure [14] in order to inform the consumers about the significance of the designation "E" and thus to eliminate the above mentioned problem. The "E" followed by a number, on the packaging of food products indicates the presence of a certain additive. Each additive is a chemical compound whose formula is well known. In the European countries is used Exxx mark, while in countries outside of Europe for is used numerous tag for the appropriate additive. The colors were marked with E and series number from 100, preservatives are marked with E and series number from 200 and antioxidants with E and the series number from 300, emulsifiers, thickening agencies with E and series number from 400, taste amplifiers with E and series number from 600, anti-foaming, sweeteners are marked with E and series number from 900, except E420 and E421 (sorbitol and mannitol).

Petrova et al. (2014) make analys in Bulgaria food labels. Results show that the 30 % of costumers respondet that the most unclear information is about additives in the produtct which are marked whid the letter E and a number that specifies the type of additive [15].

The official advices for consumers provided by the Organization of Consumers and The Agency for Food and Veterinary, are that with diverse and moderate diet there are no possibilities for people to ingest food additives more than the accepted daily amounts [11, 16].

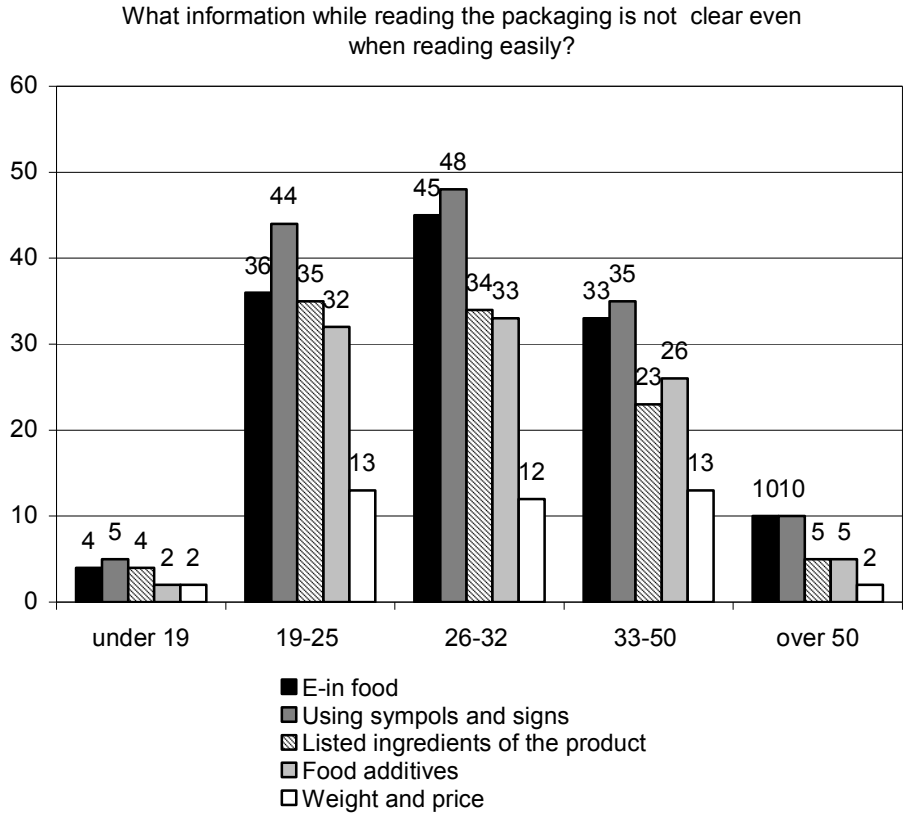

Figure 3. What information while reading the packaging is not clear even when reading easily?

During classification of the information given on the packing of the food products in the questionnaire, there were offered the following answers: duration, price, manufacturer, quantity, country of origin, information quality, information on accessories, preparation, energy and content of salt. The answers of the respondents are shown in Figure 4. The most important information is numbered with 1, while the most irrelevant with 10.

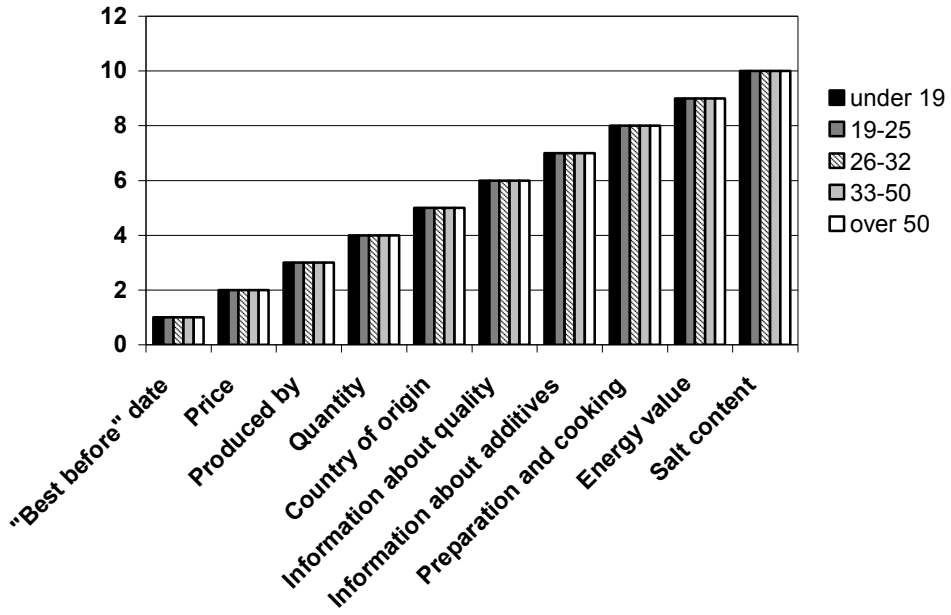

Figure 4. Classification of the information given to the packing

The Figure 4 shows that in all age groups the most important information is the shelf life, then the price, the manufacturer, the quantity, country of origin of the product, quality information, information about existing supplements, method of preparation, energy and content of salts. For all respondents is important the food product not to be with expired shelf life, because the consumption of such food products could cause some disorders. Also, the price of the product has a great influence in the choice of food products that would be purchased, due to the low purchasing power of the citizens of Republic of Macedonia.

By the respondents, as the least important information is evaluated the salt content in the food products (graded with 10), which is due to not informed consumers about the importance of salt content in the food products.

As for the energy value of the food products, in the future we expect that the information about the energy value of the products will be one of the determining factors when choosing a product that will be consumed, because most of the population in the Republic of Macedonia has become increasingly aware of the impact of the energy value of the products on health.

The Figure 5 shows the "Yes" answers to the question "What information do you think should be obligatory on the packaging of the food products?".

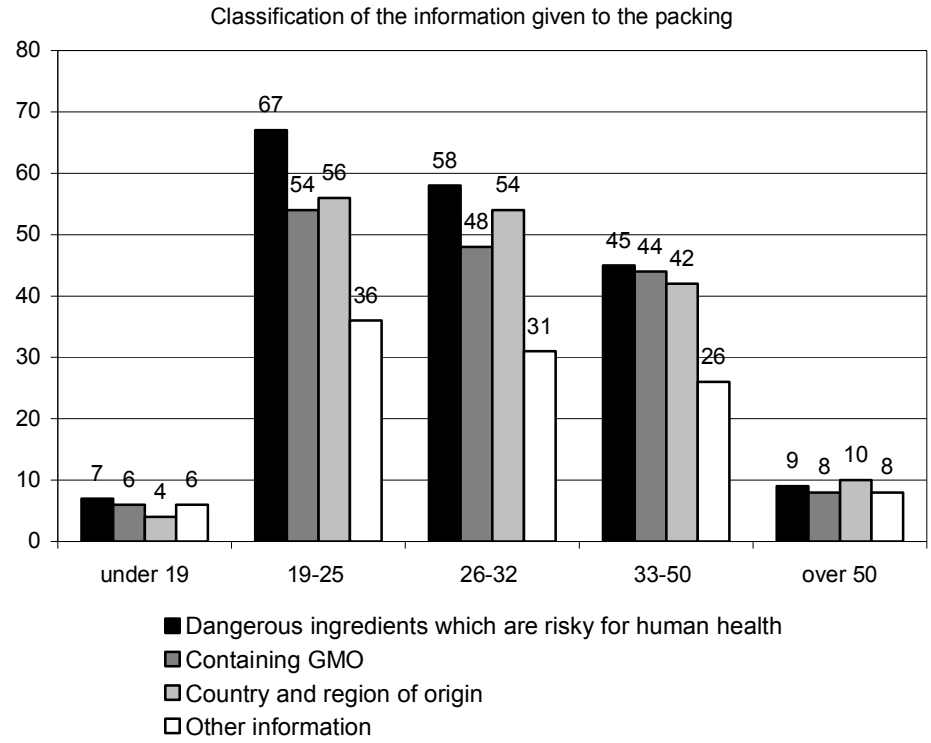

Figure 5. What information do you think should be obligatory on the packaging of the food products?

In all the groups of respondents, with most "Yes" answers were stated the dangerous components that pose a risk to human health. According to the responses, it can be concluded that the majority of respondents regardless of age believe that on the packaging should be mandatory information of dangerous components risky for the human health.

From the suggested changes that might be made on the packaging of the food products (Figure 6), respondents in all age groups (except in the group of 19–25 years) believe that on the labels should be put information about what group of spending products are intended. According to the respondents in the age group of 19–25 years on the packaging should be noted for whom the products are NOT intended (with "Yes" replied 59 out of 71 respondents).

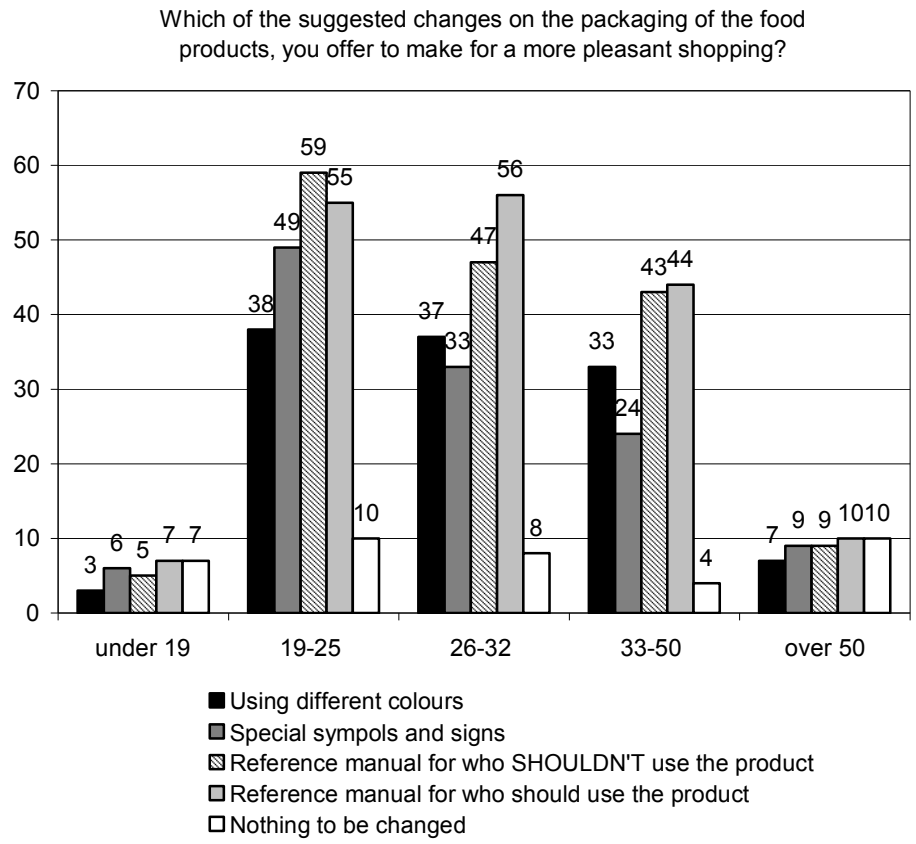

Figure 6. Which of the suggested changes on the packaging of the food products, you offer to make for a more pleasant shopping?

According to the Regulation on labeling the food products as additional and useful information that can be found on the product are: telephone number of the manufacturer, the trade name of the product if the manufacturer has, importer or distributor for additional information's, product handling, storage, delay, recycling and similar [9].

Conclusion

Based on the results of the survey, it can be concluded that consumers when choosing a food product they want to buy most often read the label with which the products are marked. From the problems they face when reading labels it should be indicated the small fund and the use of many figures and signs of unknown importance as well as marked "E". During classification of what is important when choosing a food product in the first place is the shelf life, and then the cost of the product. Respondents, regardless of age, consider mandatory that on the packaging should be an information about the presence of dangerous components that could cause certain disorders in human healthcare. For respondents of

great importance is the existence on the product of an information for which group are those products intended to be spend.

To eliminate the problems mentioned by the consumers in the future it should be increased the control of food producers, as they respect the stipulated rules and regulations set out in the Law on Food Safety of the Republic of of Macedonia, the Rulebook on food labeling and Guidelines of good practice for food operators regarding the new EU requirements for food labeling.

At the same time it is important to increase the awareness of the consumers about the importance of numbers, symbols and labels, which they meet on the labeling of food products. It should be emphasized that the Agency for Food and Veterinary of the Republic of Macedonia in cooperation with the Organization of consumers for a long time undertake a lot of activities for education and information the consumers about labeling of certain food products by placing in public a number of brochures (Food additives and consumer, Food supplements, Foods for particular nutritional uses, etc.), guides and leaflets (Guide to consumers through the law on food safety, How to read the labeling of foodstuffs, What information should include labeling of food? labeling misleading, leaflets relating to labeling of meat, dairy and processed fish, leaflets relating to labeling of foods for infants and young children, food intended for diet and nutrition for athletes and others).

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Анотації

Харчові технології

Ідентифікація бацилярних мікробних контамінантів і збудників харчових отруєнь в українській рослинній сировині і продуктах

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Вступ. Характеристика біологічних забруднень рослинних харчових продуктів – збудників харчових інфекцій і отруєнь, збудників псування та прискорене визначення потенційної їх небезпеки для споживача мають наукове і практичне значення.

Матеріали і методи. Досліджували поширені і промислово вирощувані види овочів, фруктів, ягід, ряд консервованих і сушених продуктів, а також спецій. Морфологічні, культуральні та біохімічні властивості виділених культур вивчали загальноприйнятими методами. Полімеразну ланцюгову реакцію (ПЛР) проводили з використанням групо- і видоспецифічних праймерів до послідовностей бацил та електрофорезу продуктів ПЛР в 1,5% агарозному гелі.

Результати і обговорення. Досліджені бацилярні мікробні контамінанти, потенційні збудники харчових отруєнь і псування продуктів для промислово поширених в Україні видів рослинної сировини – овочів, фруктів, ягід і продуктів їх переробки. Особливістю рослинної сировини України є домінування морфотипів *subtilis-licheniformis* серед виявлених паличковидних спороутворюючих мікроорганізмів порядку *Bacillales*. Склад мікробіоти різних видів рослинної сировини і продуктів її переробки було досліджено за комплексом їх фенотипових і молекулярно-генетичних властивостей. Встановлено, що ідентифікація аеробних і факультативно-анаеробних спороутворюючих бактерій за комплексом їх фенотипових властивостей тривала і не завжди дозволяє точно визначити вид мікроорганізмів. Апробовано методику підготовки зразків харчових продуктів і проведено ПЛР з групо- і видоспецифічними праймерами з метою прискореної діагностики в зразках штамів *B. cereus*, *Paenibacillus polymyxa*, *P. macerans*. Визначено контамінованість зразків рослинної сировини і продуктів її переробки епідеміологічно значимим мікроорганізмом *B. cereus*, яка становить від 16,7% для свіжих фруктів до 72,7% для спецій і прянощів від загальної кількості досліджених зразків.

Висновки. Ідентифіковано бацилярні мікробні контамінанти та апробовано прискорену методику підготовки зразків харчових продуктів з ПЛР для індикації регламентованих бацилярних мікроорганізмів, які впливають на безпеку продукції.

Ключові слова: *бацила, харчовий продукт, безпека, B. cereus, ПЛР, фенотип.*

Дихання грецьких горіхів (Juglans Regia l) під час зберігання

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Вступ. Вивчено показники дихання грецького горіха (**Juglans Regia l**.), і фактори, які можуть впливати на нього.

Матеріали і методи. Інтенсивність дихання грецького горіха визначали за методом замкнутої атмосфери. Використано метод уловлювання CO_2, що видаляється з продукту лужним розчином. Для оцінки впливу температури на інтенсивність дихання неочищених горіхів і ядра горіха проводилися дослідження в чотирьох режимах температур: 6 ± 2, 18 ± 2, 30 ± 2 і 50 ± 20 °С.

Результати і обговорення. Дихання є одним з окислювально-відновних процесів, які можуть призвести до окислювальної деструкції ліпідів грецького горіха і, відповідно, до їх якісного розкладання.

Вміст вологи в грецьких горіхах є одним з основних факторів, що впливають на швидкість дихання. Початкова інтенсивність дихання горіхів висока, але швидко знижується в перші 15 днів зберігання. Це зниження пов'язане зі скороченням вологи у горісі. Після 15 днів зберігання інтенсивності дихання горіхів зменшується незначно.

Встановлено зв'язок між інтенсивністю дихання і температурою навколишнього середовища. Інтенсивність дихання ядра горіхів зростає від 5 до 23 мг CO_2/кг•год зі збільшенням температури від 5 до 30 °С. При подальшому збільшенні температури до 60 °С інтенсивність дихання зменшується до 15 мг CO_2/кг•год.

Інтенсивність дихання неочищених грецьких горіхів зростає від 5 до 17 мг CO_2/кг•год зі збільшенням температури від 5 до 30 °С. Із подальшим збільшенні температури до 60 °С інтенсивність дихання зменшується до 12 мг CO_2/кг•год .

Інтенсивність дихання ядра грецького горіха більша, ніж у неочищених грецьких горіхів, оболонка служить бар'єром для безпосереднього контакту між ліпідами ядра і киснем.

Відзначається, що індекс кислотності корелює з температурою зберігання, але більше виражений для ядра і менше для неочищених грецьких горіхів.

Індекс кислотності ліпілів ядра і неочищених грецьких горіхів зі збільшенням температури від 5 до 15 °С не змінюється і становить приблизно 0,35 мг NaOH/г прод. При подальшому збільшенні температури до 40 ° С індекс кислотності ліпідів зростає до 0,8 NaOH / г прод (для ядра) і 1.1 (для неочищених грецьких горіхів). При подальшому збільшенні температури до 60 ° С індексом кислотністю ліпідів ученьшаются до 0,6 NaOH/g prod.

Висновки. Дихання грецького горіха може бути обмежене зберігання за низьких температур. Тому важливо забезпечити стабільність під час зберіганні шляхом дотримання граничних значень вмісту води в грецьких горіхах. Морфологічний стан плоду також впливає на інтенсивність дихання, причому цей параметр більший для очищених ядер, ніж для неочищених плодів, різниця зумовлена шкаралупою, яка є перешкодою для прямого контакту між ядром і киснем.

Ключові слова: *грецький горіх, дихання, зберігання, вологість.*

Вплив макухи зародків кукурудзи на процеси дозрівання пшеничного тіста та якість і харчову цінність хліба

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Вступ. Досліджено вплив макухи зародків кукурудзи на перебіг процесів дозрівання пшеничного тіста, а також харчову та біологічну цінність хліба.

Матеріали та методи. У дослідженнях використовували макуху зародків кукурудзи, борошно пшеничне першого сорту, дріжджі пресовані хлібопекарські, сіль, воду питну. Інтенсивність спиртового бродіння визначали за швидкістю газоутворення в тісті, а молочнокислого – за зміною його титрованої кислотності. Показники якості хліба, а також його харчову цінність досліджували за загальноприйнятими методиками.

Результати та їх обговорення. Результати експериментальних досліджень показали, що заміна пшеничного борошна на 10,0–20,0% макухи зародків кукурудзи сприяє інтенсифікації кислотонакопичення та газоутворення в тісті, що є підставою для скорочення тривалості його дозрівання на 6,0–17,0%. Разом з тим спостерігається зниження об'єму тіста за мірою збільшення дозування добавки. Виготовлений безопарним способом хліб з додаванням макухи зародків кукурудзи має приємний кукурудзяний присмак і аромат, більш інтенсивно забарвлену скоринку і м'якушку, вище значення показників вологості та титрованої кислотності, ніж у контрольного зразка. Додавання більше 15% добавки призводить до суттєвого зниження показників пористості та питомого об'єму хліба, що не дозволяє рекомендувати більше її дозування за безопарного способу виробництва хліба.

Хліб, виготовлений з 15% макухи зародків кукурудзи характеризується вищим вмістом незамінних амінокислот лізину, цистіну, метіоніну та треоніну, більшим вмістом харчових волокон у 1,7 рази, вітамінів B_1 – в 1,4 рази, Е – в 3,0 рази, магнію – в 2,2 рази, заліза – в 2,3 рази.

Висновок. Використання 15,0% макухи зародків кукурудзи за безопарного способу виробництва дозволяє отримати вироби високої якості, підвищеної харчової та біологічної цінності.

Ключові слова: *хліб, макуха, зародки, дозрівання, якість.*

Визначення олеїнової кислоти у зразках насіння соняшника методом біч-спектроскопії

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Вступ. Можливість використання БИЧ-спектроскопії для визначення олеїнової кислоти в насінні соняшнику не вивчений, тому дослідження в цій області є перспективним.

Матеріали і методи. Спектри зразків насіння різних сортів соняшнику з відомим вмістом олеїнової кислоти і тих самих зразків, додатково збагачених олеїновою кислотою, були досліджені методом дифузної відбивної БІЧ - спектроскопії з використанням приладу «Інфрапід-61». Для обробки отриманих результатів були застосовані методи математичного аналізу.

Результати і обговорення. У БІЧ спектрах зразків висушеного насіння соняшника порівняно зі спектрами сирого насіння спостерігається очікуване зменшення коефіцієнта дифузного відбивання у діапазоні 1920-1940 нм, що відповідає вмісту вологи в зразку. Аналіз БІЧ спектрів калібрувальної серії зразків насіння, збагачених олеїнової кислотою, показує збільшення коефіцієнта відбивання у діапазонах 1920–1940 нм і 2140–2160 нм пропорційно зростанню масової частки олеїнової кислоти. Відповідні розрахунки, калібрувальні криві і винайдене рівняння демонструють лінійну залежність коефіцієнта дифузного відбивання зразка від масової частки олеїнової кислоти при довжині хвилі 2140 нм. Знайдена залежність може бути використана для кількісного визначення олеїнової кислоти у соняшниковому насінні невідомого складу. За значенням коефіцієнта дифузного відбивання зразка з невідомим вмістом олеїнової кислоти, користуючись побудованим калібрувальним графіком, можна визначити її масову частку.

Метод БІЧ-спектроскопії дифузного відбивання може застосовуватися для аналізу як неочищеного насіння, так і насіння, відокремленого від лушпиння, оскільки спектральні характеристики таких зразків з однаковим вмістом олеатів практично ідентичні у діапазоні 1330–2370 нм.

Цей метод можна розглядати як альтернативу хімічним методам визначення показників якості жировмісної сировини.

Висновки. Метод БІЧ - спектроскопії є перспективним для визначення у насінні соняшника олеїнової та інших жирних карбонових кислот.

Ключові слова: *спектроскопія, олеїнова кислота, соняшник, насіння.*

Кваліметрична оцінка раціонів харчування

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Вступ. Метою роботи є оцінка якості раціонів харчування з позиції норм фізіологічної потреби людини та добового раціону харчування, для подальшого визначення збалансованості харчування.

Матеріали і методи. Добовий раціон харчування людини (сніданок, обід, вечеря) та норми фізіологічної потреби середньостатистичної людини – для визначення комплексно-кількісна оцінка якості раціонів харчування. Для об'єднання показників якості в узагальнений (комплексний) показник використано адитивну математичну модель як найбільш розповсюджену в кваліметрії. Методи дослідження – кваліметричні.

Результати. Враховуючи норми фізіологічних потреб середньостатистичної людини, розраховано комплексну оцінку якості одноразового прийому їжі, при цьому розроблено трирівневу ієрархічну структуру системи показників якості: одиничні показники третього рівня згруповані у показники якості, що утворюють другий рівень ієрархії структури системи, які, в свою чергу, об'єднуються у перший рівень, а потім – у комплексний показник нульового рівня, які разом характеризують якість раціону харчування.

Базові значення показників якості ($P^{баз}$) енергетичних, мінеральних речовин та вітамінів становлять: для білків – 0,15; жирів – 0,17; вуглеводів – 0,68; натрію – 0,45; калію – 0,34; кальцію – 0,07; магнію – 0,03; фосфору – 0,11; тіаміну – 0,02; рибофлавіну – 0,02; піридоксину – 0,02; аскорбінової кислоти – 0,94.

Коефіцієнти вагомості (*m*) становили для: білків – 0,50; жирів – 0,40; вуглеводів – 0,10; натрію – 0,03; калію – 0,05; кальцію – 0,25; магнію – 0,50; фосфору – 0,17; тіаміну – 0,36; рибофлавіну – 0,32; піридоксину – 0,31; аскорбінової кислоти – 0,01.

Найбільше значення комплексного показника (K_0) знайдено для сніданку – 1,60, мінімальне значення – характерно для вечері – 1,09.

Висновки. Для заданого раціону харчування визначено комплексні показники якості для групи енергетичних речовин, мінеральних речовин та вітамінів. Встановлено найбільш збалансовані значення комплексного показника якості, що характерні для вечері з оцінкою – 1,09.

Ключові слова: *кваліметрія, раціон, харчування, норма.*

ІЧ-Фур'є-спектроскопія в поєднанні з хемометрією як універсальний інструмент для оцінки якості смажених макаронних виробів

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Вступ. У досліджені проведено оцінку якості смажених на жирах макаронних виробів, які у значній кількості споживаються в багатьох країнах світу.

Матеріали і методи. З метою повної екстракції олій смажені макаронні вироби піддавали обробці в апараті Сокслета з використанням гексану як розчинника. Жирнокислотний склад добутих екстрагуванням олій встановлювали методом ГХ-МС. Для розробки простої методології кількісної оцінки груп жирних кислот та їхніх співвідношень проводили реєстрацію спектрів тих самих зразків олії із застосуванням методу ІЧ-Фур'є спектроскопії.

Результати і обговорення. У всіх досліджуваних зразках смажених макаронних виробів було виявлено високий вміст жиру (19,77 – 32,99%). Серед насичених і мононенасичених жирних кислот переважали пальмітинова (34,6 – 47.,%), стеаринова (4,76 – 10,6%), олеїнова (27,2 – 37,0%) і елаїдинова кислоти (12,0 – 24.,%). У порівняно меншій кількості було виявлено поліненасичені жирні кислоти (0,66 – 5,99%). Високий вміст транс-ізомерів жирних кислот у смажених макаронних виробах свідчить про використання гідрогенізованого жиру в процесі їх приготування. Співвідношення важливих груп жирних кислот встановлено у межах: 0,72 – 1,92 - насичені ЖК/НЖК, 0,013 – 0,130 цис-ПНЖК/насичені ЖК, 0,1 – 1,81 транс-ЖК/цис ЖК, 0,01 – 0,097 цис-ПНЖК/насичені ЖК + ТЖК, 27,7 – 37,05 цис-МНЖК + цис ПНЖК/НЖК + ТЖК. На основі результатів, одержаних методом ІЧ-Фур'є спектроскопії і співвідношень, визначених методом ГХ-МС, розроблені калібрувальні моделі для кількісного визначення груп жирних кислот та їх співвідношень із застосуванням хемометричного методу PLS. Розроблені PLS моделі в обраних діапазонах довжини хвиль високо корелюють (> 0,99) з результатами ГХ-МС.

Висновки. Якість смажених макаронних виробів є проблемою, що потребує особливої уваги з боку контролюючих органів. Запропонований метод ІЧ-Фур'є спектроскопії є швидким, простим і точним інструментом для кількісної оцінки основних груп жирних кислот та їх співвідношень.

Ключові слова: *смаження, макарони, жир, кислота, ГХ-МС, ІК-Фур'є, хемометрія.*

Особливості використання в пивоварінні хмелю та CO_2-екстракту

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Вступ. Мета дослідження полягала у вивченні особливостей використання в пивоварінні CO_2-екстракту та тонкоароматичного хмелю з низьким вмістом альфа-кислот, який може бути відходами при виробництві гранул тип 45, і винайденні способів використання та раціонального вжитку його цінних речовин.

Матеріали та методи. Досліджувались ароматичні сорти хмелю з низьким вмістом альфа-кислот, CO_2-екстракт та пиво, виготовлене з них. Використано високоефективну рідинну хроматографію для визначення кількості та складу гірких речовин хмелю, CO_2-екстракту та продуктів їх перетворення в процесі пивоваріння, а також спектрофотометричні методи контролю якості гіркоти охмеленого сусла та готового пива.

Результати. При використанні в пивоварінні CO_2-екстракту та тонкоароматичного хмелю з низьким вмістом альфа-кислот в оптимальних співвідношеннях, поліфеноли низькосмольного хмелю сприяють видаленню з сусла шляхом коагуляції високомолекулярних поліпептидів з утворенням складних комплексів. Завдяки цьому досягається більш висока колоїдна стійкість пива та підвищується ступінь використання гірких речовин на 15-20%. Кращі смакові і ароматичні якості мало пиво, приготовлене з використанням для охмеління сусла 40% гіркоти ароматичного низькосмольного хмелю та 60% гіркоти за рахунок CO_2-екстракту. Мало чим відрізнялось пиво, де екстракт і ароматичний хміль було використано в пропорції 40:60%. Поліфеноли та бета-фракція ароматичного низькосмольного хмелю позитивно впливають на грубу гіркоту CO_2-екстракту, пом'якшуючи та згладжуючи її, роблячи загальну гіркоту пива збалансованою. Також при використанні даних пропорцій спостерігається максимальне зменшення показника високомолекулярних поліпептидів, що прогнозує високу колоїдну стійкість пива. При використанні в пивоварінні лише CO_2-екстракту не можливо отримати пиво з високими смаковими якостями. Однак, надмірна кількість хмельових поліфенолів призводить до отримання в'яжучого присмаку у пиві.

Висновки. Ароматичний хміль з низьким вмістом альфа-кислот можливо використовувати в пивоварінні як поліфенольну добавку в поєднанні з CO_2-екстрактом, враховуючи кількісний вміст та якісний склад хмелепродуктів та дотримуючись при цьому певної технології.

Ключові слова: *хміль, CO_2-екстракт, поліфенол, пиво.*

Вплив м'ясного продукту з екстрактом лушпиння цибулі на метаболічний профіль щурів лінії SHR

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Вступ. Пошук нових композицій продуктів харчової промисловості є важливим для корекції порушень обміну речовин. Так цибуля містить флавоноїд кверцетин з антиоксидантною і кардіопротекторною дією.

Матеріали та методи. Для годування тварин використано м'ясний продукт з екстрактом лушпиння цибулі або кверцетину у еквівалентній дозі 2,25 мг кверцетину. Шестимісячні щури із генетично детермінованою артеріальною гіпертензією (SHR) на високофруктозній дієті (25%-а концентрація фруктози у питній воді) використані для моделювання метаболічних порушень. Через 3 місяці годування вміст глюкози вимірювали в артеріальній крові за допомогою датчиків на основі амперометричного вимірювання. Ліпідний профіль плазми визначали за ферментативними колориметричними реакціями.

Результати і обговорення. Рівень глюкози в крові у SHR без дієтичних інтервенцій (група II) був на 59% вище, ніж у контрольній групі (8,84 ± 0,3 ммоль / л проти 5,56 ± 0,86 ммоль / л, P <0, 01). Високофруктозна дієта у SHR (група III) підвищувала рівень глюкози на 5% (9,3 ± 0,4 ммоль / л, P> 0,05 порівняно з SHR групи II, які споживали питну водопровідну воду). М'ясний продукт з кверцетином не впливав на рівень глюкози крові у SHR на високофруктозній дієті (група IV) - 9,2 ±0,8 ммоль / л, P > 0,05 порівняно з SHR груп II і III. У SHR на високофруктозній дієті, які отримували м'ясний продукт з екстрактом лушпиння цибулі (група V), рівень глюкози в крові мав тенденцію до зниження - 8,0 ± 1,0 ммоль / л, P> 0,05 порівняно з SHR групи III.

Загальний холестерин мав тенденцію до збільшення в групі II порівняно з контролем (1,36 ± 0,10 проти 1,22 ± 0,05 ммоль / л, P> 0,05). У SHR групи III загальний холестерин був вище, ніж у контролі (1,45 ± 0,09 ммоль / л, P = 0,03), однак не відрізнявся від показника SHR групи II, які споживали питну водопровідну воду (1,45 ± 0,09 проти 1,36 ± 0,10, P> 0,05). У групах IV і V загальний холестерин був також значно вище, ніж у контрольній групі (1,52 ± 0,07 і 1,57 ± 0,09 проти 1,22 ± 0,05 ммоль / л, P = 0,006 і P = 0,005, відповідно).

Підвищення загального холестерину у SHR груп IV і V пов'язано зі збільшенням холестерину ліпопротеїнів високої густини (ЛПВГ), оскільки рівень не-ЛПВГ холестерину у них не змінювався. Годування SHR на високофруктозній дієті м'ясним продуктом із екстрактом з лушпиння цибулі супроводжувалося достовірним підвищенням рівня холестерину ЛПВГ, порівняно із SHR групи II (1,25 ± 0,09 проти 1,02 ± 0,05, P = 0,03). Збільшення холестерину ЛПВГ також спостерігалося у SHR, які отримували м'ясний продукт із очищеним порошком кверцетину, порівняно із SHR групи II (1,23 ± 0,08 проти 1,02 ± 0,05, P = 0,02).

Висновки. Годування SHR на високофруктозній дієті м'ясним продуктом із екстрактом лушпиння цибулі позитивно впливає на рівень глюкози. Підвищення холестерину ЛПВГ у SHR на високофруктозній дієті відображає антиатерогенний ефект розробленого м'ясного продукту.

Ключові слова: *цибуля, екстракт, глюкоза, ліпід, щур.*

Дослідження впливу технологічних факторів на в'язкість системи «пшеничний крохмаль-Твін 20 (Е432)»

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Вступ. Метою даної статті є дослідження впливу технологічних факторів (температури, цукру, лимонної кислоти) на модельну систему «пшеничний крохмаль-ПАР», яка є базовою основою для реалізації технології мусів з використанням пшеничного крохмалю.

Матеріали та методи. В'язкість модельних систем «пшеничний крохмаль-Твін 20 (Е432)» з цукром білим та лимонною кислотою під впливом температури визначали на ротаційному віскозиметрі типу ВПН-0,2.

Результати і обговорення. У літературі є достатньо інформації про перебіг процесу клейстеризації різних видів крохмалів та впливу на нього різних факторів, зокрема поверхнево-активних речовин, кислот, солей, цукру та ін., однак відсутні дані щодо впливу цих речовин на систему «пшеничний крохмаль-Твін 20 (Е432)».

Розуміння змін властивостей системи «пшеничний крохмаль-Твін 20 (Е432)» під впливом різних технологічних факторів дозволить створити наукову основу для реалізації технології нової продукції з піноподібною структурою.

У ході досліджень підтверджено доцільність використання Твін 20 (Е432) сумісно з пшеничним крохмалем в якості структуроутворювача системи, який за рахунок динамічних фазових переходів за теплової обробки забезпечить необхідну в'язкість. Присутність в системі Твін 20 (Е432) сприяє підвищенню температури клейстеризації крохмалю та зменшенню показників в'язкості на початку процесу, що забезпечує умови для піноутворення.

Внесення цукру білого та лимонної кислоти стримує наростання в'язкості в діапазоні температур 60…65 °С, подальше підвищення температури сприяє збільшенню показників.

Таким чином, раціональними параметрами модельної системи «пшеничний крохмаль-Твін 20 (Е432)», що забезпечать оптимальну в'язкість, яка необхідна для одержання високих показників з піноутворюючої здатності під час збивання є: концентрація Твін 20 (Е432) – 0,25 %, пшеничного крохмалю – 6…12 %, цукру білого – 10,0 %, температура збивання – 60…65 °С. Дані параметри дозволять отримати муси з використанням пшеничного крохмалю та Твін 20 (Е432) з новими споживчими характеристиками за рахунок реалізації функціональних властивостей пшеничного крохмалю та ПАР.

Висновки. Визначено та обґрунтовано раціональні параметри термообробки модельних систем з використанням пшеничного крохмалю та Твін 20 (Е432) з метою забезпечення найменших показників в'язкості, що сприятиме максимальній піноутворюючій здатності та дозволить реалізувати технологію мусів.

Ключові слова: *крохмаль, в'язкість, Твін 20 (Е432), цукор, кислота.*

Обґрунтування умов отримання пористих вуглецевих матеріалів із піролізованих деревних відходів методом хімічної активації з H_3PO_4

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Вступ. Метою публікації є пошук альтернативних матеріалів – відходів харчової промисловості; оцінка перспективності їх використання при виробництві пористих вуглецевих матеріалів (ПВМ) для використання в системах водопідготовки.

Матеріали і методи. Піролізовані деревні відходи (ПДВ) м'ясопереробної промисловості як сировина для виробництва сорбентів. Хімічна активація ПДВ ортофосфорною кислотою. Методом адсорбції-десорбції азоту визначали пористу структуру при температурі 77 К; розподіл мезопор за розмірами і об'єм мезопор – методом *BJH*; розподіл мікропор за розмірами – методом *QSDFT*; об'єм мікропор – методом Дубініна-Радушкевича; об'єм субнанопор – методом *QSDFT*.

Результати. Мікропориста структура має наступні характеристики: діаметри пор знаходяться у діапазоні D_{mi}=0,60–2,5 нм, які найбільш всього представлено порами з діаметром 0,87; 1,56 нм; об'єм мікропор – V_{mi}=0,091 см^3/г; диференціальний об'єм пор dV_{mi}/dD=(0,021–0,166)·10^{-2} см^3/нм·г; частка мікропор у загальному об'ємі пор складає 49%. Згідно розподілу мікропор за розмірами можна виділити область значень D_{mi}=0,5–2,5 нм з двома максимумами: при ~ 0,9 нм та при ~ 1,6 нм. Мезопориста структура має наступні характеристики: діаметри пор знаходяться у діапазоні D_{me}=3,3–50,0 нм, які найбільш представлено порами з діаметром 3,69 нм; об'єм мезопор варіюється в інтервалі V_{me}=0,005-0,049 см^3/г; площа поверхні пор – S_{me}=5,7–28,0 м^2/г; диференціальний об'єм пор dV_{me}/dD=(0,06–2,58)·10^{-4} см^3/нм·г; диференціальна площа пор dS_{me}/dD=(0,001-0,305) м^2/нм·г; частка мезопор у загальному об'ємі пор складає 3-26%. Криві диференціального об'єму пор та диференціальної площі поверхні пор для інтервалу D=15,3-50,0 нм знаходяться у стаціонарної області, а в інтервалі D=2,5–15,3 нм спостерігається один максимум в точці 3,69 нм, який розташовано в області менших діаметрів пор при диференціальному об'ємі пор dV_{me}/dD=2,58·10^{-4} см^3/нм·г. При цьому найбільша кількість мезопор доводиться на діапазон D=2,5–15,3 нм. Наведені дані свідчать, що запропонований спосіб дозволяє отримувати ПВМ з високим коефіцієнтом виходу 87,6%. При цьому отриманий ПВМ має низькі показники питомої поверхні S_{BET}=257,0 м^2/г та поровий простір – сумарний об'єм пор V_{Σ}=0,187 см^3/г.

Висновки. Вторинні «поновлювані» ресурси – ПДВ дозволяють отримувати ПВМ із низькими енерговитратами для використання в системах водопідготовки.

Ключові слова: піроліз, відхід, активація, нанопора, адсорбент.

Визначення структури і морфології комплексів циклодекстринів з йодом

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Вступ. Об'єктом досліджень є дослідження морфології поверхні комплексів включення між α- та β-циклодекстринами та молекулярним йодом, а також

визначення у отриманих комплексах стехіометричного співвідношення між цими складовими.

Матеріали і методи. Комплекси гість-хазяїн між α- та β-циклодекстринами та йодом були синтезовані згідно з методиками, наведеними в літературіМорфологія зразків поверхні була досліджена з використанням скануючого електронного мікроскопа JSM-6700F (JEOL, Японія). На поверхню зразків, попередньо, був нанесений шар платини товщиною 10 нм. Знімання зразків проводили при прискореній напрузі 15 кВ та тоці зонда 0,65 нА.

Результати і обговорення. Для дослідження морфології та структурних властивостей отриманих комплексів був використаний метод скануючої електронної мікроскопії (СЕМ). Цей метод широко застосовують для аналізу макромолекул. Його використання дозволяє точно визначити елементний вміст в зразках. Результати щодо вмісту йоду в комплексах включення з α- та β-циклодекстрином, отримані з методами СЕМ та йодометричного титрування майже тотожні. Знайдено, що вміст йоду в комплексі β-ЦД-I_2 знаходиться в межах 16,7–16,9 %, в той час як α-ЦД-I_2 містить 18,0-19,9 % активного йоду. Деякі відмінності у значеннях концентрації йоду у α-ЦД-I_2, отриманих двома методами, може пояснюватись більшою адсорбцією води на поверхні комплексу, що приводить до зменшення концентрації йоду на поверхні зразку. Експериментальні дані щодо вмісту йоду в комплексах включення вказують на те, що α- та β-циклодескстрини реагують з KI_3 , що призводить до утворення комплексу гість-хазяїн, з величиною хімічного стехіометричного співвідношення 1:1. Аналіз морфології поверхні зразків комплексів, зроблений методом СЕМ вказує на утворення крупних кристалічних структур, нетипових для органічних полімерних сполук. Порівняльні дослідження вказують на те, що співвідношення циклодекстрину та йоду в отриманих зразках складає 1:1. Підтверджено, що одна молекула циклодекстрина зв'язує одну молекулу йоду, утворюючи комплекс гість-хазяїн.

Висновки. Комплекс β-циклодекстрин-I_2 втрачає 9 % активного йоду при тривалому зберіганні протягом одного року при 4 °С. Показано, що вміст йоду можна визначити у α-ЦД-I_2 та β-ЦД-I_2 може бути визначений при використанні досить простого і швидкого методу йодометричного титрування, що є важливою властивістю зазначених комплексів при їх подальшому використанні в харчових технологіях.

Ключові слова: *скануюча електронна мікроскопія, морфологія, поверхня, циклодекстрин, йод, комплекс включення.*

Біотехнологія, мікробіологія

Антимікробна активність штамів *Lactobacillus plantarum* щодо патогенів *Salmonella*

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Вступ. Молочнокислі бактерії під час ферментації виробляють різні сполуки (органічні кислоти, діацетил, перекис водню і бактеріоцини). Всі вони можуть протидіяти зростанню деяких гнильних і патогенних бактерій у харчових продуктах.

Матеріали і методи. Для визначення антимікробної активності *Lactobacillus plantarum* D1 і *Lactobacillus plantarum* D2 щодо *Salmonella* sp. і *Salmonella abony* ATCC 6017 використано метод співкультивування. Дослідження проводились за статичних умов за температури 37±1ºС протягом 72 годин, проби відбиралися на 0, 12, 24, 36, 48, 60 і 72 годинах, контролювалися зміни в титрувальній кислотності та концентрація життєздатних клітин обох патогенів і штамів *Lactobacillus Plantarum.*

Результати і обговорення. Під час одноштамного культивування кожного штаму Lactobacillus Plantarum і кожного штаму Salmonella висока концентрація життєздатних клітин досягається на 24-й годині й підтримується до кінця культивування. У співкультивуванні кожного штаму Lactobacillus Plantarum і кожного штаму Salmonella, штам Lactobacillus істотно не залежить від наявності будь-якого з штамів Salmonella. Але число життєздатних клітин збудників значно знижується, скорочення стає штамоспеціфічним. У співкультивуванні кожного штаму Lactobacillus Plantarum і Salmonella Abony ATCC 6017 концентрація життєздатних клітин штаму патогенних мікроорганізмів знижувалася до 60-ї години. У співкультивуванні кожного штаму Lactobacillus Plantarum і Salmonella sp. концентрація життєздатних клітин штаму патогенних мікроорганізмів знижувалася до 72-ї години. Виявлена антимікробна активність виникала відповідно до закислення середовища через виробництво і накопичення молочної та інших органічних кислот.

Висновки. Описана антимікробна активність є необхідною умовою для подальших досліджень пробіотичного потенціалу двох штамів *Lactobacillus plantarum* для включення їх до складу пробіотичних препаратів і стартерів для пробіотичних функціональних продуктів харчування.

Ключові слова: пробіотик, *Lactobacillus, патоген, антимікробний, співкультивування, сальмонела.*

Процеси і обладнання харчових виробництв

Осмотичні тиски в середовищах бродильних технологій

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Вступ. Проведені дослідження з метою створення фізичної і математичної формалізації змін хімічного складу середовища, його енергетичного потенціалу і осмотичних тисків.

Матеріали і методи. Матеріали і методи дослідження визначалися на основі мети і задач теоретичних пошуків, що виключало необхідність використання фізичних матеріалів, а за базу досліджень використовувалися відомі закономірності анаеробних процесів бродіння та феноменологічні міркування з наближенням до положень термодинаміки.

Результати і обговорення. Розглядається використання біохімічної активності мікроорганізмів у бродильних виробництвах, у яких вхідні сировинні потоки

трансформуються з деструкційними впливами і утворенням речовин з різними молекулярними масами. Такі процеси можуть вважатися самоплинними і незворотними, що означає присутність ентропійних втрат у формі теплової енергії. Разом з тим деструкційні впливи супроводжуються утворенням речовин з меншими молекулярними масами, що приводить до зростання осмотичних тисків в культуральних середовищах. Досягнення критичних показників останніх припиняє подальші біохімічні перетворення з досягненням бактеріостатичних і, навіть, летальних ефектів щодо мікрофлори. Енергетичне забезпечення перебігу цих процесів досягається за рахунок хімічної енергії високомолекулярних сполук вхідних матеріальних потоків.

Перехід від розчинів з чітко визначеною структурою до середовищ харчової і мікробіологічної промисловостей означає суттєве ускладнення при визначенні осмотичних тисків. Це пояснюється, по-перше, безперервною динамікою зміни складу середовищ і, по-друге, присутністю сукупності речовин перехідних процесів. Запропоновано до використання у визначеннях осмотичних тисків принципу суперпозиції. В основу такого положення покладено відому інформацію про те, що всі перетворення і синтез проміжних речовин відбуваються на рівні ендогенних процесів в клітинах дріжджів. Відмічається ефективність організації процесів функціонування біологічних систем від сталості показників середовищ з врахуванням зовнішніх впливів і важливість напрямків осмомолекулярної дифузії. Колігативні властивості розчинів культуральних середовищ змінюються пропорційно моляльності розчиненої речовини.

Висновки. Осмотичні тиски розчинів речовин, що утворюються в результаті хімічних та біохімічних реакцій, пропорційні зрівнювальним коефіцієнтам у відповідних рівняннях, а зміни осмотичних тисків до і після перебігу хімічних і біохімічних реакцій визначаються змінами кількостей молекулярних структур, що утворюються.

Ключові слова: *бродіння, тиск, глюкоза, етиловий спирт*.

Зміна фізико-хімічних параметрів рідких бінарних систем під впливом знакозмінних імпульсів тиску

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Вступ. Проведені дослідження зметою визначення впливу безреагентного методу оброблення, а саме знакозмінних імпульсів тиску на зміну фізико-хімічних параметрів рідких бінарних систем.

Матеріали та методи. Реалізовано вплив знакозмінних імпульсів тиску на бінарні системи: воду та водно-етанольні суміші, в широкому діапазоні концентрацій від 5-90%. Для вивчення зміни фізико-хімічних параметрів бінарних систем використовувались методи прямої потенціометрії (іонометрії). Експериментальні дослідження зразків виконані з використанням лабораторного вимірювального обладнання: pH-метра-міллівольтметра pH-150M та оксиметру EZODO PDO-408.

Результати і обговорення. Під впливом оброблення із застосуванням знакозмінних імпульсів тиску рідких бінарних систем, таких як вода та водно-

етанольні суміші відбувається інтенсивне знекиснення. Величина зниження кількості розчиненого кисню у воді та водно-етанольних сумішах у порівнянні із початковим вмістом становить майже 50-55%.

Встановлено зміну водневого показника у дистильованій воді на 13%, у порівнянні із початковим значенням, а у воді, підготовленій за технологією лікеро-горілчаного підприємства, зростання водневого показника відбувалось на 14–14,5%.

Величина окисно-відновного потенціалу у порівнянні із початковим значенням знизилась на 20–60%, залежно від часу оброблення знакозмінними імпульсами тиску.

Встановлена зміна фізико-хімічних параметрів водних систем при застосуванні оброблення високочастотними осциляціями, що можна пояснити зміною реакційної здатності, внаслідок ініціювання переносу протону в асоційованих рідинах, таких як вода, аліфатичні спирти та водно-етанольні суміші з різним вмістом етанолу, а також утворення сітки водневих зв'язків, що в свою чергу впливає на структурну організацію та будову.

Висновки. Безреагентний метод обробки води і водно-етанольних сумішей з використанням роторно-пульсаційних апаратів може в значній мірі скоротити тривалість процесу змішування, знизити енерговитрати, підвищити продуктивність та замінити періодичний спосіб змішування на безперервний.

Ключові слова: *вода, етанол, суміш, тиск, імпульс.*

Економіка і управління

Опитування громадської думки споживачів щодо маркування харчових продуктів в Республіці Македонія

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3 – Healthy Food by Zegin, Скоп'є, Республіка Македонія

Вступ. Споживач повинен бути проінформований про якість і характеристики придбаного харчового продукту, що можливо лише за умови правильного маркування. Проведено дослідження з метою вивчення думки споживачів щодо маркування харчових продуктів в Республіці Македонія.

Матеріали і методи. Огляд здійснювався методом електронного опитування 200 осіб із 13 різних міст у Македонії. Учасники опитування розділені на п'ять груп залежно від віку: до 19 років, 19 – 25 років, 26 – 32 роки, 33 – 50 років та понад 50 років.

Результати і обговорення. Під час вибору продовольчих товарів більшість респондентів, незалежно від віку, читали представлену на етикетках інформацію щодо продукту. Інша проблема полягає у використанні багатьох цифр і знаків з невідомим значенням, а також знаком «Е» на упаковці. Для всіх респондентів термін придатності продукту має більший вплив під час вибору продуктів, ніж вартість продукту. Енергетична цінність продуктів і вміст солей у них не дуже важливі під час

вибору продукту. Всі респонденти згодні, що якщо харчовий продукт містить компоненти, які можуть поставити під загрозу здоров'я людини, він має бути належним чином промаркований. Респонденти вважають, що було б краще, якби етикетка, за допомогою якої продукт маркується, містила перелік групи споживачів.

Висновки. Споживачі під час вибору харчового продукту звертають увагу на маркування продукту на етикетці. Для респондентів має велике значення наявність інформації щодо призначення продукту для певної групи. У той же час важливо підвищити обізнаність споживачів з числами, символами і позначками на етикетках харчових продуктів.

Ключові слова: *маркування, харчування, споживач, опитування, Македонія.*

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, Ukrainian, Russian
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.

The background of the graphs and charts should be only in white color. The color of the figure elements (lines, grid, text) – in black color.
Figures and EXCEL format files with graphs additionally should submit in separate files.
Photos are not appropriate to use.

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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

Мови статей – англійська, українська, російська

Рекомендований обсяг статті – **8–15 сторінок** формату А4 (без врахування анотацій і списку літератури)**.**

Стаття виконується в текстовому редакторі Microsoft Word 2003, в форматі *.doc.

Для всіх елементів статті шрифт – **Times New Roman**, кегль – **14**, інтервал – 1.

Всі поля сторінки – по 2 см.

Структура статті:

1**.** УДК**.**

2. **Назва статті.**

3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озерянко).

4. *Установа, в якій виконана робота.*

5. Анотація. **Обов'язкова** структура анотації:

- Вступ (2–3 рядки).
- Матеріали та методи (до 5 рядків)
- Результати та обговорення (пів сторінки).
- Висновки (2–3 рядки).

6. Ключові слова (3–5 слів, але не словосполучень).

Пункти 2–6 виконати англійською і українською мовами.

7. Основний текст статті. Має включати такі обов'язкові розділи:

- Вступ
- Матеріали та методи
- Результати та обговорення
- Висновки
- Література.

За необхідності можна додавати інші розділи та розбивати їх на підрозділи.

8. Авторська довідка (Прізвище, ім'я та по батькові, вчений ступінь та звання, місце роботи, електронна адреса або телефон).

9. Контактні дані автора, до якого за необхідності буде звертатись редакція журналу.

Рисунки виконуються якісно. Скановані рисунки не приймаються. Розмір тексту на рисунках повинен бути **співрозмірним** (!) тексту статті. **Фотографії можна використовувати лише за їх значної наукової цінності.**

Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

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 статті та монографії іноземних авторів, які опубліковані після 2000 року.

Правила оформлення списку літератури

В Ukrainian Food Journalвзято за основу загальноприйняте в світі спрощене оформлення списку літератури згідно стандарту Garvard. Всі елементи посилання розділяються **лише комами**.

1. Посилання на статтю:

Автори А.А. (рік видання), Назва статті, Назва журналу (курсивом), Том (номер), сторінки.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

1. Приклад:
   Popovici C., Gitin L., Alexe P. (2013), Characterization of walnut (Juglans regia L.) green husk extract obtained by supercritical carbon dioxide fluid extraction, *Journal of Food and Packaging Science, Technique and Technologies,* 2(2), pp. 104–108.

2. Посилання на книгу:

Автори (рік), Назва книги (курсивом), Видавництво, Місто.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

Приклад:

2. Wen-Ching Yang (2003), *Handbook of fluidization and fluid-particle systems*, Marcel Dekker, New York.

Посилання на електронний ресурс:

Виконується аналогічно посиланню на книгу або статтю. Після оформлення даних про публікацію пишуться слова ***Available at:*** та вказується електронна адреса.

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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Додаткова інформація та приклад оформлення статті – на сайті

http://ufj.ho.ua

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УДК 663/664

Ukrainian Food Journal публікує оригінальні наукові статті, короткі повідомлення, оглядові статті, новини та огляди літератури.

Тематика публікацій в Ukrainian Food Journal:

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Мікробіологія
Фізичні властивості харчових продуктів
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Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв'язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

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Політика академічної етики. Редакція «Ukrainian Food Journal» користується правилами академічної етики, викладених в роботі Miguel Roig (2003, 2006) "Avoiding plagiarism, self-plagiarism, and other questionable writing practices. A guide to ethical writing". Редакція пропонує авторам статей і рецензентам прямо слідувати цьому керівництву, щоб уникнути помилок у науковій літературі.

Інструкції для авторів та інша корисна інформація розміщені на сайті
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