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Proteolytic systems of lactic acid microorganisms: a review

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Abstract

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Introduction. The primary objective of this review is to analyze and summarize the existing scientific information about the structure features, formation conditions and properties of proteinases and peptidases of lactic acid microorganisms, which are widely used in the production of dairy products.

Material and methods. The proteolysis of milk proteins, occurred by lactic acid microorganisms, is an investigation object of this review article. Scientific articles as well as theses and monographs of microbiology, biochemistry and dairy science have been analysed. Methodology of the investigation is based upon the use of the methods of analysis, comparison and synthesis.

Results and discussion. Cleavage of proteins and amino acids with enzymes of lactic acid and propionic acid bacteria promotes the enrichment of dairy products with nitrogen-containing and nitrogen-free compounds, and as a result, the product obtains necessary consistency, taste and smell. In addition to providing organoleptic properties, the formation of a large number of peptides with different types of biological activity occurs also in the process of proteolysis of milk proteins in the production of dairy products.

The proteolytic system of lactic acid bacteria consists of three parts: proteinases, which that provide the initial cleavage of casein to peptides with formation of a large number of oligopeptides; peptidases, which cleavage peptides to amino acids; transport system, which provides transfer of proteolysis products through the cytoplasmic membrane. Proteinases function outside microbial cells, produce them, and peptidases – in cells of lactic acid bacteria.

By the specificity of the effect on the fractions of the casein complex of milk proteinases of lactic acid microorganisms are divided into 2 types – *PI* and *PIII*. Proteinases *PI* are able to cleavage β -caseins and don't cleavage α_{S1} - and κ -caseins, but proteinases *PIII* hydrolyse all three fractions: α_{S-} , β - and κ -caseins.

None of the peptidases with carboxypeptidase activity were revealed among large number of lactic acid bacteria peptidases. *PepN*, *PepC*, *PepA* are referred to the aminopeptidases, found in lactic acid microorganisms. In addition to aminopeptidase, dipeptidases and tripeptidases were revealed in lactobacilli.

Conclusion. It is recommended to use systematized characteristics of proteinases and peptidases of appropriate microorganisms with the purpose of providing quality organoleptic parameters of dairy products as well as the formation of biologically active peptides in the process of selecting the species composition of starter cultures.

Introduction

At production and sale of food and dairy products, in particular, organoleptic properties (taste, smell, consistency) of the finished product are the main factors, which guarantee a high demand level among consumers. Special taste and smell, typical for each product, are provided with various food substances (proteins, fats, carbohydrates) and their cleavage products [1-4]. A significant amount of taste and flavoring substances in dairy products are formed as a result of proteolysis of milk proteins [1,2,5,6]. In particular, proteolysis actively occurs in the production of fermented milk products (kefir, koumiss, cottage cheese, etc.). And very intensively – in the production of hard cheeses, in the aging of which there are biochemical changes in milk proteins. Cleavage of proteins and amino acids with enzymes of lactic acid and propionic acid bacteria promotes the enrichment of dairy products with soluble in water nitrogen-containing and nitrogen-free compounds, and as a result, the product obtains necessary consistency, taste and smell [7-14].

In addition to providing organoleptic properties, which are important for the consumer and demand in the market, the formation of a large number of peptides with different types of biological activity occurs also in the process of proteolysis of milk proteins in the production of dairy products [15-17]. Among the casein proteolysis products, bioactive peptides, having opioid affect, antihypertensive and immunomodulating properties, ability to influence blood coagulation processes, transport of calcium ions in the intestine etc., were revealed [18-24]. Inhibitors of angiotensin converting enzyme, peptides with opioid and bactericidal action, immunomodulating and hypocholesterolemic, as well as peptides, affecting intestinal motility, were found among bioactive peptides from milk whey proteins [25-27]. It was defined that β -actoglobulin is the precursor of all these types of bioactive peptides, except for immunomodulating peptides. Among bioactive peptides, formed from α -lactalbumin, there are no peptides with hypocholesterolemic action and peptides affecting intestinal motility, and only two types of biological activity are inherent in peptides with lactoferrin (bactericidal and immunomodulating).

It is known that proteolysis of proteins occurs gradually under the influence of lactic acid microorganisms [13]. The casein proteins are the most sensitive to proteolytic enzymes. First the caseophosphate complex decomposes into high molecular weight polypeptides, then medium and low molecular weight peptides and amino acids dominate among the products of proteolysis. The majority transformations during the initial stages of proteolysis occur under the influence of extracellular and cell-wall-bound proteinases, and more profound transformations of the peptides – under the influence of membrane and intracellular peptidases of lactic acid bacteria. [28-33].

Lactic acid bacteria (lactococci and lactobacilli), which are a part of different types of starter preparations for dairy products, are auxotrophs, that is, their ability to develop in a dairy medium depends on the activity of the proteolytic system, which ensures the liberation of essential amino acids during the cleavage of proteins of the casein complex, used by microorganisms in the synthesis of proteins [32, 33]. The proteolytic system of lactic acid bacteria consists of three parts:

- proteinases, which that provide the initial cleavage of casein to peptides with formation of a large number of oligopeptides [32];
- peptidases, which cleavage peptides to amino acids [30];
- transport system, which provides transfer of proteolysis products through the cytoplasmic membrane [12, 33].

It is known that proteinases function outside microbial cells, which produce them, and peptidases – in cells of lactic acid bacteria.

Proceeding from the aforesaid, the purpose of this work is to analyze and summarize the existing scientific information about the structure features, formation conditions and biochemical properties of proteinases and peptidases of lactic acid microorganisms, which are widely used in the production of dairy products.

Material and methods

The proteolysis of milk proteins, occurred by lactic acid microorganisms, is an investigation object of this review article. Scientific articles as well as theses and monographs of microbiology, biochemistry and dairy science have been analysed. Methodology of the investigation is based upon the use of the methods of analysis, comparison and synthesis. Literature referenced in this review article was obtained from searches from bibliographic information in CAB abstracts, AGRICOLA, SciFinder, Google Scholar, PubMed, ScienceDirect database and Web of Science.

Results and discussion

Proteinases

Localization of proteinases. Proteinases of lactic acid microorganisms are monomeric serine proteinases with molecular weight 180 000–190 000 Da (Table 1), which are connected with the bacterial cell wall and are called extracellular proteinases or in abbreviated form *PrtP*.

Table 1
Characteristics of proteinases of lactic acid microorganisms
 (adapted from Kunji (1996)) [12]

Types and strains of lactic acid microorganisms	Molecular weight *, kDa	Substrate, which is cleaved with proteinase	pH optimum
<i>L. lactis ssp. cremoris</i> WG2		κ -, β -caseins	
<i>L. lactis ssp. cremoris</i> HP		κ -, β -caseins	6,4
<i>L. lactis ssp. cremoris</i> SKII	187 ⁿ	α_{S1} -, κ -, β -caseins	
<i>L. lactis ssp. cremoris</i> AC1		α_{S1} -, κ -, β -caseins	
<i>L. lactis ssp. cremoris</i> AM1		α_{S1} -, κ -, β -caseins	
<i>L. lactis ssp. cremoris</i> H2	180 ^e	κ -, β -caseins	6,0
<i>L. lactis ssp. cremoris</i> NCD0763		α_{S1} -, κ -, β -caseins	
<i>Lb. casei ssp. casei</i> NH14		β -casein	
<i>Lb. casei ssp. casei</i> NCD0151			6,5
<i>Lb. delbrueckii ssp. bulgaricus</i> CNRZ397	170 ^e	α_{S1} -, β -caseins	5,5
<i>Lb. helveticus</i> CNRZ303		α_{S1} -, β -caseins	7,5
<i>Lb. helveticus</i> CP709	45 ^e	α_{S1} -, β -caseins	6,5
<i>Lb. helveticus</i> L89	180 ^e	α_{S1} -, β -caseins	7,0

Notes: The molecular weight of the enzyme was defined with polyacrylamide gel electrophoresis (mark – e) or calculated by the primary structure (mark – n).

Primary PrtP structure and the structure of gene, which encodes their synthesis [12, 34], was defined for most types of lactic acid microorganisms. Thus, in lactococci and *Lb. paracasei* cell-wall-bound proteinase includes 1902 amino acid residues in *Lb. delbrueckii* – 1946, and in *Lb. lactis* – 1962. Primary PrtP structure in different lactococci is identical for 98% and is identical for 95% with *Lb. paracasei*. The analysis of the primary structure of proteinases shows their similarity with subtilisins, which are also serine proteinases with similar catalytic domains [35]. Wherein, N-end part of the formed enzyme contains a catalytic domain with several conserved amino acid residues, which participate in the catalytic process and substrate binding. The next segment shows no similarity to proteins with similar functions and, evidently, is responsible for placing the catalytic domain on the surface of the cell wall [35]. C- terminal part of cell-wall-bound proteinases is similar to that found in many Gram-positive bacteria and includes signal sequence and α - helix section, connected with the membrane [36].

Extracellular localization of proteinases is possible in cases of microorganisms placing in the solutions without calcium [37], or when microorganism cells are exposed to enzyme lysozyme affect [38]. In the first case, the enzyme is formed with less molecular weight (165000 Da) in comparison with lysozyme affect (180000 Da), which can happen due to auto-proteolysis.

In the laboratory of biochemistry of dairy products of Ternopil Ivan Puluji National Technical University, it has been obtained the evidence of the existence of cell-wall-bound extracellular proteases in *St. salivarius ssp thermophilus* (strain 9₁) during proteolysis of purified casein fractions by microorganism cells [39].

Substrate specificity of proteinases. Some authors defined, that cell-wall-bound proteinases are characterized with wide substrate specificity [37, 40, 41]. Those sectors, on which proteolysis uniquely occurs, were not defined on the basis of analysis of many products of proteolysis. Only those sectors were found, which were sensitive mainly to the affect of different types of proteinases. It should be noted, that di- and tripeptides, as well as free amino acids are formed in small quantities under affect of cell-wall-bound proteinases of lactic acid bacteria on α _S-, β - and κ -caseins. However, many slightly larger peptides are formed (4-8 amino acid residues), which contain all essential amino acids, necessary for normal growth of lactic acid bacteria. All products of proteolysis, formed due to the affect of cell-wall-bound proteinases, are located in the medium, outside the bacterial cell.

By the specificity of the effect on the fractions of the casein complex of milk cell-wall-bound proteinases of lactic acid microorganisms are divided into 2 types – *PI* and *PIII*. Proteinases *PI* are able to cleavage β -caseins and don't cleavage α S1- and κ -caseins, but proteinases *PIII* hydrolyse all three fractions: α _S-, β - and κ -caseins [12, 32, 44].

Cleavage of β -casein fraction with proteinases. Recently they conduct intensive research for the purpose of detailed study of caseins proteolysis products with cell-wall-bound proteinases of lactobacilli. It was established that β -caseins are the most sensitive to the affect of these enzymes. Specificity of the proteinases activity at incubation the purified casein fraction with intact bacterial cells was studied in the early works [42]. At the same time it was proved, that only cell-wall-bound proteinase shows proteolytic action. Later in the experiments in vitro they used purified enzymes obtained from various strains of lactic acid bacteria, and the appropriate fraction of casein. In particular, they investigated the influence of cell-wall-bound proteinase of lactic acid microorganisms *L. lactis* and *Lb. helveticus* on β -casein [43]. They separated the products of β -casein proteolysis by liquid chromatography method, purified and installed the primary structure by Edman. The first results showed that only part of β -casein is cleavaged under affect of cell-wall-bound proteinase. In this case, large fragments are mainly formed. Further research, using liquid

chromatography method under high pressure and mass spectrometry, allowed to analyze more than 95% peptides, formed at β -casein cleavaging with proteinase of *PI* type [40]. More than 100 peptides, consisting of 4-30 amino acid residues were found. Most peptides contained 4-10 residues.

It was established that half of the peptides is formed from C- terminal part of β -casein molecule. Analysis of products of β -casein proteolysis, formed under the affect of proteinase of the type *PIII*, allowed to identify thirteen identical links, which are always cleavageted with proteinases of the type *PIII* and *PI*, and six links, which are often cleavageted with cell-wall-bound proteinases of bacteria of different strains. The aforesaid peptides are formed mainly from C- terminal part of β -casein molecule. In addition to the proteinases, typical for *Lb. helveticus* and *L. lactis* in *Lb. helveticus* CP790, much smaller cell-wall-bound proteinase (45000 Da), which belongs to the class of serine proteinases and shows specificity in relation to β -casein [43], was also revealed.

Cleavage of α_{S1} - i α_{S2} -casein fractions, occurs mainly due to the affect of *PIII*-type proteinases or mixed-type proteinases. Proteinases *PI* do not hydrolyze the fractions of α_S -caseins [44]. 25 main oligopeptides, half of which is formed as a result of C-terminal part cleavageting, were identified among the products of proteolysis, [41, 45]. Besides, the number of small peptides, formed from sectors, adjoining to peptide connections, sensitive to proteinase, were identified.

The analysis of specificity of proteinases Exterkate F.A., Albing A.C., Bruinenberg P.G. [34] was conducted on the fragment of α_{S1} -casein, including amino acid residues 1-28. In this case, they used proteinases, extracted from sixteen different *L. lactis* strains. Based on the results of these studies, they separated proteinase of lactococcus into 7 groups, which differed in the specificity of cleavageting of the aforesaid fragment of α_{S1} -casein. Comparison of amino acid sequences responsible for substrate binding, of proteases with different specificity showed, that their specificity is caused by minor genetic variations of the structural proteinase gene. The primary structure of the catalytic domain is conservative not only in lactococci, but also in lactobacilli with cell-wall-bound proteinases. So, in *Lb. paracasei* two substitutions of amino acid residues in this domain were found, and in *Lb. delbrueckii* – three substitutions [46]. In proteinase *Lb. helveticus* (strain L89) the same specificity as in the proteinase lactococci was revealed. Differences between them were due to different ratios of proteolysis products [47].

Cleavage of κ -casein fraction with proteinases. Products of proteolysis of κ -casein were studied under the influence of cell-wall-bound proteinase of different types in the number of strains of lactococcus *L. lactis* [41, 48, 49]. Cleavage of κ -casein causes the formation of large number of small peptides predominantly from C- terminal part of molecule. Most peptide connections are constantly subjected to hydrolysis with all types of proteinases, however, the peptides were also found, which are formed under affect of certain types of specific proteinases.

Peptidases

Peptidases – are the enzymes of hydrolase class, which cleavage one by one amino acid from the carboxyl or amine end from peptide molecules. There are many works in the scientific literature, devoted to structure, properties and specificity of peptidases, main results of which are systematized in the Table 2.

Table 2

Peptidases of lactic acid microorganisms (adapted from Kunji (1996)) [12]

Name of the enzyme	Substrate	Strain of lactic acid microorganisms	Molecular weight, kDa	Quaternary structure	Peptidase type ¹
Aminopeptidases N PepN	X↓(X) _n	<i>L. lactis ssp. cremoris</i> Wg2	95	monomer	M
		<i>L. lactis ssp. cremoris</i> MG1363	95		
		<i>L. lactis ssp. cremoris</i> HP	95		
		<i>Lb. casei ssp. casei</i> LGG	87	monomer	M
		<i>Lb. casei ssp. casei</i> IFPL731	95	monomer	M
		<i>Lb. delbrueckii ssp. lactis</i> DSM7290	95	monomer	M
		<i>Lb. delbrueckii ssp. bulgaricus</i> B14	95	monomer	M
		<i>Lb. helveticus</i> ITGL1	97	monomer	M
		<i>Lb. helveticus</i> SBT2171	95	monomer	M
		<i>Lb. sanfrancisco</i> CB1	75	monomer	M
		<i>S. salivarius ssp. thermophilus</i> CNRZ302	97	monomer	M
Aminopeptidases C PepC	X↓(X) _n	<i>L. lactis ssp. cremoris</i> AM2	50	hexamer	C
		<i>Lb. delbrueckii ssp. lactis</i> DSM7290	51		C
		<i>Lb. delbrueckii ssp. bulgaricus</i> B14	54	tetramer	C
		<i>Lb. helveticus</i> CNRZ32	50		C
		<i>S. salivarius ssp. Thermophilus</i>	50	hexamer	C
Aminopeptidases A PepA	X↓(X) _n	<i>L. lactis ssp. cremoris</i> AM2	40	hexamer	M
		<i>L. lactis ssp. cremoris</i> MG1363	38		
		<i>S. salivarius ssp. Thermophilus</i>	45	octomer	M

Continue of the Table 2

Name of the enzyme	Substrate	Strain of lactic acid microorganisms	Molecular weight, kDa	Quaternary structure	Peptidase type ¹
Dipeptidases V PepV	X↓X	<i>L. lactis ssp. cremoris</i> Wg2	49	monomer	
Dipeptidases D, PepD	X↓X	<i>L. lactis ssp. cremoris</i> MG1363	51		M
		<i>L. lactis biov. Diacetylactis</i>	50		M
		<i>Lb. delbrueckii ssp. lactis</i> DSM7290	52		M
		<i>Lb. delbrueckii ssp. bulgaricus</i> B14	51	monomer	M
		<i>Lb. helveticus</i> SBT2171	50	monomer	M
		<i>Lb. casei ssp. casei</i> IFPL731	46	monomer	M
		<i>Lb. sace</i>	50	monomer	M
		<i>Lb. sanfrancisco</i> CB1	65	monomer	M
		<i>Lb. helveticus</i> 53/7	54	octomer	T
Tripeptidases PepT	X↓X-X	<i>L. lactis ssp. cremoris</i> Wg2	52	dimer	M
Prolidases Q PepQ	X↓Pro	<i>L. lactis ssp. cremoris</i> AM2	52	dimer	M
		<i>L. lactis ssp. cremoris</i> IMN-C12	23	trimer	C
		<i>L. lactis ssp. cremoris</i> AM2	42	monomer	M
X- rolyldipeptidyl-aminopeptidase PepX	X- Pro↓ (X) _n	<i>Lb. delbrueckii ssp. lactis</i> DSM7290	41		M
		<i>Lb. delbrueckii ssp. Bulgaricus</i>	41		M
		<i>Lb. delbrueckii ssp. bulgaricus</i> CNRZ	41	dimer	
		<i>Lb. casei ssp. casei</i> IFPL731	41	monomer	M
		<i>L. lactis ssp. lactis</i> H1	83	dimer	S

Name of the enzyme	Substrate	Strain of lactic acid microorganisms	Molecular weight, kDa	Quaternary structure	Peptidase type ¹
Prolineimmuno-peptidases PepI	Pro↓X-(X) _n	<i>L. lactis ssp. cremoris</i> P-8-2-47	90		S
		<i>L. lactis ssp. cremoris</i> AM2	59	dimer	S
		<i>L. lactis ssp. cremoris</i> nTR	88	dimer	S
		<i>Lb. casei ssp. casei</i> LLG	79		S
		<i>Lb. delbrueckii ssp. lactis</i> DSM7290	88		S
		<i>Lb. delbrueckii ssp. bulgaricus</i> B14	95	dimer	S
		<i>Lb. helveticus</i> 53/7	91	dimer	S
		<i>Lb. helveticus</i> LHE-51	87		S
		<i>Lb. helveticus</i> CNRZ32	90		S
		<i>S. salivarius ssp. thermophilus</i> ACA-DC4	80	dimer	S
		<i>L. lactis ssp. cremoris</i> HP	50		M
Endopeptidases Pep E		<i>Lb. delbrueckii ssp. lactis</i> DSM7290	33		S
		<i>Lb. delbrueckii ssp. bulgaricus</i> CNRZ	33		S
		<i>Lb. helveticus</i> 53/7	34	dimer	S
		<i>Lb. helveticus</i> CNRZ32	52		C
Pep G		<i>Lb. delbrueckii ssp. lactis</i> DSM7290	50		C
Pep O		<i>Lb. helveticus</i> CNRZ32	71		M
PepF1, PepF2		<i>L. lactis</i>	71		M
		<i>L. lactis</i>	70		

¹Note. M – metallopeptidase; S – serine; C – cysteine peptidase.

Peptidases localization. The question of the peptidases localization in the cells of lactic acid bacteria has been changed since the time of its rising. In earlier works it was written about their localization on cell membranes and even outside the cells [13]. At present most researchers tend to think about intracellular localization of all peptidases of lactic acid microorganisms [50-53]. The absence of signal sequences and anchor sections for fixation on the membrane in all peptidases, for which the primary structure was established, can be the evidence of this. Besides, transport system of oligopeptides of lactic acid bacteria can provide entering of large peptides, formed with casein proteolysis, into the cell. And there is no need to cleavage peptides outside the cell or on cell membranes.

Substrate specificity of peptidases. In accordance with the effect on substrates, we can distinguish

- *aminopeptidases*, hydrolyzing the peptide connection, formed by the amino group of the polypeptide chain and the carboxyl group of the terminal amino acid,
- *carboxypeptidases*, acting on the peptide connection, formed by the carboxyl group of the polypeptide chain and the amino group of the final amino acid,
- *dipeptidases*, which provide hydrolysis of dipeptides.

None of the peptidases with carboxypeptidase activity were revealed among large number of lactic acid bacteria peptidases, different by specificity. *PepN*, *PepC*, *PepA* are referred to the aminopeptidases, found in lactic acid microorganisms. In addition to aminopeptidase, dipeptidases *PepD* and *PepV* [50, 52] were revealed in lactobacilli.

Aminopeptidase N (PepN). Study of genes *PepN* in different bacteria showed a high level of their identity [50], at the same time the primary structure *PepN* is homologous to aminopeptidase N in mammals [54]. *PepN* can cleavage off N-end amino acids in di- and tripeptides. However, dipeptides, which contain proline residue in the first or second positions, are not cleavaged with *PepN*, whereas such connection in tripeptides undergoes hydrolysis [55,56]. *PepN* dipeptides better the hydrolyses, in which N-end amino acid residue is arginine. Dipeptides, containing lysine and leucine in the first position, are hydrolyzed less [57]. The enzyme activity increases with increasing of hydrophobicity C-end amino acid residue of dipeptide Arg-X. *PepN* with *Lb. helveticus* has similar properties with respect to dipeptides Ala-X and Lei-X [55].

The affect of *PepN* on oligopeptides was studied in several works [56,57]. *PepN* ability to cleavage oligopeptides, including from 4 to 14 amino acid residues, is shown on the example of using products of trypsin hydrolyzate of β -casein as a substrate. It was found that hexapeptide is the optimal substrate for *PepN* [57]. Aminopeptidase N with *Lb. helveticus* is capable of hydrolyze the peptides, containing up to 10 amino acids, at that, the proline residue may be in the first position. It is also known that the enzyme is capable to split the end tyrosine from the fragment β -CNf193-209, containing 16 amino acid residues [58].

Regulation of *PepN* expression in *L. lactis* depends on the bacterial strain, as well as from the nutrient medium [50]. At lactococci growth in milk the *PepN* activity is higher than at growth on artificial nutrient media. It is known that the dipeptide Pro-Lei reduces *PepN* expression in *L. lactis* MG1363 [59]. They used the mutants of *Lb. helveticus* and *L. lactis* with deletion of the gene *pepN* [58, 60] in order to clarify the physiological role of peptidase N. Slight reduction of lactobacilli growth in the dairy medium was revealed, whereas difference in their growth was not revealed on the artificial complex nutrient medium. Similarly, mutants and wild strains *L. lactis* grow on the artificial nutrient medium, however they grow much more slowly in milk media.

Aminopeptidase C (PepC) was defined from many strains of lactic acid bacteria [50,61]. They established high activity of *PepC* at cleavageting the peptide connections,

created with basic (Arg, Gls, Lys), acidic (Glu, Asp), hydrophobic (Ala, Leu) and aromatic (Phe) amino acids. At the same time the connections, formed with the proline of the type: Pro-pNA, Pro-βNAP, X-Pro-pNA, X-Pro-βNAP, remained discontinuous. Structural modeling of *PepC* with *L.lactis* showed that C-terminal residues, participating in the interaction of α-carboxyl group *PepC* and α-amino group of the substrate [62], are the part of the enzyme active center. This was also confirmed at studying of the mutants without C-terminal residue *PepC*. The mutants *L.lactis* with deletion of the gene *PepC* did not lag behind in growth in nutrient medium, but in milk they decreased by 10% [60].

Aminopeptidase A (PepA) is able to cleavage off acidic N-terminal amino acid residues, to hydrolyse well Glu- and Asp-pNA and much less Glu- and Asp-βNAP [63,64]. *PepA* is able to cleavage off N-terminal Glu and Asp in peptides of different sizes (from 2 to 10 residues). The mutants *L.lactis*, in which there is no *PepA*, somewhat lag behind in growth at lag- phase, but in the final version they reach the same concentration as in wild strains.

X-prolyl-peptidyl-aminopeptidase (PepX). X-prolyl-dipeptidyl-aminopeptidase (*PepX*), which cleavages off dipeptides of type X-O with N-terminal part of peptides was found in strains of many kinds of lactic acid bacteria. Besides, *PepX* shows amidase and esterase activity [65,66]. The highest activity of *PepX* is revealed at cleavageting of X-o-PNA substrates, in which N-terminal amino acid is not charged (Ala, Gly) or is basic (Arg). It is known that *PepX* does not hydrolyze dipeptides, but cleavages peptides, including from 3 to 7 amino acid residues [65–67]. Dipeptides, which are released under *PepX* affect, can contain residues of basic amino acids (Arg, Gls, Lys), aromatic (Phe, Tir) and hydrophobic (Ala, Ile, Val, Gly) amino acids in the first position. *PepX* specificity to substrates of the type X-Ala-(X)_n was established and obtained at cleavageting of two dipeptides Lys-Ala and Val-Pro [66,67], using the fragment of β-casein *f* 176-182 (Lys-Ala-Val-Pro-Tir-Pro-Gln). Besides, *PepX* is able to hydrolyze the substrates of the type Pro-Pro-(X)_n, but almost does not cleavage X-Pro-Pro [51].

The original aminopeptidase *PepP*, which releases N-terminal amino acids from the peptides of the type X-Pro-Pro-(Y)_n [68,69], was found only in lactococci *L.lactis*. *PepP* showed the highest activity for pentapeptides, including from 3 to 9 amino acid residues. *PepP* specificity towards the next N-terminal amino acids (X): Arg, Met, Lys, Leu and Tir was established. Difference in the growth rate in artificial and dairy medium of the mutants with deletion gene *PepP* and wild strains *L.lactis* is small.

Dipeptidases. Dipeptidase *PepD* has a wide specificity, but does not hydrolyze AA-pNA, dipeptides, containing proline residues, and dipeptides with N-terminal remains of glycine. In contradistinction to *PepD*, peptidase *PepV* is more important for lactic acid bacteria growth. It was shown on the example of *L.lactis*, that strains, which didn't contain *PepV*, lagged behind in growth in 22% [70].

Proline-iminopeptidase (PepI), which cleavages off N-terminal proline residue in peptides, is common among lactic acid bacteria. [70, 71]. *PepI* shows hydrolytic activity to peptides of type Pro-X, where X may be a hydrophobic residue (Ala, Ile, Leu, Val), acidic (Glu) or aromatic residue (Phe, Tir). Use of peptides of different sizes as substrates showed, that *PepI* mainly cleavages off N-terminal proline in di- and tripeptide (rarely in tetrapeptide, for example, Pro-Phe-Gly-Lys), but not in pentapeptides [72]. By its specificity *PepI* of lactococci and lactobacilli differ between themselves: *PepI* of lactococci – metallopeptidase, and *PepI* of lactobacilli – serine. The absence of proline-iminopeptidase in the mutants with deletion gene *PepI* does not affect their growth in complex artificial nutrient medium. Wherein The time of doubling of microorganisms in dairy medium is increased by 9%.

Peptidase, which cleavages off N- terminal amino acid, when the second position is the proline residue – prolidase (*PepQ*) [53, 73]. Prolidase is enzyme, which hydrolyses dipeptide X-Pro. However, not all of the prolidase are dipeptidases, and they are capable to hydrolyze not all substrates of the type X-Pro. First of all *PepQ* hydrolyses dipeptides, which in the first position contain residues of hydrophobic (Ala, Ile, Leu, Val), main (Gln), aromatic (Phe, Tyr) and sulfur-containing (Met) amino acids. Some prolidases show an incomprehensible high ability to cleavage peptides without residues of proline, or contained it in the first position (Pro-Ala, Pro-Pro, Pro-Val). In a dairy medium the strains *Lb. helveticus*, with *PepQ* deficit, developed by 13% slower. Study of bacteria strains, in which *PepQ* functions normally, and strains without this enzyme showed, that almost 100% dipeptides Met- Pro, Leu-Pro and Phe-Pro are hydrolyzed with *PepQ* participation.

Tripeptidases. Tripeptidase *PepT*, separated from *L. lactis*, hydrolyses tripeptides, except peptides of the type X-Pro-Y. They are not able to hydrolyze di-, tetra- or large peptides [74]. Other tripeptidases are characterized by greater ability to cleavage tripeptides with hydrophobic and aromatic amino acid residues [75, 76]. Physiological role of *PepT* was studied little. It is only known that *PepT* absence in lactococci delays their growth in milk [60].

Peptidase *PepO* cleavages oligopeptides, which include from 5 to 35 amino acid residues [76-78]. Like thermolysin, *PepO* hydrolyses peptide connections, are formed with leucine and phenylalanine. Though *PepO* cleavages a series of casein fragments, the native proteins of the casein complex are not hydrolyzed. Growth of mutants with deletion gene *PepO* and wild strains *Lb. helveticus* were examined in various nutrient medium [77]. They observed a slight lag in growth of mutants *L. lactis*, using milk as a nutrient medium [60].

One more peptidase (*PepF*), which cleavages the oligopeptides, was found only in лактококки [79]. *PepF* hydrolyzes the oligopeptides, which include from 5 to 17 amino acid residues [79]. *PepF* shows the highest cleavaging ability for substrates, consisting of 8 or 9 residues. *PepF* hydrolyses three connections, releasing peptides from 3 to 5 residues in the fragment AKTG (f 1-24). Lack of activity of *PepF* towards β -chain of insulin (30 residues), glucagon (29 residues) and the fragment AKTG (f 1-24) allows you to determine the limits of substrates size (less than 24 residues). *PepF* doesn't cleavage native proteins of the casein complex of proteinase. This enzyme plays an important role in the processes of lactococci growth in a dairy medium. Generation time of the mutants with lack of *PepF* increases by 16% [9].

Conclusion

Based on the analysis of scientific sources, it is established that microorganisms widely used in technologies of dairy products, can produce a number of proteases (proteinases and peptidases), which play important role in proteolytic processes of industrial production of protein dairy products – primary cleavaging of the casein complex proteins and release of amino acids from exogenous peptides. Proteinases function outside microbial cells, which produce them, and peptidases – in the cells of lactic acid bacteria. In most cases, the mutants, deficient in each of the peptidases, do not differ in their growth from wild strains of lactobacilli in complex artificial nutrient media, and in a dairy medium they significantly lagged behind in growth.

It is recommended to use systematized characteristics of proteinases and peptidases of appropriate microorganisms with the purpose of providing quality organoleptic parameters of dairy products as well as the formation of biologically active peptides in the process of selecting the species composition of starter cultures.

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Influence of adding of laurel essential oil extracts on salad dressings properties

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Abstract

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Introduction. The objective of this study was to characterize essential oil extracts from laurel (*Laurus nobilis* L.) leaves and to develop sensory profiles of salad dressings with these extracts.

Materials and methods. Laurel leaves (*Laurus nobilis* L.) originating from the Athos peninsula, northern Greece were used and they were picked in October 2016. The salad dressings, which are belonged to oil-in-water emulsions, were produced with the addition of essential oil extracts from dried and humid laurel leaves.

Results and discussion. There were identified 46 components in the extracts which are represented approximately 97% of the total content. The main components in dry leaves extract are: 1,8-cineole (43.65%), α -terpinyl acetate (15.10%), calarene (8.48%), β -bisabolene (3.89%) and *p*-cymene (3.12%); in humid leaves extract – 1,8-cineole (45.94%), α -terpenyl acetate (15.89%), calarene (8.92%), β -bisabolene (5.09%), *p*-cymene (3.28%) and terpinen-4-ol (3.03%).

The two extracts had difference by content of aromatic components from those obtained with ethanol. There were differences in the composition of the essential oils, and this was probably due to the method of production.

In the extract obtained from dry leaves dominated monoterpene oxygen-containing derivatives (68.47%), sesquiterpene hydrocarbons (13.65%), aliphatic hydrocarbons (7.90%), aromatic compounds (4.10%), monoterpene hydrocarbons (2.33%), triterpene (1.43%), sesquiterpene oxygen-containing derivatives (1.23%), diterpene (0.52%) and aliphatic oxygen-containing derivatives (0.37%). In the extract obtained from humid leaves dominated monoterpene oxygen-containing derivatives (72.19%), sesquiterpene hydrocarbons (15.41%), aromatic compounds (4.32%), aliphatic hydrocarbons (3.64%), monoterpene hydrocarbons (2.45%), triterpene (0.66%), sesquiterpene oxygen-containing derivatives (0.70%), aliphatic oxygen-containing derivatives (0.39%) and diterpene (0.24%).

Dressings with an oil extract of humid leaf had most intensive smell of laurel leaf. The same is true when this sample was also perceived with the most intensive taste of laurel leaf. The sour and salt taste was equally appreciated for all three samples.

The oil extract obtained from humid leaves was preferred and between the oil extract obtained from dry leaves and the control sample the evaluators didn't not express a preference. A higher total score was obtained by salad dressing with an oil extract obtained from humid leaves.

Conclusion. Oil extract obtained from humid leaves was preferred and between the oil extract obtained from dry leaves and the control sample the evaluators didn't express a preference. A higher total score was obtained by salad dressing with an oil extract obtained from humid leaves.

Introduction

Laurel (*Laurus nobilis* L.) is a perennial plant of the family Lauraceae. It is believed that it originates from Asia Minor from where it was transferred to the Balkan Peninsula and the Mediterranean. Nowadays the laurel is distributed area of Europe, North Africa and Asia. In Bulgaria, this tree or shrub is cultivated in gardens of the homes and in the most southern regions – the cities Petrich and Sandanski as well as in the northeastern parts of the country [3, 4, 5, 12].

Fresh or dried laurel leaves are used widely in the food industry as flavors and preservatives for marinating meat and vegetables dishes, canned foods, fish dishes, sauces, soups, food emulsions *etc.* [4, 9, 16]. Antimicrobial and antioxidant activities are other factors for aromatic products from laurel leaves to be used in the food products as a food preservative [4, 5, 12].

Emulsions take place in the structures of many natural and processed foods and significant part of these foods are mayonnaise-type products. An oil-in-water emulsion can be used in the production of sweet sauces and salad dressings. Today, their formulation include not only glyceride oils rich in polyunsaturated fatty acids [6, 7, 8], but also essential oil extracts containing different biologically active substances [2, 4].

No studies have been reported on the obtaining of essential oil extracts from laurel (*Laurus nobilis* L.) leaves and their practice application in food products.

The objective of this study was to characterize essential oil extracts from laurel (*Laurus nobilis* L.) leaves and to develop sensory profiles of salad dressings with these extracts.

Materials and methods

Plant material

Laurel leaves (*Laurus nobilis* L.) originating from the Athon peninsula, northern Greece were used and they were picked in October 2016.

Moisture content determination

The raw materials moisture content was determined by drying up to constant weight, at 105 °C [11].

The wetness of the leaves – fresh (36.69%) and air-dry after shade drying (4.76%) was determined by drying to constant mass at 105 °C [11]. The essential oil content of the leaves was 2.34% [10].

Aromatic compounds extraction

Extraction was carried out as a batch static process by maceration in the solvent at a ratio of raw material to solvent = 1:10 under the following conditions: solvent – sunflower oil; temperature – 60 °C; size of material particles – 1.0×1.5 cm; duration of extraction 5, 7 and 9 h. As a criterion for effectiveness of the process the quantity of aromatic compounds was determined.

The oils were prepared by hydrodistilled for 3 h in laboratory glass apparatus of British Pharmacopoeia, modified by Balinova and Diakov [1]. The oils were dried over anhydrous sulfate and were stored in tightly closed dark vials at 4 °C until analysis.

The separation of the raw material from the obtained extraction aromatic products was made by filtration through filter paper.

Aromatic compounds determination

The content of aromatic products in oil extracts was determined by water distillation in laboratory glass apparatus of British Pharmacopoeia, modified by Balinova and Diakov [15]. The distillation was continued for 3 h and was ended when two consecutive measurements in 30 minutes didn't show an increase in the amount of essential oil [11].

The amount of essential oil non-extracted from the raw material was determined by water distillation in the apparatus described above under the same technological parameters.

After distillation, the leaves could be used to fertilize or to produce other biologically active substances.

GC/MS analysis of oil extracts

The physico-chemical properties of experimental extracts were measured [11]. GC analysis was performed using gas chromatograph Agilent 7890A; column HP-5 ms (30m × 250µm × 0.25µm); temperature: 35 °C/3 min, 5 °C/min to 250 °C for 3min, total 49 min; carrier gas helium 1 ml/min constant speed; split ratio 30:1. GC/MS analysis was carried out on a mass spectrometer Agilent 5975C, carrier gas helium, column and temperature the same as the GC analysis.

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

Technology of Dressing's production

The salad dressings, which belong to oil-in-water emulsions, were produced by established technology [8] with the addition of essential oil extracts from dried and humid laurel leaves.

The following ingredients for salad dressings were used: dry egg melange – 4%, refined sunflower oil – 5% and oil extracts from laurel leaves – 5%.

Starch – 4% and gum (mix of gum guar and gum xanthan) – 0.1% were used as structure stabilizers of products.

The starch, gum and water were heated to 80 °C and then the mixture was cooled to 20 °C. The sunflower oil and extract were added to the mixture and homogenized together with citric acid – 0.1% and salt – 1%.

A control sample without essential oil extracts was developed.

Sensory analysis of salad dressings

Sensory evaluation was performed by a trained sensory panel consisting of 10 trained assessors. The samples were at a temperature of 10 °C±1 °C and equal quantities (5 g) placed on white plastic glass, labelled with a three-digit code and served to the panel in random order.

Specific attributes and sensory descriptors of salad dressings were defined (Table 1).

Table 1

Main parameters used for sensory evaluation of salad dressings

№	Specific sensory attributes	Sensory descriptors
1	Appearance	Color (intensity of yellow color (white to yellow), brightness, emulsion stability)
2	Texture	Consistency (fluid to firm), adhesion, oiliness, homogeneity
3	Smell	Laurel leaf, rancidity
4	Taste	Salty, laurel leaf, rancidity, sour
5	Aftertaste	Bitter, laurel leaf
6	Overall acceptability	Bad to very good

Each attribute was quantified by intensity of perception (amplitude) with a numeric value from 0 to 9, corresponding to "no stimulus" to "extremely strong stimulation". Each attribute had individually scale and after the statistical evaluation, the results were graphically presented. Sensory profiles of salad dressings were demonstrated.

All measurements were conducted in triplicate and the mean values were presented in the tables and graphs.

Results and discussion

The amount of flavoring substances (relative to the extracts) was as follows: at 5 h – 0.02%, at 7 h – 0.03%, at 9 h – 0.03%. With increasing the duration of extraction from 5 to 7 hours, increase the content of flavoring substances by 50% and then remains unchanged regardless of time.

The air-dry leaves were moistened with water to reach humidity of the fresh leaves and after being kept in a closed vessel for 12 hours (for a more complete diffusion of water in the dry leaves) were extracted. The quantity of flavoring substances in the oil extracts was 0.03% and it did not differentiate each other. In the processed raw material, the content of flavoring substances ranged from 2.2 to 2.25%.

Sensory attributes and chemical content in the oil extracts were measured after 7 h extraction and then the same extracts were added in salad dressing's formulation.

The oil extracts were different regarding to their aroma and the sample with humid leaves had more pronounced smell (Table 2).

Table 2

Attributes of essential oil extracts

Attributes	From dry leaves	From humid leaves
Appearance	Oily fluid	
Color	Yellow	
Smell	Specific	Strong, Specific

Chemical composition of the extracts was determined and is listed in Table 3.

Table 3

Percentage composition of the extracts, %

№	Components	RI	From dry leaves	From humid leaves
1	α -pinene	939	0.35	0.37
2	Camphenan	954	0.31	0.31
3	Sabinene	971	0.10	0.11
4	β -pinene	979	0.28	0.30
5	β -myrcene	991	0.11	0.12
6	δ -2-carene	1001	0.05	0.06
7	δ -3-carene	1007	0.21	0.21
8	p-cymene	1025	3.12	3.28
9	1,8-cineole	1032	43.65	45.94
10	β -ocimene	1040	0.15	0.16
11	γ -terpinene	1055	0.52	0.54
12	Terpinene	1087	0.33	0.35
13	β -linalool	1096	0.67	0.70
14	n-nonanal	1128	0.18	0.19
15	Verbenol	1131	0.20	0.21
16	L-trans-pinocarveole	1137	0.23	0.25
17	cis- β -terpineol	1143	0.55	0.58
18	Pinocarvone	1152	0.26	0.28
19	terpinen-4-ol	1179	2.88	3.03
20	α -terpineol	1189	2.31	2.44
21	Nerol	1229	0.10	0.10
22	2-decanal	1230	0.18	0.19
23	Bornyl acetate	1269	0.21	0.22
24	α -terpenyl acetate	1333	15.10	15.89
25	eugenol	1363	0.15	0.16
26	β -elemene	1368	0.23	0.24
27	methyleugenol	1371	0.52	0.55
28	ilangene	1387	0.13	0.14
29	calarene	1426	8.48	8.92
30	β -caryophyllene	1426	0.22	0.23
31	α -humulene	1453	0.09	0.09
32	Germacrene D	1484	0.43	0.45
33	β -bisabolene	1502	3.89	5.09
34	Caryophyllene oxide	1574	0.39	0.18
35	(-)-spathulenol	1619	0.58	0.27
36	n-heptadecane	1700	0.33	0.15
37	n-heneicosane	2100	1.05	0.49
38	Phytol	2105	0.50	0.23
39	n-docosane	2200	1.00	0.46
40	n-tricosane	2300	0.66	0.31
41	n-tetracosane	2400	0.64	0.29
42	n-pentacosane	2500	0.94	0.43
43	n-hexacosane	2600	1.20	0.55
44	n-heptacosane	2700	1.37	0.63
45	octacosane	2800	0.48	0.22
46	squalene	2817	1.39	0.64

* unidentified

In extract from dry leaves as seen 46 components representing 97.06% of the total content were identified. Twelve of them were in concentrations over 1% and the rest 34 constituents were in concentrations under 1%. The main components (above 3%) were: 1,8-cineole (43.65%), α -terpinyl acetate (15.10%), calarene (8.48%), β -bisabolene (3.89%) and *p*-cymene (3.12%).

In extract, from humid leaves as seen 46 components representing 96.91% of the total content, were identified. Seven of them were in concentrations over 1% and the rest 39 constituents were in concentrations under 1%. The main components (above 3%) were: 1,8-cineole (45.94%), α -terpenyl acetate (15.89%), calarene (8.92%), β -bisabolene (5.09%), *p*-cymene (3.28%) and terpinen-4-ol (3.03%).

The two extracts had difference by content of aromatic components from those obtained with ethanol (30, 50, 70 and 95%) [10], which might be explained by the selectivity of the extractants. There were differences in the composition of the essential oils [10], and this was probably due to the method of production.

The distribution of the major aromatic compounds in the two oil extracts is shown in Figure 1.

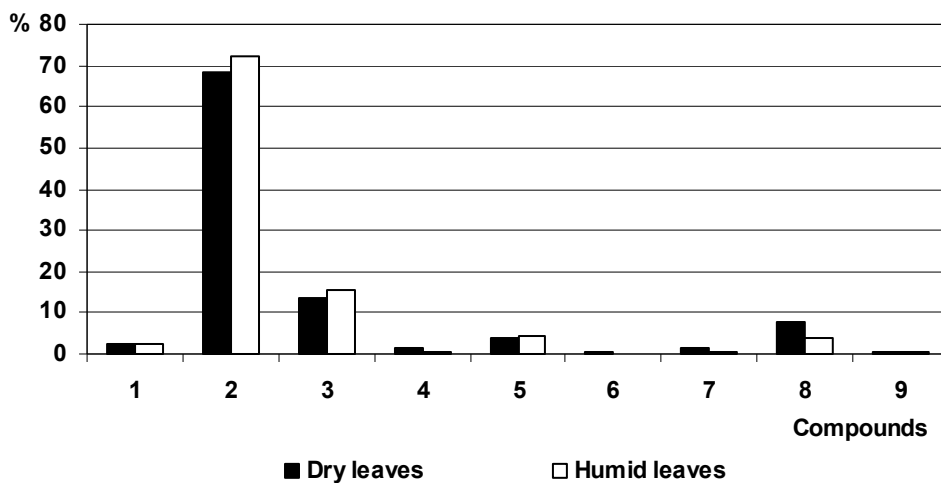


Figure 1. Group of components in essential oils from extracts, %

1 – monoterpene hydrocarbons; 2 – oxygenated monoterpenes; 3 – sesquiterpene hydrocarbons; 4 – oxygenated sesquiterpenes; 5 – phenyl propanoids; 6 – diterpenes; 7 – triterpenes; 8 – aliphatic hydrocarbons; 9 – oxygenated aliphatics.

The data showed that:

- In the extract obtained from dry leaves dominated monoterpene oxygen-containing derivatives (68.47%), followed by sesquiterpene hydrocarbons (13.65%), aliphatic hydrocarbons (7.90%), aromatic compounds (4.10%), monoterpene hydrocarbons (2.33%), triterpene (1.43%), sesquiterpene oxygen-containing derivatives (1.23%), diterpene (0.52%) and aliphatic oxygen-containing derivatives (0.37%).
- In the extract obtained from humid leaves dominated monoterpene oxygen-containing derivatives (72.19%), followed by sesquiterpene hydrocarbons (15.41%), aromatic compounds (4.32%), aliphatic hydrocarbons (3.64%), monoterpene hydrocarbons (2.45%), triterpene (0.66%), sesquiterpene oxygen-containing derivatives (0.70%), aliphatic oxygen-containing derivatives (0.39%) and diterpene (0.24%).

Oil extracts had difference from essential oil and ethanol extracts [10] by content of the essential monoterpene oxygen-containing derivatives that were odor-determining components, although they were derived from the same raw material (Figure 2). This can be attributed the way of production for the other two products – oil distillation and extraction and the use of different technological parameters – extractor, temperature, and duration.

Other authors [4] had found similar dependencies on the differences in the composition of different flavoring products obtained from the same raw material.

The results of sensory evaluation of the salad dressings are shown in Table 4. The color perception of the samples was perceived as equal according to the data from the analysis of appearance. According to the evaluators, dressings had a bright, almost white color, due to the low content of the oil in the formulation. The addition of extracts from laurel leaves had no effect on the color characteristics of the food products. Other authors also confirm the bright color of low-fat food emulsions, which, in their opinion, is also due to the presence of thickening agents (starch and gums) [14].

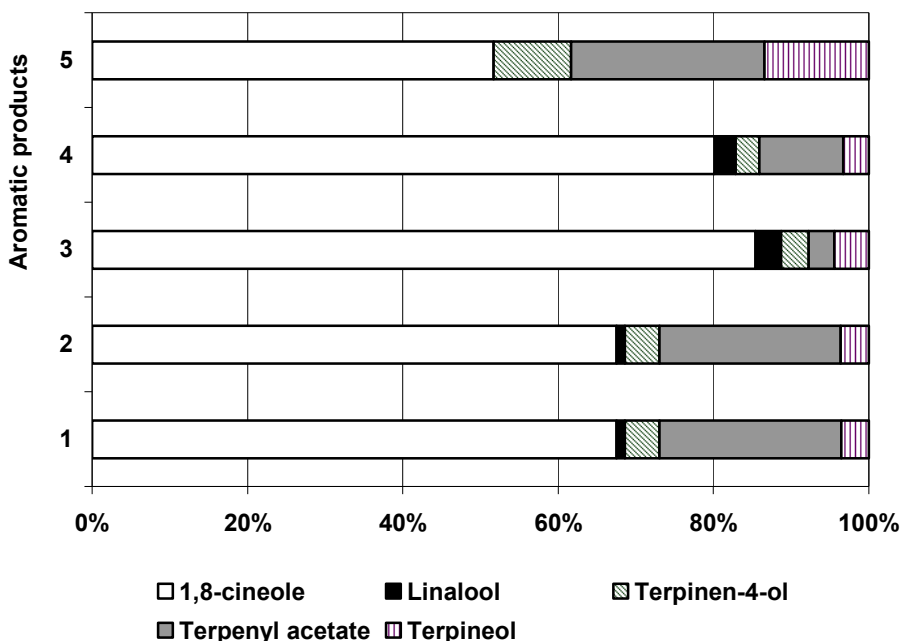


Figure 2. Distribution of monoterpene oxygen-containing derivatives
 1– oil extracts from dry leaves; 2– oil extract from humid leaves; 3– extract with 30% ethanol;
 4– extract with 50% ethanol; 5– essential oil

Table 4

Sensory evaluation of salad dressings with extracts from laurel leaves

Attributes	Control sample	Salad dressings with extract from dry leaves	Salad dressings with extract from humid leaves
Yellow color	3.0±1.4a	3.7±1.4a	3.0±0.9a
Brightness	3.0±0.9a	2.7±0.8a	2.5±1.0a
Stability	8.0±1.3a	7.5±1.8a	8.8±0.4b
Consistency (fluid to firm)	4.0±1.8a	3.8±1.5a	4.2±1.9a
Adhesion (adhesiveness)	1.8±1.0a	1.7±0.8a	1.7±0.8a
Oiliness	3.2±1.2a	3.5±1.4a	3.5±1.4a
Homogeneity	7.3±1.0a	7.7±0.5a	7.8±0.8a
Smell – laurel leaf	1.3±0.8a	4.8±1.0b	7.5±1.2c
Rancidity smell	1.5±0.5a	1.5±0.5a	1.5±0.5a
Salty taste	4.0±1.4a	4.2±1.0a	4.5±1.0a
Taste – laurel leaf	1.2±0.4a	5.8±0.8b	7.7±1.0c
Rancidity taste	1.3±0.5a	1.3±0.5a	1.3±0.5a
Sour taste	2.2±1.0a	2.8±1.2a	2.7±1.2a
Bitter aftertaste	1.2±0.4a	1.8±0.8a	1.8±0.8a
Bitter aftertaste	1.2±0.4a	1.8±0.8a	1.8±0.8a
Aftertaste – laurel leaf	1.8±1.0a	6.0±1.1b	7.2±0.8c
Overall acceptability	5.5±1.4a	5.2±1.3a	7.3±1.2b

Means ± SD values followed by the same letter in each line are not significant different at $p \leq 0.05$ by ANOVA

In terms of stability, all products were accepted at equal sensory stability. There was no separation of oil on the surface of the products. Regarding to the viscosity, the evaluators defined dressings as products with a flowing consistency.

It was observed that dressings with an oil extract of humid leaf had most intensive smell of laurel leaf. This is explained by the higher content of monoterpenic oxygen-containing derivatives that are responsible for taste and aroma. The same is true when this sample was also perceived with the most intensive taste of laurel leaf. It was also found out that the sour and salt taste was equally appreciated for all three samples because of the same amounts of salt and citric acid used in their composition.

The evaluators didn't take into account the rancid flavor of the products, which is an indicator of the vegetable oil quality.

After consumption of the emulsion products, the after taste of the laurel leaf, determined with the highest intensity of perception, was more pronounced in products with oil extract obtained from humid leaves. Bitter aftertaste was almost unrecognizable in all three samples.

The results for the overall acceptability of the three products showed that the oil extract obtained from humid leaves was preferred and between the oil extract obtained from dry leaves and the control sample the evaluators didn't not express a preference. A higher total score was obtained by salad dressing with an oil extract obtained from humid leaves.

Experimental data from Figure 3 and Figure 4 shows the perceived attributes of the investigated samples graphically presented.

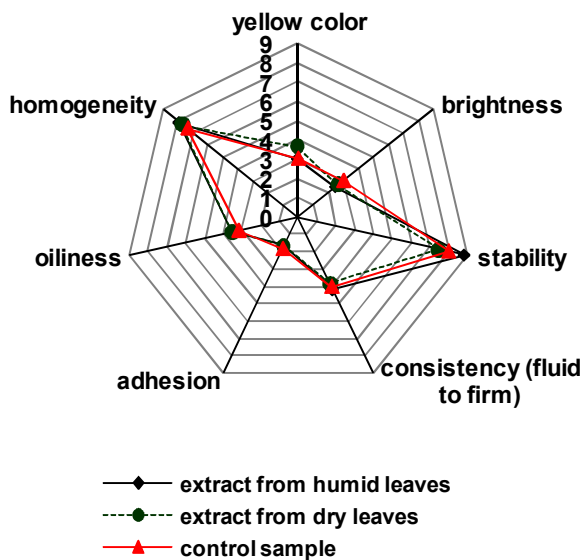


Figure 3. Appearance and texture sensory profiles of salad dressings with oil extracts from laurel leaves

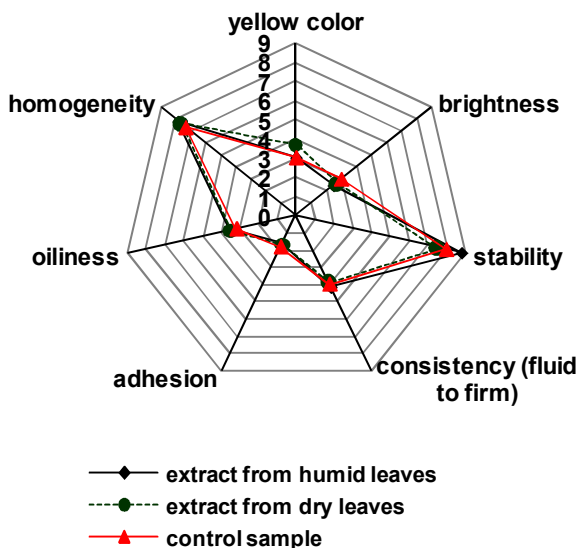


Figure 4. Smell and taste sensory profiles of salad dressings with oil extracts from laurel leaves

Conclusion

Extracts from laurel leaves are appropriate ingredients of salad dressings and they improve sensory profiles of food products. Oil extract obtained from humid leaves was preferred and between the oil extract obtained from dry leaves and the control sample the evaluators didn't express a preference. A higher total score was obtained by salad dressing with an oil extract obtained from humid leaves.

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Production of active coal from pyrolyzed wood wastes by alkaline activation of KOH

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Abstract

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Introduction. The purpose of this publication is to evaluate an alternative renewable raw materials obtained from the food industry wastes (pyrolyzed wood wastes – PWW) as precursors for production of active coal (AC) used in a process of water purification in alcoholic beverages' production.

Materials and methods. PWW of meat processing industry. PWW will be used as a raw material for a production of AC. Chemical activation of PWW by alkaline activation of KOH. Method of adsorption–desorption of nitrogen to determine a porous structure at 77 K; mesopores' distribution by size and by mesopores' volume – BJH-method; micropores' division by size – QSDFT-method; volume of micropores – Dubinin-Radushkevich method; subnanopores' volume – QSDFT-method.

Results and discussion. The microporous structure has the following characteristics: pores' diameters are in the range of $D_{mi}=0,61-2,5$ nm, most represented pores' diameters are 0,61; 1,19; 1,54 nm; volume of micropores – $V_{mi}=0,11-0,30$ cm³/g; pores' surface area – $S_{mi}=407-852$ m²/g; pores' differential volume – $dV_{mi}/dD=(0,023-1,400) \cdot 10^{-2}$ cm³/g; pores' differential area – $dS_{mi}/dD=(0,18-45,60)$ m²/g. There are 70,31% of micropores in a total pores' volume. Dominant contribution of micropores into specific surface of the pores shows a proportional dependence between pores' volume and surface area of pores. It is also confirmed by the linear dependence between the pores' differential volume and the differential area. The smallest pores – subnanopores with $D \leq 1$ nm were defined at the micropores structure. Subnanopores' diameters are in the range of $D_{1nm}=0,61-1,00$ nm. Subnanopores' volume varies in the range of $V_{1nm}=0,11-0,25$ cm³/g. Pores' surface area is $S_{1nm}=407-783$ m²/g; pores' differential volume: $dV_{1nm}/dD=(11,3-140,0) \cdot 10^{-4}$ cm³/g; differential area is $dS_{1nm}/dD=(2,33-45,60)$ m²/g. The subnanopores' portion at the micropores' volume is 84,12%. The share of subnanopores' at the total pores' volume is 59,15%. It can be argued that the alkaline activation of KOH leads to a development of subnanopores in the porous structure of the adsorbent. The cited data shows that the proposed method allows to obtain AC with an output ratio of 70,4%. The obtained AC has a developed specific surface of $S_{BET}=777$ m²/g and porosity. Total pores' volume is $V_{\Sigma}=0,421$ cm³/g.

Conclusion. An energy-saving method is proposed for the production of high porous AC from the secondary «renewable» resources – PWW. It is advised to use it in alcoholic beverages production.

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Introduction

A search for economically feasible ways of obtaining cheap sorbent materials in a purification of contaminated environment remains an urgent problem for all the countries around the world. Carbon adsorbents occupy a significant place among such materials. This kind of raw material has a gigantic range of precursors (natural coal, peat, wood, carbonaceous wastes of various origins, etc.) [1–12]. Therefore, there is an urgent need to obtain AC from an alternative material. The search for these materials could involve existing technologies of food industry. Wastes from these industries can be used to produce the adsorbents [4–8, 11–26].

There two ways of getting AC that are known today: chemical [1, 4–6, 10–13, 15, 16, 19, 21–23, 26–28] and physical activation [1, 10, 15, 17, 21]. Benefits of chemical activation are one-step process; low activation temperature; short activation time; large yield; high surface; well-developed controlled microporosity [28]. Chemical activation involves usage of activating agent ($ZnCl_2$ [4], H_3PO_4 [9, 11, 12, 16, 23, 26], $NaOH$ [28], KOH [27, 28], et al.), entered by impregnation, followed by carbonization of raw materials in the atmosphere of inert gases and activation [1].

There are many ways of receiving AC (Kumar, Jena, 2017; Yorgun, Yildiz, 2015; Kucherenko et al, 2010; Lillo-Rodenas, 2003) [4, 11, 27, 28], (Pat. 61059 Ukraine): grinding carbon-containing material with $(1-2) \cdot 10^{-3}$ m, mixing it with KOH in solid form in a weight ratio 1:1, carbonizing and activating at heatstroke mode, cleaning with water and drying. This method (Pat. 61059 Ukraine) has its 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 a gaseous components; high temperature carbonization and activation of AC; activation in a heatstroke mode causes tearing of the structure and reduction of AC shares; low rate of AC release.

The most promising raw material for AC is PWW. PWW is formed by pyrolysis of wood chips (Kuzmin, Shendrik, 2016) [10]. In a proposed method grinding materials are not required as AC wood chips' size is $l \times b \times h = (6 \times 12 \times 3) \cdot 10^{-3}$ m; AC fractional increases up to $3,6 \cdot 10^{-3} > d \geq 1,0 \cdot 10^{-3}$ m; temperature reduction of charcoal's carbonization and activation within $T = 773-973$ K; absence of activation heat stroke due to carbonization at non-isothermal heating and isothermal heating at activation; yield increases of AC ratio.

KOH is one of the promising activating agents (Kucherenko V.A. et al, 2010; M.A. Lillo-Ródenas et al, 2007) [27, 28]. It is added to the brown coal. It can withstand up to full impregnation, allowing alkali to interact with organic and mineral components, with the formation of water-soluble substances washed with AC.

Thus, the use of KOH allows to receive AC with a formed pores' space. Variation of mass part (MP) of activating agent in relation to PWW can affect the surface pores' factor, yield ratio of AC and volume of wastewater [29–37].

A blend of raw material/agent during carbonization and activation undergoing non-isothermal heating up to an activation temperature during the subsequent isothermal aging. At the same time low molecular parts of thermal distraction of organic matter of PWW and products of PWW's chemical reactions with alkali are formatted in a PWW's volume. It's outflow from the PWW's volume creates a spatial framework within PWW. It leads to a formation of micropores and subnanopor and, consequently, increases the pores' specific surface area and total volume. This improves adsorption characteristics of AC (Shendrik et al, 2003; Kucherenko et al, 2010; Zubkova, 2011) [27, 29, 30]. AC's fractional composition is determined by MP's residue on sieves with holes with a diameter of 3,6 mm, 1,0 mm and on the pallet itself.

It has been shown that PWW can be an alternative carbon-containing raw material for AC

production (Kuzmin, Shendrik, 2016) [10]. The aim of this work is to evaluate an alternative renewable raw materials from the food industry wastes (pyrolyzed wood wastes – PWW) as precursors for production of active coal (AC) which can be used for water purification in alcoholic beverages' production.

Materials and methods

Conditions for AC production are presented at Table 1.

Table 1

Terms of AC

Sym bol	Characteristic	Experimental data	Rationed data
T_1	Drying temperature 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	PWW's outdoor drying time, s	$336 \cdot 60^2$	$(336-504) \cdot 60^2$
T_2	Drying temperature in the drying cabinet, K	373	373–383
W_2	MP of moisture of PWW,%	6,58	4–8
	MP of <i>KOH</i> in aqueous solution,%	50	30–70
	Mass ratio (MR) of PWW/alkali, kg/kg	1:1	1:0,5–1:1
τ_2	Time withstand of PWW with alkali, s	$24 \cdot 60^2$	$(18-24) \cdot 60^2$
T_3	PWW alkali holding temperature, K	294	291–295
T_4	Drying temperature, K	381	373–383
W_3	MP of moisture of PWW,%	6,78	4–8
Q_1	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	$\leq 0,07$
	MP of sulfuric acid,%	96	96
T_5	Activation temperature, K	1073	873–1073
τ_3	Time of activation, s	$1 \cdot 60^2$	$1 \cdot 60^2$
	Non-isothermal cooling, deg./s	0,1	$\leq 0,1$
T_6	Final temperature after cooling of AC, K	323	≤ 323
τ_4	Time cleaning of AC from activating agent, s	600	300–600
T_7	Drying temperature in the drying cabinet, K	378	373–383
W_4	MP moisture AC,%	5,84	4–8
Y_1	AC yield ratio,%	70,4	70–80
	MP of remnant of AC (%) in the sieve with holes, m: $d \geq 3,6 \cdot 10^{-3}$ $3,6 \cdot 10^{-3} > d \geq 1,0 \cdot 10^{-3}$ $d < 1,0 \cdot 10^{-3}$	0,2 87,6 12,2	MP<2,5 MP≥95,5 MP<2,0

Obtained PWW is dried in the open air ($T_1=293-298$ K; $W_1=67-82\%$; $v_1=1-2$ m/s) during $\tau_1=(336-504) \cdot 60^2$ s, followed by more drying at $T_2=373-383$ K up to air-dry state with humidity of $W_2=4-8\%$.

KOH (MP *KOH* in aqueous solution – 30–70%) used as an activating agent for impregnating

of PWW/alkali in MR 1:0,5–1:1. The received mixture withstands for $\tau_2=(18-24)\cdot 60^2$ s at $T_2=291-295$ K and PWW dried to receive a constant weight of MP moisture $W_2=4-8\%$ at $T_2=373-383$ K. Activation carried out in a stream of argon with a volumetric flow of $Q_1\leq 5,6\cdot 10^{-7}$ m³/s with drying bubbling after 96% in sulfuric acid under non-isothermal heating at 0,07 deg./s up to activation temperature $T_5=873-1073$ K and isothermal aging for $\tau_3=1\cdot 60^2$ s at the temperature activation and non-isothermal cooling at 0,1 deg./s in a stream of argon upto a temperature $T_6=323$ K.

The received AC cleaned from activating agent with a usage of water for $\tau_4=300-600$ s and dried at a temperature $T_7=373-383$ K up to a level of humidity $W_4=4-8\%$ with the yield of AC $Y_1=70-80\%$, followed by fractioning with the help of MP residue on sieves with holes: $d\geq 3,6\cdot 10^{-3}$ m – MP $\leq 2,5\%$; $3,6\cdot 10^{-3}>d\geq 1,0\cdot 10^{-3}$ m – MP $\geq 95,5\%$; $d<1,0\cdot 10^{-3}$ m – MP $\leq 2,0\%$ with the following selection of working faction on a sieve with holes $3,6\cdot 10^{-3}>d\geq 1,0\cdot 10^{-3}$ [9].

Figure 1 shows the stages of AC production; Figure 2 – general scheme of AC obtaining as per experimental data at Table 1.



Figure 1. Stages of receiving AC:

a – technological chips of oak large $(6\times 12\times 3)\cdot 10^{-3}$ m; *b* – PWW with MP moisture $W=43,01\%$; *c* – PWW after drying of moisture MP $W=6,58\%$; *d* – AC to fractionation; *e* – AC after fractionation of $d\geq 3,6\cdot 10^{-3}$ m; *f* – AC after fractionation of $3,6\cdot 10^{-3}>d\geq 1,0\cdot 10^{-3}$ m; *g* – AC after fractionation of $d<1,0\cdot 10^{-3}$ m

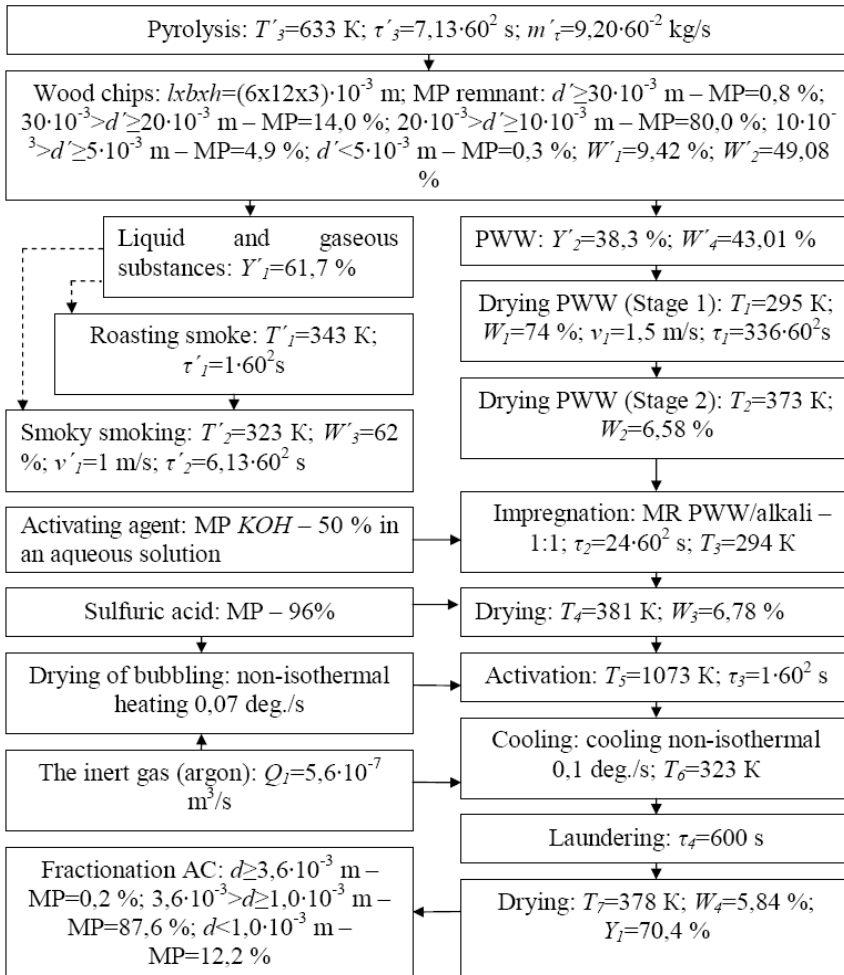


Figure 2. The general scheme of AC production as per experimental data

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 – $W_2=6,58\%$. Potassium hydroxide with MP $KOH - 50\%$ in an aqueous solution, injected by impregnation of PWW – KOH and kept for $\tau_2=24\cdot60^2$ s at temperature $T_3=294$ K, dried up to a moisture obtained at MP PWW $W_3=6,78\%$ at $T_4=381$ K. The volume of solution has been chosen to create MR PWW/alkali – 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 $Q_1=5,6\cdot10^{-7}$ m³/s, drained bubbling through concentrated sulfuric acid (96%). The heating of reactor's furnace has been switched on after $0,17\cdot60^2$ 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 $\tau_3=1\cdot60^2$ s and rapid cooling in a

stream of argon cooled at non-isothermal 0,1 deg./s to $T_6=323$ K. Activation temperature was $T_5=1073$ K when activated via *KOH*.

Samples of AC activating agent washed with distilled water for $\tau_4=600$ s and dried at $T_7=378$ K to humidity $W_4=5,84\%$ of the yield of AC $Y_1=70,4\%$. Fractionation AC remnant of MP conducted on sieves with holes: $d \geq 3,6 \cdot 10^{-3}$ – MP=0,2%; $3,6 \cdot 10^{-3} > d \geq 1,0 \cdot 10^{-3}$ – MP=87,6%; $d < 1,0 \cdot 10^{-3}$ (pallet) – MP=12,2% with the following collection of working fractions on sieves of 3,6 mm and 1,00 mm MP – 87,8%.

Results and discussions

Characteristics of porous structure was determined on a basis of isotherms of an 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 3).

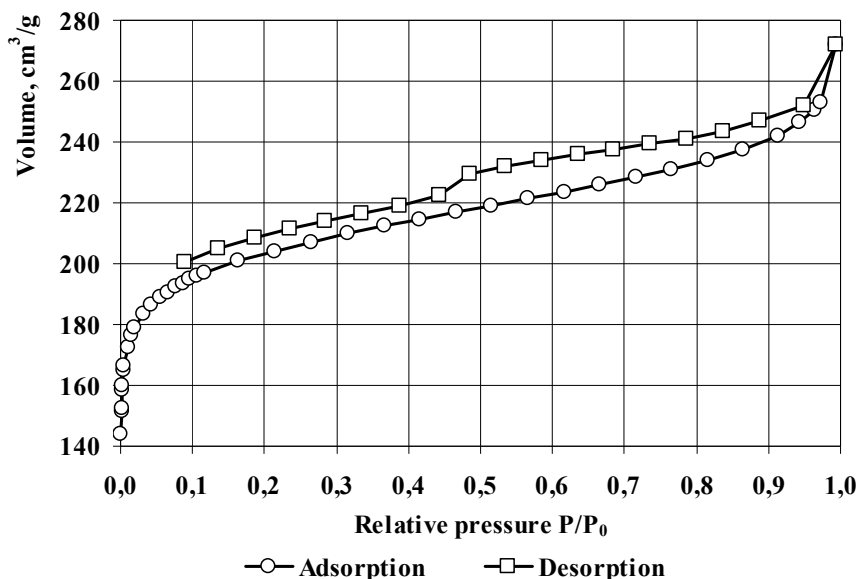


Figure 3. Isotherms of an adsorption-desorption of nitrogen at AC at $T=77$ K

The obtained isotherms of type II – according to Brunauer S. et al, 1938 [31] classification, 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.

Figures 4–7 shows the distribution of micropores (*QSDFT*–method), the size of the sample and the corresponding volumes accumulated in these pores.

The microporous structure has the following characteristics (Figure 4–5): pore diameters are in the range of $D_{mi}=0,61-2,5$ nm, mostly represented by pores with a diameter of 0,61; 1,19; 1,54 nm; volume of micropores – $V_{mi}=0,11-0,30$ cm^3/g ; pores' surface area – $S_{mi}=407-852$ m^2/g ; pores' differential volume $dV_{mi}/dD=(0,023-1,400) \cdot 10^{-2}$ cm^3/g ; pores' differential area $dS_{mi}/dD=(0,18-45,60)$ m^2/g ; micropores are about 70,31% of the total pore volume.

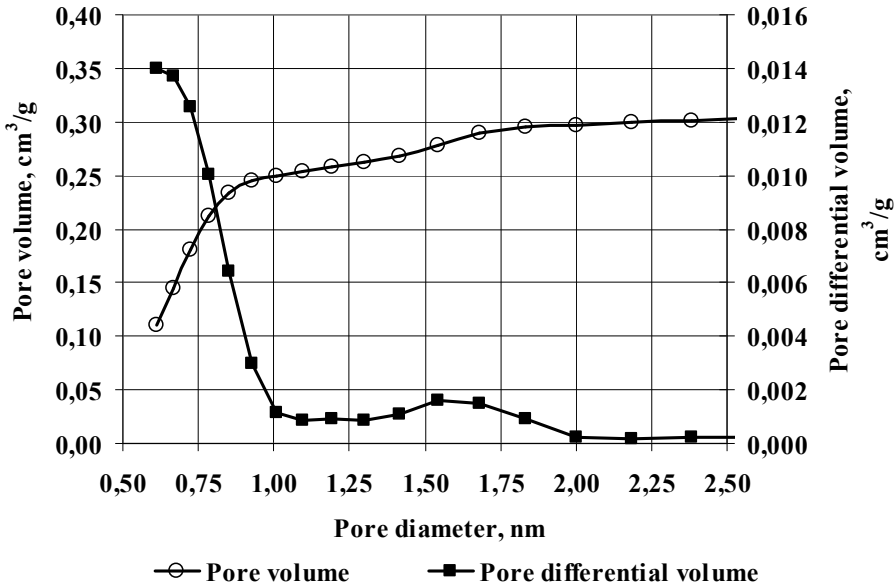


Figure 4. Distribution of micropores by size of AC sample – (dependence of pores' volume and pores' differential volume on pores' diameter) by *QSDFT*-method

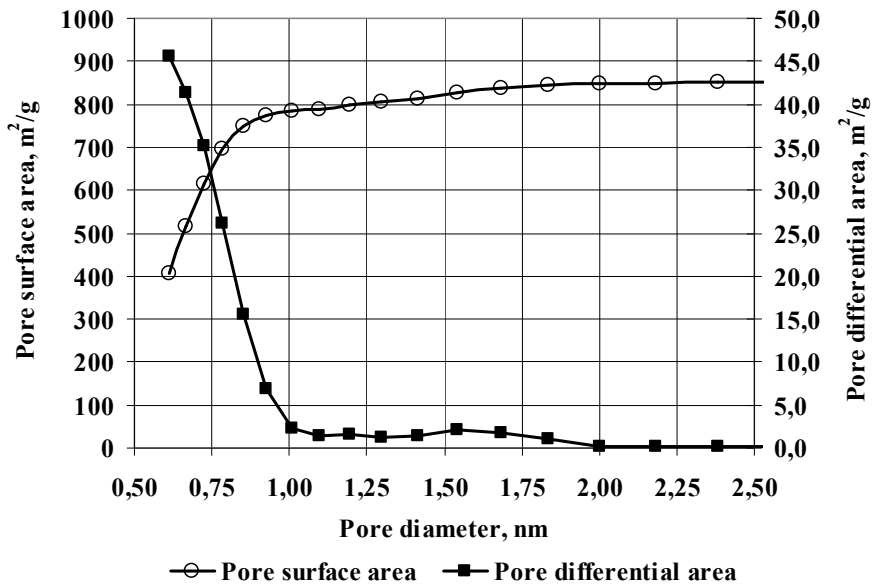


Figure 5. Distribution of micropores by size of AC sample – (dependence of surface area and pores' differential surface area on pores' diameter) by *QSDFT*-method

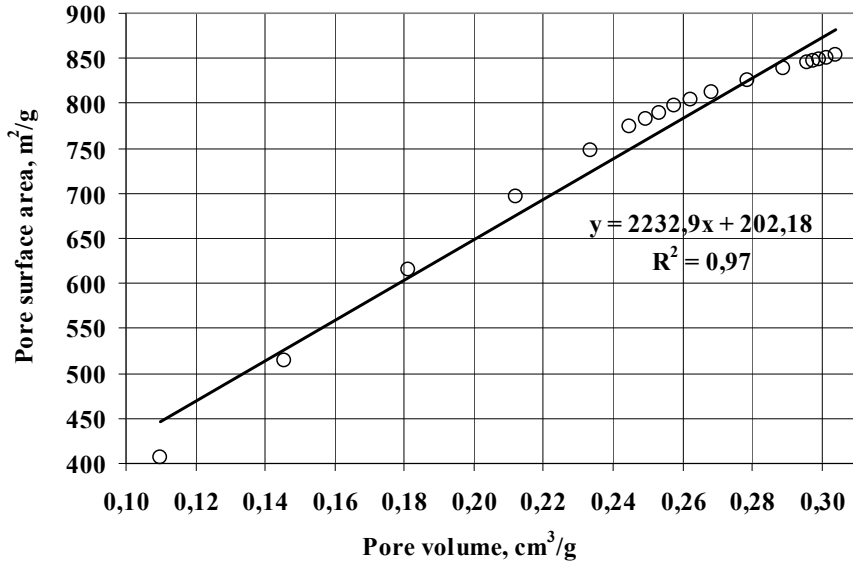


Figure 6. Distribution of micropores by size of AC sample – (dependence of pores' volume on pores' surface area) by *QSDFT*-method

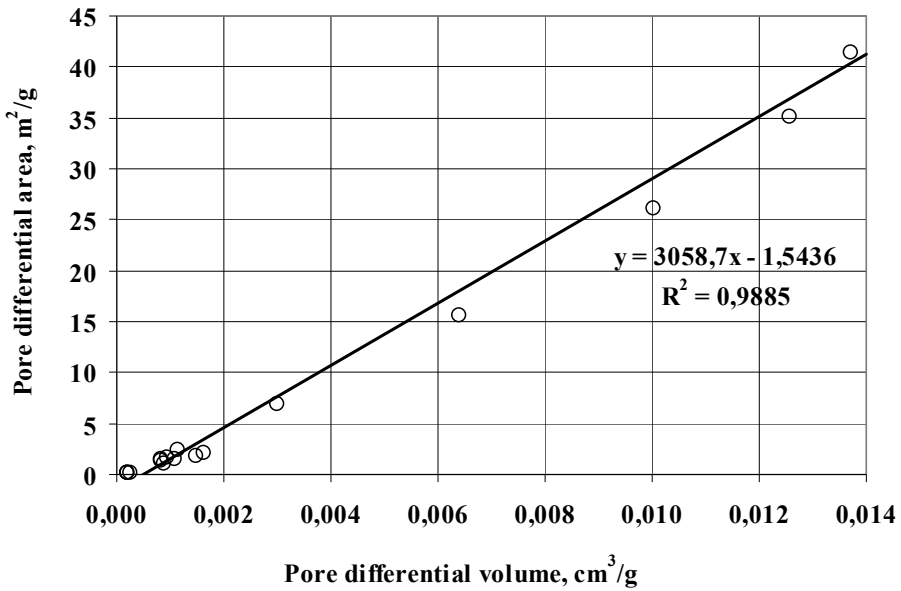


Figure 7. Distribution of micropores by size of AC sample – (dependence of pores' differential volume on pores' differential surface area) by *QSDFT*-method

According to distribution of micropores by size, two areas of values can be distinguished: a dynamic range ($D_{mi}=0,5-2,0$ nm) of values with several maxima; a stationary range of values ($D_{mi}=2,0-2,5$ nm). The main differences are fixed at the dynamic range of values ($D_{mi}=0,5-2,0$ nm). We can observe three maximum values: at $\sim 0,6$ nm, weakly expressed at $\sim 1,2$ nm, maximum at $\sim 1,5$ nm. The differential pore volume is in the range of $dV_{mi}/dD=(1,9-2,1)\cdot 10^{-4}$ cm³/g at the static range of values $D_{mi}=2,0-2,5$ nm. The differential area is in the range of $dS_{mi}/dD=(0,18-0,20)$ m²/g.

The dominant contribution of micropores in the specific surface of the pores shows a proportional relationship between the pores volume and the surface area of pores. This is also confirmed by the linear dependence between the pores' differential volume and the pores' differential area (Figure 6–7).

The subnanopores with $D\leq 1$ nm – the smallest pores were considered in the micropores' structure (Figure 4–5): pores' diameters are in the range of $D_{Inm}=0,61-1,00$ nm; subnanopore's volume varies in the range of $V_{Inm}=0,11-0,25$ cm³/g; pores' surface area: $S_{Inm}=407-783$ m²/g; pores' differential volume: $dV_{Inm}/dD=(11,3-140,0)\cdot 10^{-4}$ cm³/g; pores' differential area: $dS_{Inm}/dD=(2,33-45,60)$ m²/g. The subnanopore's portion in the micropores volume is 84,1%. The share of subnanopore's in the total pores' volume is 59,2%. It can be argued that the alkaline activation of *KOH* leads to the development of a subnanopore's in the porous structure of the adsorbent.

Figures 8–13 show the distribution of mesopores (*BJH*-method) by size in the sample and the corresponding volumes accumulated in these pores.

In Figure 8, the curve of the pores' size set with its size increasing smoothly, not reaching the plateau, indicating the presence of mesopores with a wide distribution in size.

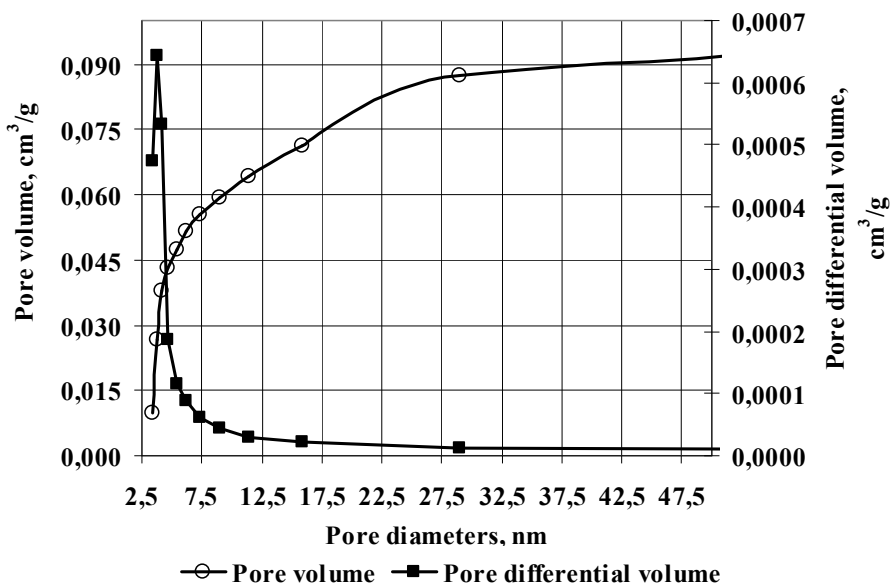


Figure 8. Distribution of mesopores by size of AC sample – (dependence of pores' volume and pores' differential volume on pores' diameter) by *BJH*-method

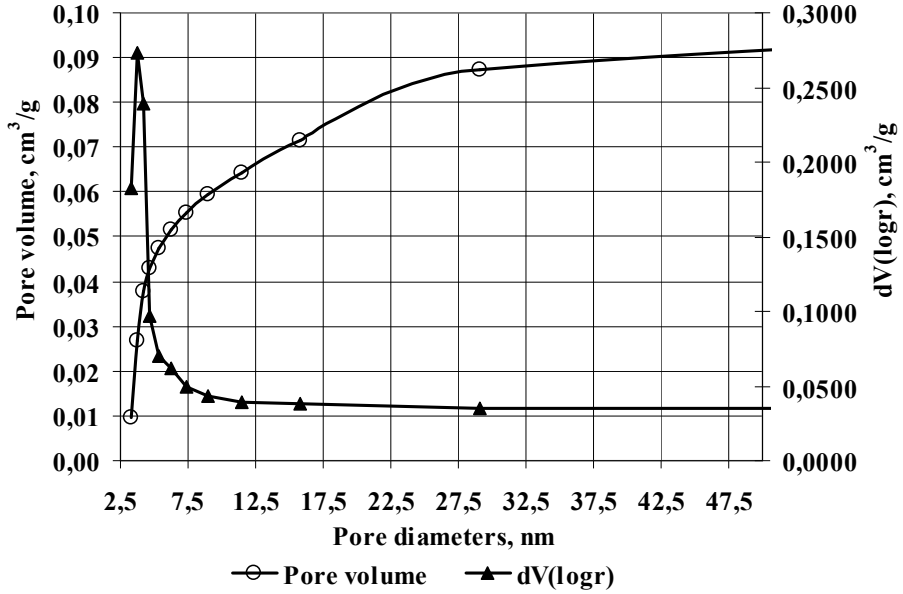


Figure 9. Distribution of mesopores by size of AC sample – (dependence of pores' volume and pores' $dV(\log r)$ on s' diameter) by *BJH*-method

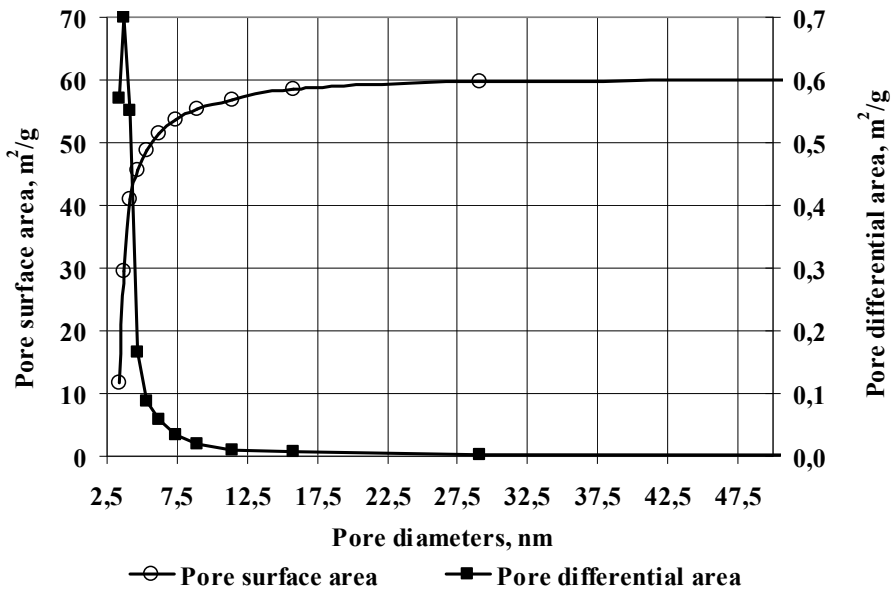


Figure 10. Distribution of mesopores by size of AC sample – (dependence of pores' surface area and pores' differential surface area on pores' diameter) by *BJH*-method

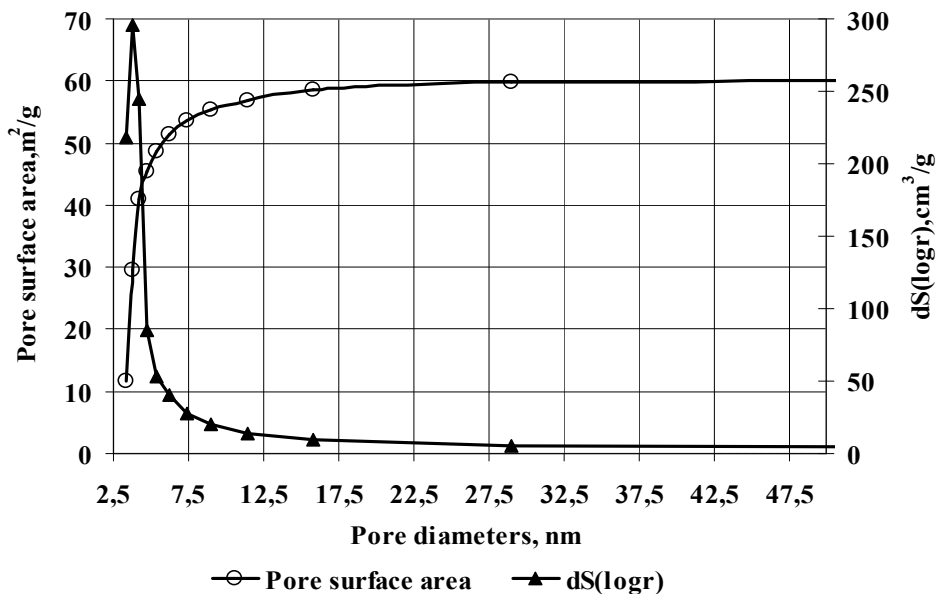


Figure 11. Distribution mesopores the size of AC sample – (dependence of pores' surface area and pores' $dS(\log r)$ on pores' diameter) by the *BJH*-method

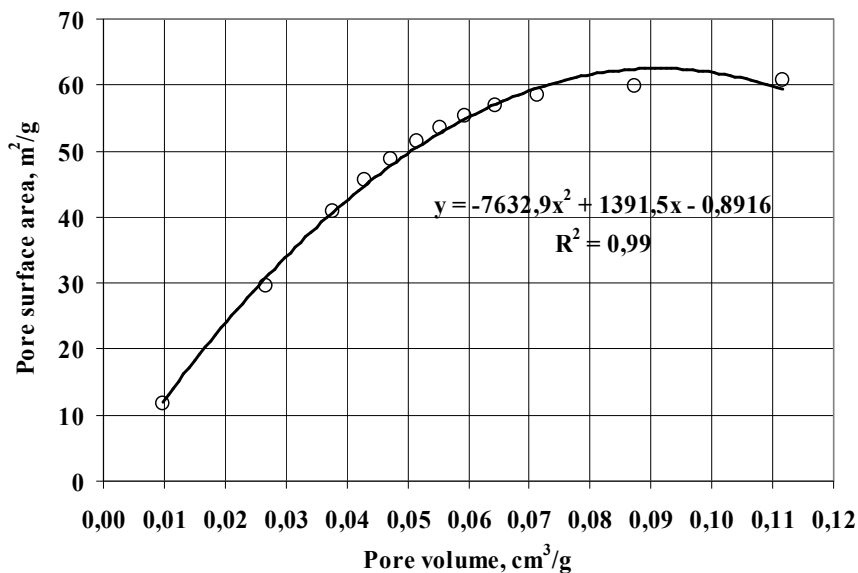


Figure 12. Distribution of mesopores by size of AC sample – (dependence of pores' surface area on pores' volume) by the *BJH*-method

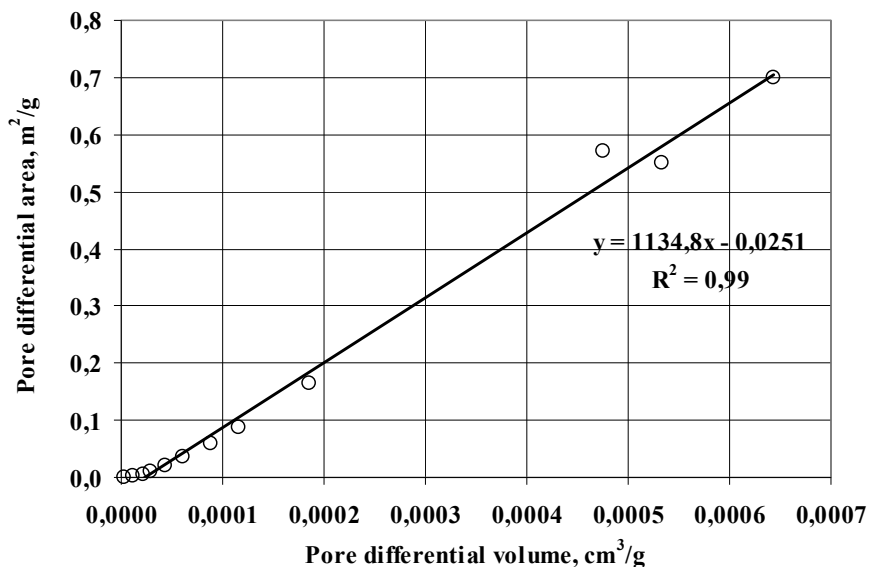


Figure 13. Distribution of mesopores by size of AC sample – (dependence of pores’ differential area on pores’ differential volume) by the *BJH*-method

Mesoporous structure has the following characteristics: pores’ diameters are in the range of $D_{me}=3,3-50,0$ nm, most represented pores with a diameter of 3,73 nm; mesopore volume varies in the range of $V_{me}=0,010-0,091$ cm³/g; pores’ surface area – $S_{me}=11,7-60,0$ m²/g; pores’ differential volume $dV_{me}/dD=(0,02-4,75) \cdot 10^{-4}$ cm³/g; pores’ differential area $dS_{me}/dD=(0,002-0,570)$ m²/g; fraction of mesopores in the total pores’ volume is 2,14–21,6% (Figure 8–13).

Curves of pores’ differential volume and pores’ differential surface area at the interval of $D=15,8-50,0$ nm are in the static area. Maximum location of pores with a smallest diameter is observed at the pores’ differential volume $dV_{me}/dD=6,43 \cdot 10^{-4}$ cm³/g at the point of 3,73 nm within $D=2,5-15,8$ nm. The biggest number of mesopores are located at the range of $D=2,5-15,8$ nm.

The terms of AC and its characteristics are shown at the Table 2. The following characteristics of AC were measured: Y – yield (%); S_{BET} – specific surface area; V_{Σ} – pores’ total volume; V_{ma} – macropores’ volume; V_{me} – mesopores’ volume; V_{mi} – micropores’ volume; V_{Inm} – subnanopores’ volume; A_{phenol} – sorption capacity toward phenol; A_{Pb} – sorption capacity toward Plumbum; A_{MB} – sorption capacity toward methylene blue.

Comparison of distribution of porous space according to (Pat. 61059 Ukraine) to the experimental data is presented at the figure 14.

A method that allows the production of AC from PWW, generated after the process of food products’ smoking has been proposed. Moreover, PWW is subsequently heated non-isothermally and chemically activated in the presence of *KOH*. As a result, AC is produced with a high yield of 70–80%, developed specific surface, porous space and a high sorption capacity. The results of AC production can be adapted for the technology of alcoholic beverages’ production at the expense of 1,0–3,6 mm particles’ fractional composition.

Table 2

Terms of AC and its characteristics

Characteristic	Method of AC production (Pat. 61059 Ukraine)		Method of AC experimental production	
Type of raw material	Lignite (brown coal)		PWW	
Activation temperature, K	1073		1073	
Activating agent	KOH		KOH	
State of the activating agent	solid		solution 50%	
MR raw/agent, kg/kg	1:0,5		1:1	
$Y, \%$	39,0		70,4	
$S_{BET}, m^2/g$	890		777	
$V_{\Sigma}, cm^3/g$	0,580	100%	0,421	100%
$V_{ma}, cm^3/g$	0,010	1,73%	0,034	8,08%
$V_{me}, cm^3/g$	0,250	43,10%	0,091	21,61%
$V_{mi}, cm^3/g$	0,320	55,17%	0,296	70,31%
$V_{1nm}, cm^3/g$	0,230	39,66%	0,249	59,15%
$A_{Phenol}, mg/g$	120		200	
$A_{Pb}, mmol/g$	-		0,7	
$A_{MB}, mg/g$	92		150	

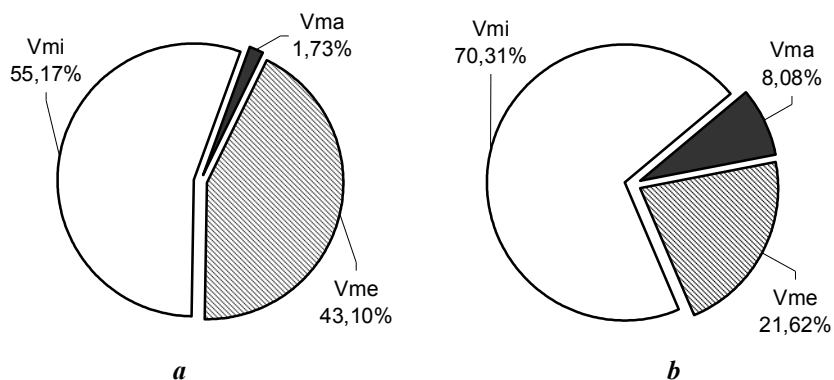


Figure 14. Distribution of pores in AC:

a – according to Pat. 61059 Ukraine; *b* – according to experimental data.

The attention is drawn to the volume of pores' with $D \leq 1$ nm. It accounts to 59,15% of the total pores' volume in AC. The obtained data allows us to hope that the studied raw materials can be used for the purification of water-alcohol mixtures.

Conclusions

The data show that the proposed method allows to obtain AC with a high yield of 70,4% compared to the method of obtaining AC from lignite (Pat. 61059 Ukraine) – 39,0%. Experimentally received AC has a lower specific surface $S_{BET}=777 \text{ m}^2/\text{g}$ with respect to AC (Pat. 61059 Ukraine) $S_{BET}=890 \text{ m}^2/\text{g}$ and pores' space: total pores' volume $V_{\Sigma}=0,421 \text{ cm}^3/\text{g}$ to $V_{\Sigma}=0,580 \text{ m}^3/\text{g}$. Nevertheless, the ratio of micropores in the experimental sample (70,31%), increased in relation to the prototype (55,17%), and the ratio of subnanopores in the experimental sample (59,15%), increased in relation to the prototype (39,66%). The ratio of macropores in the experimental sample (8,08%), increased in relation to the prototype (1,73%). At the same time the ratio of mesopores in the experimental sample (21,61%) reduced relatively to the prototype (43,10%).

It can be concluded that the proposed method of AC production from PWW, produced of smoked foods, with further carbonization at non-isothermal heating and activation at temperature of 873–1073 K in the presence of *KOH*, leads to sorbents with a high yield of 70–80% and fractional composition of particle size of 1,0–3,6 mm (~ 90%). An energy-saving method is proposed for a production of cheap AC from secondary «renewable» resources – PWW. These AC can be examined for water purification in alcoholic beverages' production.

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The nutritional value of desserts with the addition of Gooseberry family raw materials from the Northern Black Sea Region

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Abstract

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Introduction. The studies of new berry raw materials in order to determine the balance of its chemical composition, sensory and technological characteristics in the light of use in dessert production. The technology of jelly production from jostaberry was developed.

Materials and methods. Berries off. *Grossulariaceae* (actinidia, jostaberry, feijoa) were chosen as subject of these studies. The analysis of technical literature and sources of patent information related to utilization of new raw materials and development of new recipes was carried out. Structural strength of jelly was determined by penetration method.

Results and discussion. It was shown, that berry raw materials of Black Sea Region, such as feijoa, actinidia and jostaberry can be used for production of desserts with improved nutrition value. The nutritional value of mentioned berries is specified by presence of broad range of biologically active components in forms, which are available for human organism. In particular, iodine content in feijoa berries reaches 0,07–0,1 mg/100 g. Actinidia and jostaberry contain vitamin C in high concentrations, equal to 400–800 mg/100 g and 450–600 mg, respectively. These berries are the natural concentrates of vitamins A, B, C, P, PP, β -carotene and mineral compounds, such as potassium and iron and can be considered as products with high nutritional value. Due to high pectin content makes actinidia, jostaberry, feijoa are the perspective raw materials for structured desserts, such as jellies, mousses and sorbets. The results of studies of technological characteristics of jellies with jostaberry were presented. It was shown, that introduction of jostaberry in jelly allows to eliminate gelatin from recipe without significant changes of product's rheological characteristics. The values of density and shear stress value of jellies containing 15% of jostaberry are equal to 1,27 kg/m³ and 5,53 kPa, respectively. Therefore the product meets all requirements to this category of desserts. The jellification time of jellies with jostaberry significantly decreases in comparison with samples without it.

Conclusion. New ingredients from plants of Ukraine's Southern region, such as feijoa, actinidia and jostaberry are prospective for broadening the range of desserts with improved nutritional value. The optimal composition of ingredients in recipes of jellies with jostaberry was developed.

Introduction

At present time the problem of diet inadequacy and deficiency is typical for modern world in general as well as for most countries of Eastern Europe. It is connected with consumption of refined product with high energy-value which are lean in terms of content of biologically active components. Imbalance of nutrients in diet and ecological problems lead to the decrease of organism resistance and causes the range of diseases. Health, ability to work and longevity of human organism are based on supply of all needed nutrients. These compounds are to be supplied regularly, in full quantity corresponding to physiological needs.

According to this concept, the structure of typical modern people's diet needs significant correction. This goal can be reached by development of food products with improved nutrition value and their introduction in people's diet. These products may be based on new and non-traditional raw materials as it seems to be the effective way of diet enrichment with biologically active components. Being introduced into foodservice industry, such products can become one of effective methods of diet structure improvement and increasing of healthy food share in it.

Rationalization of nutrition should be reached by increase of fresh fruits and berries share in ration as well as products of their processing as it can become an additional source of natural biologically active components. Exotic fruits and berries which are rich on biologically active components, so their introduction in people's ration can be one of the ways of nutrition structure correction. The introduction of corresponding plants in the agriculture as well as development of processing technologies and corresponding food products is needed to reach this goal. The usage of winter-hardy subtropical cultures in agriculture of the Black Sea region becomes an important part of this strategy. Feijoa, actinidia, jostaberry are among these cultures.

Last years demonstrated that climate the Black Sea region became warmer, with hot and dry summer and mild winter. It enables gardeners to cultivate exotic cultures of fruit and berry plants in this region and in the southern regions of Ukraine including Odessa.

Long-term experiments with subtropical plants enabled selectioners and agriculture specialists to breed new winter-hardy breeds and cultivation technics for gooseberry, actinidia, fig, feijoa, kiwi, jostaberry and date plum for cultivation in open ground with excellent results. This practice is actual for the Black Sea region.

Subtropical berries, including feijoa, actinidia and jostaberry are considered to be herbal sources of biologically active nutrients. The combination of properties, good for human health lets to place these cultures among the most useful for human health.

Feijoa originates from Southern America. It is one of the most winter-hardy subtropical plants and able to stand during short-term frosts (to -15°C) without harm. Due to this specific feature it is successfully cultivated in the Black Sea region of Ukraine, such as Odessa region.

Feijoa berries are green oblong fruits covered with waxy film [1]. They are harvested at the end of November or early December. Feijoa is a new product for the Black Sea region, but it already became popular among nutritionists, diet experts and endocrinologists. It is recommended to people with disorders of thyroid gland and intellectual stresses. The main feature of feijoa is high iodine content (Table 1), which is comparable to this in seafoods. Feijoa berries contain organically bound iodine in concentration, equal to 0,07–0,1 mg/100 g, while the recommended daily consumption for grown-up is equal to 0,14–0,200 mg/100 g. The feijoa berries which are cultivated in maritime regions are especially rich to iodine. Moreover, this iodine is water-soluble and can be effectively consumed by organism.

Table 1

Chemical composition of feijoa, actinidia and jostaberry [2, 3]

Component	Feijoa	Actinidia	Jostaberry
Proteins, g	0,98	0,9	0,7
Fats, g	0,8	0,6	0,2
Carbohydrates, g	10,0	11,9	9,1
Pectin, g	1,5-2,5	0,9	1,1
Ash, g	0,74	0,6	0,9
Vitamins, mg/100g			
Beta-carotene	0,002	0,26	0,2
Vitamin B ₁	0,1	0,02	0,01
VitaminB ₂	0,04	0,05	0,03
VitaminB ₃	0,46	0,4	0,3
Vitamin B ₅	0,23	-	0,18
VitaminB ₆	0,05	0,2	-
VitaminB ₉	0,04	0,02	0,004
VitaminC	32,4	600	450
Minerals, mg/100g			
K	172,0	332	275
Ca	17,0	26	36
Mg	9,0	30	17
Na	3,0	4	21
P	19,0	31	33
Fe	0,8	0,8	1,2
I	0,07	0,035	0,012
B	0,03 (50% daily intake)	-	-
Mn	0,09	0,21	0,26
Cu	0,06	0,14	0,9
Zn	0,04	0,3	0,27
Energy value, ccal	49,0	61,0	45,0

Materials and methods

The subject of studies of desserts with high nutritional value development was selected new raw materials, namely: Feijoa, Actinidium and jostaberry, which are rich in chemical composition. All three selected samples of the raw materials studied in the work are berries of the gooseberry family, therefore, due to many similarities (texture, consistency, etc.) they will give a good combination. While the new sweet dish technology development, in a jelly was added jostaberry adding in the amount of 5–15% to the mass of the product, with a complete gelatin replacement.

For the whole quality control of the new product, a complex of its properties was studied: organoleptic and physical properties of the jelly mass. There were also studied some changes of its structural and mechanical properties provided to replace gelatin to jostaberry.

To determine the density of samples, a picnometric method was used, which is based on measuring the mass of a certain volume of the product at a temperature from the following absolute and relative density.

Structural-and-mechanical properties of the dough quality were determined with the help of the penetrometer of firms "Labor" of the OV-2G5, modification by determining the resistance of the food masses to the penetration of the body of immersion with strictly defined dimensions, mass and material at a precisely defined temperature for a certain time [4].

Results and discussion

Feijoa doesn't only contain iodine compounds in high concentration, but is rich to biologically active catehins and leicoanthocyanins, ascorbic acid, essential oils. These biologically active compounds are present in fruit's skin and act as powerful antioxidants and immune modulators, which decrease the risk of oncology disease and slow down the aging processes. Feijoa skin contains high concentration of pectin, which is able to bond ions of heavy metals and radioactive elements and useful for people, who contact with heavy metals or stay in polluted environment [5].

Feijoa a isusefulin treatment of anemia as it is considered to be natural source of iron.

The high content of vitamin C makes feijoa an excellent natural antioxidant. Even seasonal consumption of this fruit can help human organism to resist stress and makes it more resistant to infection [6, 8]. Feijoa is an autumn product which is very actual in period of increased risk of acute respiratory diseases and flue. Not only vitamins, but also the essential oils of feijoa fruit are important for prevention of respiratory diseases caused by viruses or bacteria [7].

There is information, that feijoa is recommended for patients with diabetes of type II, as it can lower blood glucose level. This fruit contains minimal quantity of sugar with fructose as main component, so it is considered to have low-calorie product.

In feijoa fruit not only flesh, but skin possess high biological activity. Fruit skin contains catehins and leicoanthocyanins, which have high anti-oxidant activity. Consumption of feijoa skin contributes in prevention of oncology diseases and premature aging, as well is in lowering of cholesterol level. Strong anticarcinogenic effect of feijoa fruits was also reported [9].

Studies of flavonoid composition of feijoa fruits showed presence of valuable biologically active compounds, such as quercetin-3- α -arabofuranoside (avicularine), quercetin-3- β -D-galactoside (hyperine), quercetin-3- β -D-xyloside (reinoutrine), quercetin-3- α -L-arabopiranoside (gaudjaverine) [10].

Studied the influence of impact of water extract, 30% and 50% tinctures of fresh feijoa fruits to synthetic function of thyroid gland. Experiments were carried out with intact rats using the model of «goiter reaction». As a result the strong thyreo-stimulating effect of fresh feijoa fruit water extract was demonstrated. Thus, future studies of feijoa thyreo-stimulating action and development of corresponding pharmaceuticals seem to be very prospective [11].

Feijoa extract demonstrated powerful antibacterial effect. It also possessed high antioxidant activity [12].

In recent times the growth of actinidia popularity was noted. This culture is also called winter-hardy kiwi or mini-kiwi as some actinidia species, such as *Actinidia purpurea*, *A. arguta*, *A. kolomikta* can be cultivated in region with mild climate and are close to real «Tropicana kiwi» (*A. deliaosa*), which grows only in tropical or sub-tropical climate. This woody vine is a dioecious plant. It originates from Far East, where it is called Amur gooseberry [13].

Today the international kiwi-fruit industry has more than 170,000 ha of orchard planted and able to produce more than 1.8 million tonnes of fresh fruit. The constitution of actinidia berries is similar to this of kiwi, but smaller in size. Weight of wild actinidia berries usually differs from 2 to 15 g depending of variety. Berry has thin skin without indumentum, and juicy delicate flesh with numerous small soft seeds. It has moderately sweet taste [14].

As opposed to kiwi, winter-hardy actinidia breeds have some important advantages. First of all, they can stand short-term frost down to -30 °C, which are common for Black Sea region. Secondly, this culture is resistant to pests and diseases and doesn't need pesticide treatment. Actinidia doesn't stand high concentration of mineral fertilizers, so the production of high quality «green» berries is possible. Such features of tasty and stable in cultivation culture makes it very important for Black Sea region, where numerous health-related complexes, sanatoriums and summer camps for children are located. Thirdly, actinidia fruit contains nutritional and biologically active components in quantities, which are comparable with real kiwi fruit. Taste of berries of some actinidia breeds, such as Figurna, Veresneva and other is even better than this of kiwi fruit.

Actinidia is considered to be one of the most valuable plants as it bears numerous useful features [15, 16, 17].

Actinidia berries are the natural concentrates of vitamins A, B, C, P, PP, β-carotene and mineral compounds (Table 1). Moreover, they contain biologically active compounds, including enzyme actinidine with action close to papaine, which helps to digest food in stomach.

Glucose and fructose are the main sugars of actinidia berry. Content and composition of organic acids varies depending on cultivation conditions. Actinidia berry may contain 0,3–1,5% of organic acids, including 40–50% of citric acid, 40–50% of quinic acid and up to 10% of malic acid.

Actinidia berry is a valuable source of vitamins with nutritional and medical importance [17]. It has the highest vitamin C content among all fruit and berry cultures, which can reach values from 400 to 800 mg/100 g depending on breed (Table 2). It is 10–15 times higher, than in lemon fruit and 2–3 times higher, than in black currant berry which is considered to be one of main sources of ascorbic acid. As grown-up person needs about 70 mg of ascorbic acid per day, 2-3 actinidia berries can supply the recommended daily intake of this vitamin. This berries can be stored like black currant berries (in frozen state, in form of pulp, mixed with sugar etc.).

Concentration of vitamin P in actinidia berries reaches 26 mg/100 g, which can be considered to be a significant amount. Flavonoid compounds, which belong to vitamin P group, are powerful antioxidants and are associated with normalization of blood vessel permeability and elasticity. Biologically active compounds are known to interact with other essential compounds enhancing their activity. Vitamin P act in a similar way as it is essentially important for normal functioning of vitamin C. Actinidia contains both these vitamins in significant amounts and appears to be an ideal supply of these biologically active compounds in diet.

Table 2

Comparison of nutrition value of fruits and berries [2, 3]

Product	Content, g/100 g		Content, g/100 g					Energy content, ccal/100 g
	Carbo-hydrates	Cellulose	Vitamin C	β-carotene	Ca	Mg	K	
Actinidia	14.9	1,10	600	0,26	26	30	332	61
Jostaberry	9,1	1,0	450	0,2	36	17	275	45
Lemon	3,6	1,3	40	0,01	40	12	163	31
Black currant	8,0	3,0	200	0,1	36	35	372	40
Gooseberry	9,9	2,0	30	0,2	40	22	224	41
Apple	14.8	0.54	4	0,03	4	5	115	57
Banana	23.4	0.50	9.1	0,12	6	29	346	92
Strawberry	7.0	0.50	57	0,03	14	10	166	30
Grapefruit	8.4	0.20	33.3	0,02	12	9	148	33
Orange	11.7	0.43	53.2	0,05	40	10	181	47
Peach	11.1	0.64	6.6	0,5	5	7	197	43
Grape	16	0.60	6.0	зал.	45	17	255	64

Actinidia berry contain β-carotene in concentration close to 0,26 mg/100 g, which is 2 times higher, than in black currant or banana. It is known, that daily intake of vitamin P and β-carotene should be equal to 25–50 mg and 15–25 mg, respectively. It means that 10–12 actinidia berries can supply organism with recommended daily dose of these biologically active components.

Actinidia is the source of vitamin E, which acts as powerful antioxidant. These berries contain vitamin E in concentration, which is 2 times higher, than in avocado while having 60% of its energy value.

Actinidida is used in traditional folk medicine as tonic and preventive cure, as well as for stimulation of blood circulation and liquification, for fever treatment and enhancing of lactation. Actinidia intake improves functioning of stomach, improves immune resistance and promotes the excretion of antibiotics and radionuclides. Berries contain iodine, which enables its usage for prevention of some diseases, including malfunction of thyroid gland [18, 19, 20].

Medics recommend to use actinidia berries in complex treatment of acute and chronic intestinal diseases, dental caries, tuberculosis, scorbutus and disbacteriosis as well as cure for prevention and treatment of avitaminosis, for rehabilitation after serious diseases, exhaustion or mental stress [13].

Actinidia berries are used in fresh state or after processing in jam, confiture, juice, compote, liquor or wine. These berries ripen in late autumn and can be stored in a fresh state for a long time. They stand well during the transportation in case of adequate packing [18, 19, 20, 21].

Jostaberry is the hybrid of gooseberry and currant. High content of biologically active compounds is its main advantage as jostaberry contain components of gooseberry and currant at the same time. Comparison of chemical composition of gooseberry, currant and jostaberry as shown in Table 2 allows to recommend its usage for dessert production. At

present time jostaberry is widely spreaded in Western Europe while in Eastern Europe this culture is used mainly for decoration [22].

Jostaberry has high technological and consumer characteristics and is considered to be the rich source of natural biologically active compounds (Table 1,2). Together with black currant jostaberry contains high concentrations of vitamins, in particular vitamin C. Consumption of 30 g of jostaberry supplies human organism with daily dose of ascorbic acid.

Jostaberry contains iron, which makes berries useful for those with anemia. Potassium ion of jostaberry positively influences on cardiovascular system and helps to reduce risk of heart-attack and stroke. Jostaberries are recommended for prevention of gastrointestinal diseases [22].

It is reported that jostaberry contain polyphenol compounds, such as catehins, anthocyanins, flavonols and other. Total content of bioflavonoids in jostaberry is close to 320–380 mg/100 g.

Jostaberry berries contain significant amount of cellulose and pectin. In case of regular intake they can perform detoxication function and stimulate the excretion of heavy metal ions and radionuclides. Jostaberry has low calorific value (45 ccal/100 g) and can be considered as diet product.

Therefore, the analysis of literature and patent sources enables to state, that feijoa, actinidia and jostaberry can be economically grounded raw materials for production of different food products. Although these cultures are new for Ukraine, all of them are gaining popularity and are broadly cultivated at Southern region.

Introduction of new raw materials into recipes of sweet products for production in food-service industry will promote not only the development of this branch, but the development of agriculture and processing industry of Southern Ukraine. It will help in complex development of region's economy.

Monitoring of chemical composition of feijoa, actinidia and jostaberry showed that these berries contain iodine in significant amounts and can be used for healthy and therapeutical nutrition. They contain vitamin C in high concentrations and at the same time are rich to vitamins of B-group, vitamins P, E and β -carotene, organic acids, mineral elements, in particular iron and potassium. This data enables to classify feijoa, actinidia and jostaberry as products with high nutrition value and shows the opportunity to use them as biologically active food supplements.

Feijoa, actinidia and jostaberry will be used as raw materials for future studies as they belong to *Grossulariaceae* family and have similar texture, consistency and other technological characteristics resulting in good compatibility in dessert recipes.

Chosen cultures can be processed in a complex processing cycle, such as separate processing of flesh and skin. The development of technology for seasonal production of semi-finished products from stated berries for their future use in technology of finished products is also planned.

Berries of feijoa, actinidia and jostaberry have sweet taste with piquant spicy shades, so the development of desserts with improved nutrition valley on their basis seemed to be logical. Berries of feijoa, actinidia and jostaberry are rich in pectin, so they can be good base for structured desserts, such as jellies, mousses, sorbets etc. Such desserts correspond to modern trends in foodservice industry, in particular, trend to consume "light" foods, opportunity of shock-freezing, ice-mixing and other modern technologies.

The analysis of information concerning studies of the chemical composition, properties, physico-chemical and organoleptic characteristics of jostaberry enabled us to start the development of jelly production technology based on this raw material.

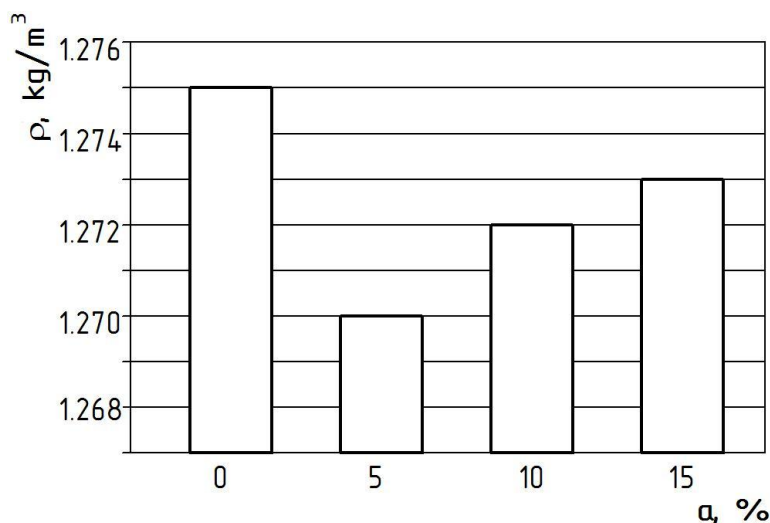


Figure 1. The dependence of the jelly density ρ , kg/m³ on the jostaberry mass fraction a , %

In a jelly was added jostaberry adding in the amount of 5–15% to the mass of the product, with a complete gelatin replacement.

When the new dishes are developing, some ingredients are replaced by other. That's why it definitely affect on the technological and consumer properties of the newly created product, on its nutritional value. Therefore, the first step in the development of the new jostaberry jelly technology are theoretical justification and planning the compositions of ingredients, methods of processing raw materials, modes of cooking, taking into account the processes that form the desired structure with a given composition of the final product, physical, chemical and technological properties.

Structural and mechanical properties of the jelly mass are qualitatively outer expression of the inner essence of objects that define the state of aggregation, dispersion, structure and species interactions in the middle of the product. There were also studied some changes of its structural and mechanical properties provided to replace gelatin to jostaberry.

It shown (Figure 1) that the density of the samples with the jostaberry addition slightly decreases compared to the control sample. Since density is associated with structural jelly strength, the jostaberry additives adding will affect the rheological properties jelly. The particular importance for the development of gelatinous foods technology is studying the effect of additives on the sliding properties of the finished dishes.

The dependence of limiting voltage of the jelly offset on the jostaberry mass fraction is shown in Fig. 2. Since the structure-gelatin is completely excluded by the chemical composition of jostaberry, the value of the limiting voltage of samples offset was slightly decreased. The most important indicator near the limiting voltage offset to the control sample indicator is a sample of jelly with 15% content of jostaberry and which is close to the reference value. Thus, the growth rate of the dessert limiting voltage offset with increasing mass fraction of jostaberry (15%), characterizes strengthening structure of jelly as appropriate. The structure strength increase is a favorable factor in the stages of solidification, forming, storage and implementation of the gelatinous foods.

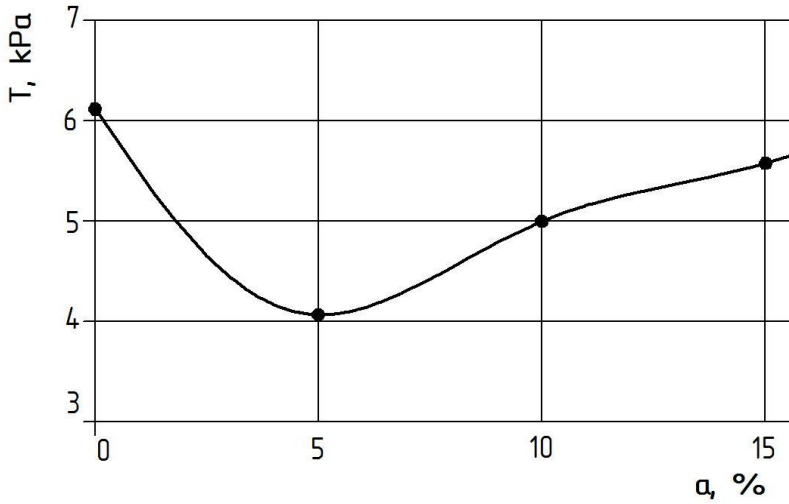


Figure 2. The dependence of limiting voltage of the jelly offset T , kPa on the jostaberry mass fraction a , %

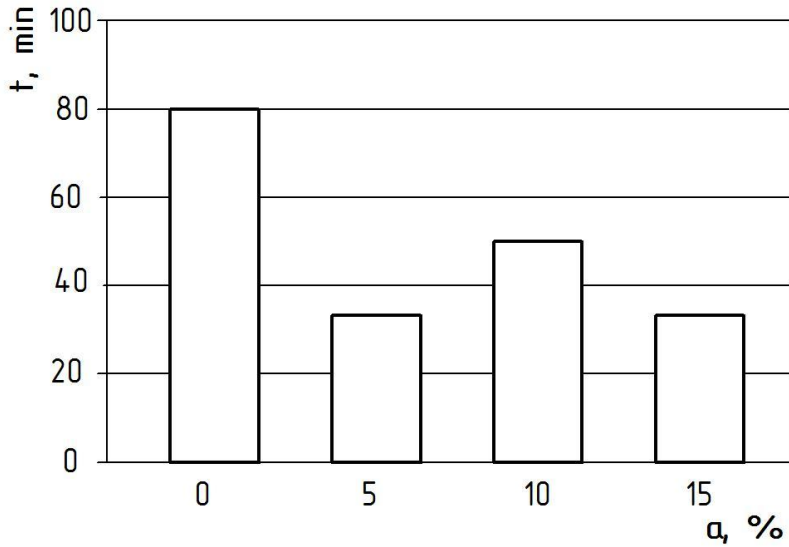


Figure 3. The dependence of jelling time t , minutes on the jostaberry mass fraction a , %

The data regarding product density and structure strength correlate with results of jellification time studies (Figure 3).

In particular, jellification time of jelly containing no gelatin and 15 % of jostaberry decreases if compared with control sample. Hydrocolloids of raw materials used are able to ensure sufficient structure characteristics of jelly.

Evaluation of structural and mechanical properties of jelly with the addition of jostaberry in the context of positioning the possibility of obtaining stable gelatinous system showed that the proposed formula and technology gives a product with high technological properties, attractive consumer properties and high nutritional value.

Conclusion

The usage of non-traditional fruits and berries from the Black Sea region, in particular feijoa, actinidia and jostaberry, enables us to broaden the range of desserts with improved nutrition value and consumer properties and, as a result, improve the structure of nutrition for population.

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Influence of genotype and crop year on carotenoids content of peels from Bulgarian tomato cultivars

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Abstract

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Introduction. The aim of this study is to determine the effect of genotype and crop year on the quantity of waste peels from six Bulgarian tomato cultivars generated during their peeling and the carotenoids content of the obtained peels.

Materials and methods. Six Bulgarian tomato cultivars, were grown under open-field conditions at the Maritsa Vegetable Crop Research Institute, Plovdiv, Bulgaria. The combined effect of the investigated factors on the quantity of the waste generated during tomato peeling was established by the two-factor dispersion analysis and by the HPLC analysis the carotenoids contained in tomato peels were determined.

Results and discussion. It was found that tomato genotype has a major effect on the percentage of generated peels during tomato peeling and on its carotenoids content. The average percentage of peels from tomatoes harvested in 2013 year ranged from $2.45 \pm 0.13\%$ to $5.33 \pm 0.09\%$. The highest percentage of peels was found for “Carobeta” cultivar and at least for “Topaz”. For tomato cultivars cultivated in 2014 crop year the average percentage of the obtained peels varied from $2.98 \pm 0.13\%$ to $3.50 \pm 0.25\%$ and the highest quantity of peels was generated from the “Aquarius F1” cultivar and at least from “Carobeta” cultivar of tomato. The obtained peels contained mainly lycopene, beta-carotene and lutein. In the first crop year the highest contents of lycopene (97.16 ± 0.81 mg/100g) and lutein (21.22 ± 0.10 mg/100g) were found in the peels of the “Stella” cultivar of tomato and those of “Carobeta” cultivar had the highest content of beta-carotene (108.48 ± 1.36 mg/100g), whereas in the second year of survey most of the lycopene (241.14 ± 1.24 mg/100g) was contained in the “Aquarius F1” peels, and the beta-carotene (293.36 ± 2.00 mg/100g) and lutein (13.58 ± 0.15 mg/100g) in the “Stella” tomato peels. Tomato peels of cultivars „Stella“, „Topaz“, „Aquarius F₁“ and „Jacqueline“ are reached in lycopene and beta-carotene, whereas the peels of cultivars „Marigold“ and „Carobeta“ are suitable source of beta-carotene only. The results indicated the greatest influence of the tomato genotype on lutein content (69.43%), followed by beta-carotene (57.52%) and peels percentage (46.55%). The environmental conditions were found to had a strong influence on the content of peels (41.66%) and lycopene (38.73%), while the effect on beta-carotene was lower (14.92%) and on luteine was very low (1.63%).

Conclusions. The amount of lycopene in tomato peels is dependent on genotype and crop year, whereas the beta-carotene and lutein contents were affected mainly by the tomato genotype.

Introduction

Tomatoes have an important economic significance in the countries with advanced vegetable production. The good tomato taste and suitability for technological processing in various types of products determine the great importance of this vegetable. The wide distribution and use of tomatoes are mainly due to the established cultivars with different vegetation period, high and stable productivity, resistance to economically important diseases and excellent technological quality.

Production of fresh tomatoes in the world for 2012 amounted to 161.8 million tones and in the EU-27 to 15.2 million tones. The production of tomatoes in Bulgaria for the same year amounted to 94016 tones. According to FAO data, 65-85% of the fresh tomatoes produced are processed into canned foods [5]. This industrial processing of tomatoes released around 10-40% of waste products [1].

The tomato peeling operation applied in processing industry generates tomato skin and outer pericarp tissue, named peels, usually creating big environmental problems. However, the by-products of tomato processing contain important biological active substances (vitamin C, polyphenols, lycopene, beta-carotene and etc.), which made this waste material suitable for using in the food industry [10, 15].

The quantity of tomato wastes combined with the beneficial characteristics of components of these wastes justifies the great interest of researchers and manufacturers in extracting of carotenoids from this low cost material [16].

The amount of carotenoids in industrial tomato cultivars depends from different factors such as genotype, agricultural practices, soil, climate factors, harvesting date, degree of maturity and post-handling. The reported amount of lycopene in tomato peels ranging from 5 to 100 mg/100g [8, 9, 12, 13, 14].

The valorisation of generated huge quantities of value-added waste tomato material is among the most important global challenges. However, it is necessary to study the quantity and composition of each tomato processing waste to know its potential use for food purposes.

Bulgarian tomato cultivars „Stella“, „Topaz“, „Aquarius F₁“, „Jacqueline“, „Marigold“ and „Carobeta“ are of the great interest for the canning industry. There are not data in the literature for the effect of tomato genotype and crop year on the quantity of the waste during the tomato peeling and the content of carotenoids in the peels generated from these Bulgarian tomato cultivars. Therefore, to establish this effect was the main aim of present study.

Materials and methods

Materials

Bulgarian tomato cultivars „Stella“, „Topaz“, „Aquarius F₁“, „Jacqueline“, „Marigold“ and „Carobeta“, were grown under open-field conditions at the Maritsa Vegetable Crop Research Institute, Plovdiv, Bulgaria. HPLC grade acetone, methanol, tetrachloromethane, acetonitrile and methyl tert-butyl ether (MTBE) of analytical grade were purchased from Sigma, Germany. Carotenoid standards were supplied by Extrasynthese, France.

Sample preparations

The average laboratory sample (10 kg) of fresh red-ripe tomatoes was blanched at 95 °C for 2 min, cooled in tap water and hand peeled. The obtained tomato peels quantity after

peeling of each sample of different tomato cultivars was weighed and expressed as average percentage of peels. Then the samples were subsequently air-dried at 25 ± 1 °C, ground in a laboratory mill (Bosh MKM 6003, Germany) and sieved through a 1.0 mm sieve. The resultant material was kept in glass jars closed with aluminium foil at -20 °C until the start of the experiments. The moisture content of the dry ground tomato peels was determined by gravimetric method at 105 °C.

Carotenoids extraction

To 0.1 g of dried and milled tomato peels sample was added 2 ml of methanol and 5 ml of tetrachloromethane and methanol mixture (1:3) and 0.5% of butylhydroxytoluene. The sample was placed for 15 min in an ultrasonic bath (35 kHz) and after carotenoid extraction the 1 ml of 10% NaCl solution was added. The obtained extract was then centrifuged for 10 min at 5000 min^{-1} and the clear fraction was placed in a 5 ml volumetric flask.

HPLC analysis of carotenoids

For the determination of carotenoids, the obtained extracts were analyzed using an HPLC system (Waters, Milford, USA) composed of a UV-VIS detector (Waters 2487 Dual), a Waters 1525 binary pump and thermostat (LCO 102). The HPLC system was equipped with a C_{18} column, 25 cm x 4.6 mm, 5 μ l particle (Suspelco Discovery HS). Mobile phases of methanol:acetonitrile (A) in 8:2 ratio and MTBE (B) were used (Table 1). The flow rate was maintained at 1 ml/min, the column temperature at 30 °C, and detection was carried out at 270 nm and 290 nm. The results are expressed in mg/100 g dry matter.

Environmental conditions measurement

Data for average air temperature (°C) and rainfall amount (L/m^2) of the tomato open-field growing period in 2013 and 2014 crop years were obtained from the local research station of the Maritsa Vegetable Crop Research Institute, Plovdiv, Bulgaria.

Statistical analysis

All experiments were run in triplicate. The data were analyzed and presented as mean values with standard deviation. Statistical analysis was conducted using Statgraphics Centurion XVI Version 16.2.04 (Statpoint Technologies Inc., USA) и Microsoft Excel 2003 software. Statistical techniques, incl. Two-factor dispersion analysis, ANOVA and Duncan's Multiple Range Test, were applied. The significant differences were determined at 95% confidence ($P < 0.05$) level.

Table 1

Gradient profile of HPLC system for carotenoid analysis of tomato peels

Runs	Time, min	A, %	B, %
1	3.0	95	5
2	3.0	95	5
3	4.5	80	20
4	5.0	65	35
5	10.0	65	35
6	10.1	95	5
7	15.0	95	5

Results and discussion

Six tomato cultivars for industrial processing were studied in the first year (2013) of survey. However, in the second crop year (2014), cultivars were reduced to four for the following reasons. The “Aquarius F1” and “Jaqueline” cultivars have almost the same chemical composition [6] and the average percentage of the peels was almost the same (Figure 1). In addition, “Aquarius F1” is a new and hybrid cultivar with a higher productivity and is preferred by the manufacturers in comparison to “Jaqueline” cultivar of tomato. Furthermore, the cultivars of “Marigold” and “Carobeta” are the same sort and the peels average percentage and beta-carotene content in the peels of “Marigold” is less than these in “Carobeta” (Figure 1 and Table 2). That’s why the ‘Jaqueline’ and “Marigold” tomato cultivars were dropped out of the 2014 survey.

The results obtained for average percentage of peels generated during the peeling of studied tomato cultivars are shown in Figure 1. The average percentage of peels from tomatoes harvested in 2013 year ranged from 2.45 ± 0.13 to $5.33 \pm 0.09\%$. The highest percentage of peels was found for “Carobeta” cultivar and at least for “Topaz”. For tomato cultivars cultivated in 2014 crop year the average percentage of the obtained peels varied from $2.98 \pm 0.13\%$ to $3.50 \pm 0.25\%$ and the highest quantity of peels was generated from the “Aquarius F1” cultivar and at least from “Carobeta” cultivar of tomato. No significant differences ($P > 0.05$) were observed between the average percentage of peels for both “Aquarius F1” and “Stella” cultivars of tomato in 2013 crop year and for “Aquarius F1”, “Stella” and “Topaz” for 2014 crop year.

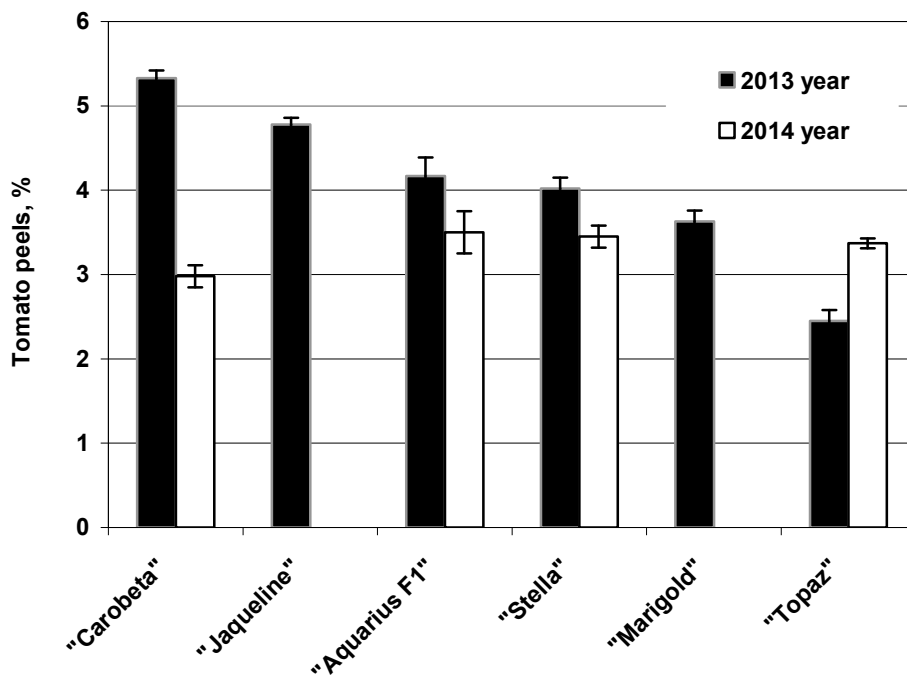


Figure 1. Average percentage of peels from different Bulgarian tomato cultivars (The data are means \pm standard deviation of three independent replicates)

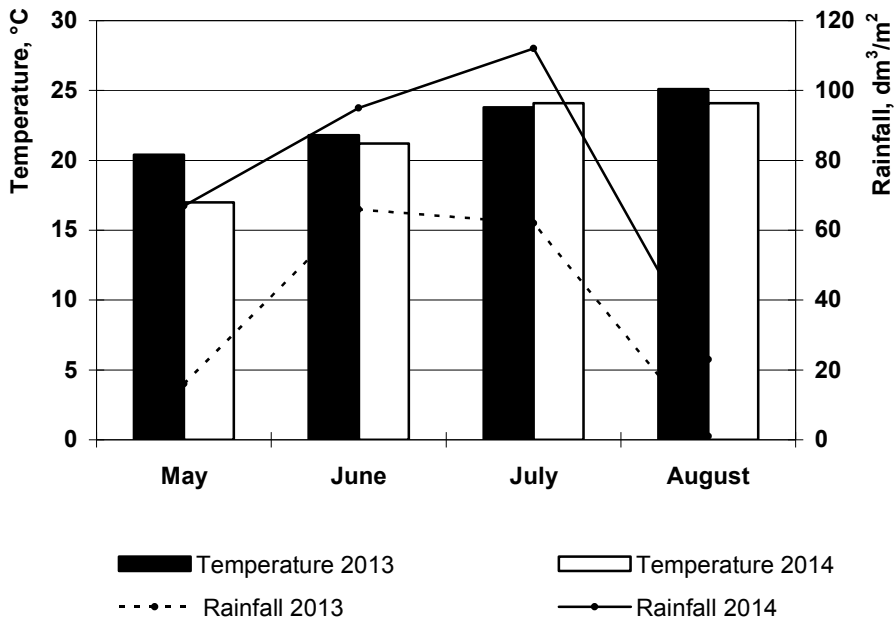


Figure 2. Average air temperature and rainfall amount of the tomato open-field growing period in 2013 and 2014 crop years

The results for average percentage of peels generated from different Bulgarian tomato cultivars (Figure 1) indicated that in addition to the tomato genotype, the environmental conditions of the investigated crop years probably had effect on peels quantity also. This fact is confirmed by the data of average air temperature and the amount of rainfall during tomato growing period in the two crop years which are presented in Figure 2. Data indicated that the air temperatures in 2013 and 2014 crop years were very closed, but the rainfall amount in the first year was much less than the second, which probably had affected the quantity of peels from the investigated tomato cultivars.

A quantitative and qualitative determinations of the carotenoids contained in tomato peels from different samples were performed by the HPLC analysis and the results obtained are summarized in Table 2. The data from carotenoids determination showed that the peels of studied tomato cultivars consisted mainly of lycopene, beta-carotene and lutein. In the first crop year the highest contents of lycopene (97.16 ± 0.81 mg/100g) and lutein (21.22 ± 0.10 mg/100g) were found in the peels of the “Stella” cultivar of tomato and those of “Carobeta” cultivar had the highest content of beta-carotene (108.48 ± 1.36 mg/100g), whereas in the second year of survey most of the lycopene (241.14 ± 1.24 mg/100g) was contained in the “Aquarius F1” peels, and the beta-carotene (293.36 ± 2.00 mg/100g) and lutein (13.58 ± 0.15 mg/100g) in the “Stella” tomato peels.

Table 2

Carotenoid content in the peels of different Bulgarian tomato cultivars

Tomato cultivars	Lycopene, mg/100g		Beta-carotene, mg/100g		Lutein, mg/100g	
	2013 year	2014 year	2013 year	2014 year	2013 year	2014 year
Stella	97.16± 1.81 ^{aA}	167.86± 2.15 ^{aB}	88.38± 2.65 ^{aC}	293.36± 2.00 ^{aD}	21.22± 0.10 ^{aE}	13.58± 0.15 ^{aF}
Topaz	54.26± 1.60 ^{bA}	167.40± 1.42 ^{bB}	55.66± 0.46 ^{bA}	46.03± 0.44 ^{bC}	15.54± 0.13 ^{bD}	11.48± 0.10 ^{bE}
Aquarius F ₁	26.97± 1.09 ^{cA}	241.14± 1.24 ^{bB}	38.17± 0.91 ^{cC}	45.88± 0.26 ^{bD}	11.65± 0.09 ^{cE}	11.21± 0.10 ^{cF}
Jacqueline	20.34± 0.25 ^{dA}	*	32.52± 0.49 ^{dB}	*	11.56± 0.16 ^{cC}	*
Marigold	15.89± 0.15 ^{eA}	*	83.52± 0.10 ^{eB}	*	11.30± 0.28 ^{cC}	*
Carobeta	14.91± 0.21 ^{fA}	14.51± 0.57 ^{eA}	108.48± 1.36 ^{fB}	155.47± 1.42 ^{cC}	2.27± 0.06 ^{dD}	9.28± 0.09 ^{dE}

* Not determined. The data are means ± standard deviation of three independent replicates. The values with different small letters (a-f) and different capital letters (A-F) indicate significant differences between means values in the columns and rows, respectively (P<0.05).

The results obtained for carotenoids content in the tomato peels (Table 2) were in agreement with data reported from other researches [9, 10, 14, 15] and showed differences in carotenoids content for different tomato cultivars which may be due to the genotype features. Differences in carotenoids content among tomato cultivars has been previously reported [7, 11]. However, differences in carotenoids content between two crop years of the same cultivars were found also, probably due to different environmental conditions in 2013 and 2014 years, as indicated in Figure 2. Although tomatoes are irrigated crops, air temperature and humidity is important for the synthesis of the substances in them. It has been reported that lycopene formation is favoured at temperatures ranging from 16 to 21 °C and unfavoured at temperature values above 30 °C [3]. Other studies have highlighted that the tomato nutrients, including lycopene, is affected by the soil water depletion even if it seems to be cultivar dependent [3, 4]. Therefore, probably due to the less rainfall amount during tomato growing in 2013 crop year differences in both the percentage of the peels and their carotenoids content for the same tomato cultivars grown in 2013 and 2014 were observed.

The effects of genotype and crop year on the percentage of peels in tomatoes (Figure 3) and on the content of carotenoids in peels (Figures 4, 5 and 6) were established by performing of a two-factor dispersion analysis. The results indicated the greatest influence of the tomato genotype on lutein content (69.43%), followed by beta-carotene (57.52%) and peels percentage (46.55%). The environmental conditions were found to had a strong influence on the content of peels (41.66%) and lycopene (38.73%), while the effect on beta-carotene was lower (14.92%) and on luteine was very low (1.63%).

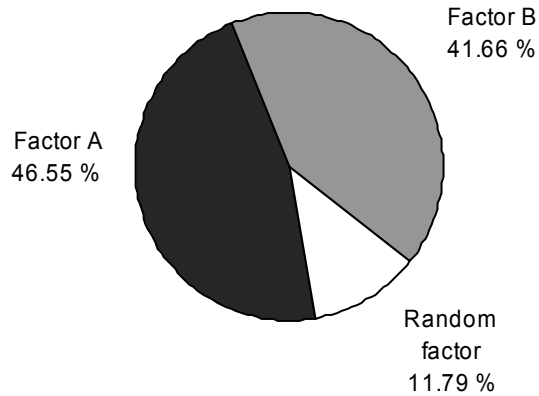


Figure 3. Influence of tomato genotype (Factor A) and crop year (Factor B) on the percentage of peels from six Bulgarian tomato cultivars

The results of the two-factor dispersion analysis (Figures 3, 4, 5, and 6) showed the major influence of the tomato genotype on the contents of tomato peels, beta-carotene and lutein, while the combined effect of genotype and crop year was found for percentage and lycopene content of the tomato peels. Data were in good accordance with other researches carried out for different tomato cultivars [2, 11].

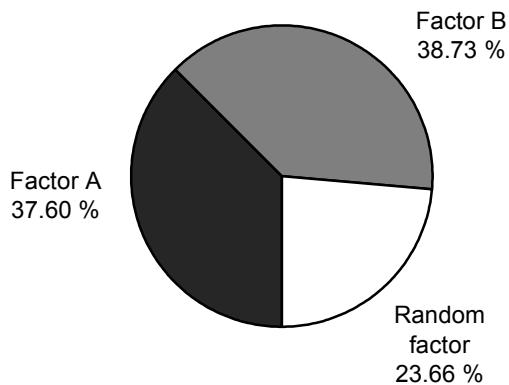


Figure 4. Influence of tomato genotype (Factor A) and crop year (Factor B) on the lycopene content of peels from six Bulgarian tomato cultivars

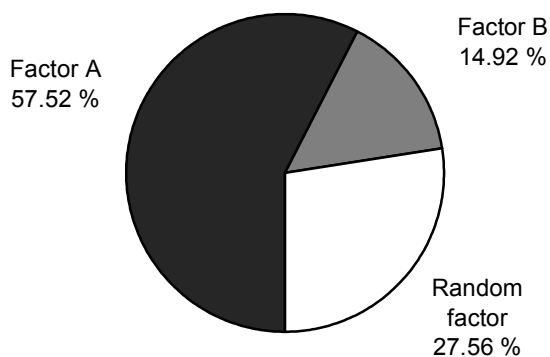


Figure 5. Influence of tomato genotype (Factor A) and crop year (Factor B) on the beta-carotene content of peels from six Bulgarian tomato cultivars

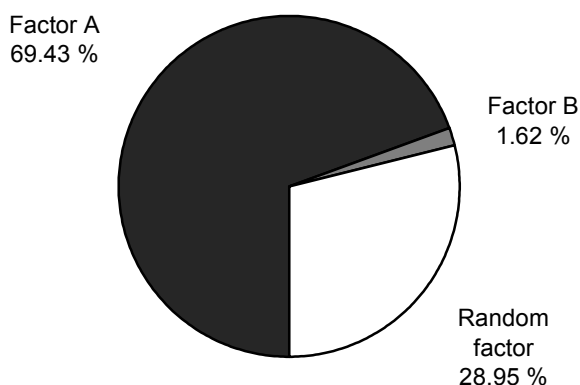


Figure 6. Influence of tomato genotype (Factor A) and crop year (Factor B) on the lutein content of peels from six Bulgarian tomato cultivars

Conclusion

The two-factor dispersion analysis was carried out to determine the combined effect of the tomato genotype and crop year on the amount of the waste peels generated during tomato peeling and by the HPLC analysis a characterization of the carotenoids contained in the tomato peels was made. The results indicated that obtained tomato peels contained mainly lycopene, beta-carotene and lutein. HPLC analysis showed that tomato peels of cultivars „Stella“, „Topaz“, „Aquarius F₁“ and „Jacqueline“ are rich in lycopene and beta-carotene, whereas the peels of cultivars „Marigold“ and „Carobeta“ are suitable source

of beta-carotene only. Tomato genotype was found to had a major effect on the percentage of generated peels and on its carotenoids content. The amount of lycopene in tomato peels was dependent on both genotype and crop year, whereas the beta-carotene and lutein contents were affected mainly by the tomato genotype.

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Nutritional value and consumer properties of bakery products with fructose for diabetic nutrition

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Abstract

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Introduction. Nutritional value and consumer properties are decisive for assessing the quality of products which are attractive for the consumer. In this paper a study of these characteristics in products for the diabetic direction is presented.

Materials and methods. The dough was prepared in an unoccupied way after the developed recipes. These characteristics were determined by the organoleptic parameters by the expert estimation method, the structural and mechanical properties of the crumb on the automated penetrometer, the degree of freshness conservation by the indexes of lidding and moisture content, distribution and forms of moisture communication by differential thermal analysis on the derivatograph, the content of aromatic substances by the amount of bisulfite binding compounds.

Results and discussion. Currently, diabetic bakery products made after common recipes have a low nutritional value and a short expiration date without loss of freshness. An expert assessment of the diabetic products developed by us «Bakery product 1» and «Bakery product 2», enriched with the components of casein, powder of artichoke, cellulose of buckwheat bran, calcium citrate, magnesium, zinc and iron showed an improvement of the organoleptic qualities of the products when adding these components. The determination of the deformation of the crumb and the hydrophilic properties revealed that the developed products strung slowly due to increasing of water absorption capacity. This correlates with the better preservation of the associated moisture during storage. These products, in comparison with the control sample, contain more aromatic compounds both in the crust and in the crumb. The calculation of the nutritional value of products showed a significant increase of the nutrient content in samples with additives.

Conclusion. The developed products have a higher nutritional value and better quality characteristics, they are slowly striking.

Introduction

The nutritional value of bread depends on the type and variety of flour, recipe additives and the moisture content of the product. Bread is well absorbed by the organism, because it has a loose elastic crumb, in which proteins are optimally denatured, starch is pasteurized, sugars are dissolved. This state of the constituents of bread makes them available for the action of enzymes of the gastrointestinal tract [1-3]. The chemical composition of bread, its taste, smell, state of proteins and carbohydrates, that form its structure, the presence of biologically active substances - vitamins, minerals in it, give high physiological value to the bread [4,5]. The influence of the constituents on various systems of vital activity of the organism - immune, cardiovascular, digestive, etc. forms its physiological value. However, according to the current requirements of the science of nutrition, bread products need improving their composition. There isn't the optimum ratio of proteins and carbohydrates, calcium and phosphorus in bread, there is also insufficient content of such essential amino acids as lysine, methionine, tryptophan [6]. Recently, diabetes has become widespread, but on the world market, the range of bakery products for diabetic nutrition, especially enriched with useful nutrients, is small [7-9].

At the present stage among bakery products diabetic products with a low nutritional value and a relatively high glycemic index, deprived of physiologically useful components such as complete proteins, fiber, vitamins and minerals dominate [10], [11-16]. As substitutes for sugar, polyols such as sorbitol, xylitol, mannitol, etc. are mainly used. However, natural substances, in particular sugar - fructose should be preferred.

The deterioration of the quality of bakery products, and especially the products of special diabetic nutrition, is connected with the number of factors: low quality of raw materials, non-compliance with the technological process, etc. [17]. Consumer properties are determined by the chemical composition, assimilation of nutrients, energy value, biological and organoleptic characteristics of bread [18]. In the case of use of raw materials of reduced quality, errors in the technological process or in the wrong mode of storage, the consumer properties of bread are reduced [19].

The problem of drawing of bread, caused by changes in the structure of starch: retrogradation, reorganization of polymers in the amorphous region, loss of moisture and distribution of water between amorphous and crystalline zones [20].

The modern way of life prompts the necessity of making bread of long-lasting freshness. In connection with this, near the use of packaging materials, it is relevant to make supplements aimed at improving the quality of bread and slowing down its drawing. The purpose of our research was to determine the influence of the components of the recipes of developed bakery products «Bakery product 1» and «Bakery product 2» for diabetic nutrition on their consumer properties and preservation of freshness in comparison with the product without additives.

Materials and methods

Materials

The products were produced with such ratio of the recipe components, %.

Control sample:

Flour – 91,3; Yeast – 2,7; Salt – 1,5; Fructose – 4,5.

Bakery product 1:

Flour – 79,6; Yeast – 2,4; Salt – 1,2; Fructose – 4,0; Corn oil – 1,6; Mixture of calcium, zinc, magnesium and iron citrates – 0,8; Casein – 7,2; Artichoke powder – 3,2.

Bakery product 2:

Flour – 77,3; Yeast – 2,3; Salt – 1,2; Fructose – 3,9; Corn oil – 1,5; Mixture of calcium, zinc, magnesium and iron citrates – 1,4; Casein – 6,2; Buckwheat fiber – 6,2.

Conducting an expert assessment of organoleptic parameters of finished products

Sampling: a medium sample was taken from a batch of products. The average sample was selected from the batch of products, its external features characterize the entire party. Organoleptic parameters were evaluated by the tasters using sensory organs.

Firstly, the color, shape, condition of the crust, and then - the smell, consistency, taste were evaluated.

Determination of structural and mechanical parameters of the crumb by the penetrometer AP-4/1

The bread is cut in a 40-mm thick slip, which is stacked on the stand of the appliance. In the beginning, the upper stem position should correspond to zero on the scale. On the immersion body the variable load is put and it is set to a position where it will touch the surface of the sample. The start button is pressed. The height of the sample at the place of deformation is recorded in units of penetration.

Determination of the cockiness of the crumb

Two pieces in the form of a parallelepiped of 5 g each are cut from the loaf of bread and transferred to a conical flask of 250 cm³. The content of the flask is stirred for 5 minutes on a vibrating mixer. The crumb, formed as a result of friction of two pieces, is collected and weighed on scales. The cockiness (X,% to the weight of the crumb), is determined by the formula 1:

$$X = \frac{G_1}{G_2} \times 100 \quad (1)$$

where G₁ - mass of crumb, g; G₂ - the weight of bulk of bread, g.

Determination of the amount of water absorbed by the crumb of bread

3 g of crumb are chopped and weighed. Bulk is transported to the sieve and add 17 ml of distilled water during 5 minutes from the pipette. The soaked crumb is collected and weighed. The amount of water absorbed by the crumb (V,% on dry matter), is calculated by the formula 2:

$$V = \frac{(G_1 - G_2) \times 100 \times 100}{G_2 - (100 - W)} \quad (2)$$

where G₁ - mass of bread after wetting, g; G₂ - weight of bread bulk, g, W - mass fraction of moisture in bread, %.

Determination of the forms of bonding of moisture in bread by derivatograph Q-1500

The essence of the method is that the sample and the standard are loaded into the working volume and heated at a constant rate. In this case, the temperature of the sample and the difference between the temperature of the sample and the standard reference temperature difference, sample mass change, and the difference in masses of the reference and working samples are measured. In two crucibles a standard sample and a test sample weighing 1 g is loaded. They are heated and at a rate of 1.25 °C/min in the temperature range of 20-250 °C. The recording device captures the graphs. On the curve of the difference in sample masses, a clear endeavor is observed, which corresponds to the additional absorption of heat by the sample. Tangents are held to it. From the point of intersection of the tangents, the vectors are carried to the intersection with the curves of the change in mass and temperature of the sample. On a scale of mass and temperature the mass loss of the sample is determined.

Analysis of derivatograms was made according to the method of A. Litvinenko.

Determination of aromatic compounds

The methodology is to determine the bisulfite-binding compounds according to the method of R. Tokareva and V. Kretovich and is based on the ability of binding of aldehydes and some ketones by sodium bisulfite. The crumb or crust weighing 20 g is triturated in a mortar with 0.15% solution of sodium bisulfite and transferred quantitatively to a 200 cm³ volumetric flask. Content is brought to the mark and shaken for 10 minutes. The suspension is filtered, 20-25 cm³ of filtrate is transferred to a conical flask of 250-300 cm³ and 1 cm³ of 1% starch solution is added. The excess of bisulfite is oxidized firstly by 0.1 and then by 0.01 mol / dm³ of iodine solution to a weakly violet color.

To destroy the bisulficarbonyl compounds and bring to pH of 8,3, 25 cm³ of alkaline-boron solution is added to the flask and titrated from the micro burette the isolated bisulfite 0.01 mol / dm³ by iodine solution to a violet-blue color that does not disappear for 15s. The volume spent on titration is fixed. To the titrated solution 90-95% of the volume of 0.01 mol / dm³ of iodine solution spent on the previous titration is added, then 25 cm³ of alkaline-boron solution is added and titrated by 0.01 mol/dm³ of iodine solution until a violet blue color, which does not disappear for 15s. From the received titration results the data from the control analysis is subtracted.

Work out the results. The content of bisulfite binding agents, X, mg-eq per 100 g of dry matter, is calculated by the formula 3:

$$X = \frac{V_1 \times N \times V_2 \times 100 \times 100}{V_1 \times p \times (100 - W)} \quad (3)$$

where V₁ – volume of 0,01 mol / dm³ of iodine solution spent on titration, cm³; V₂ – the volume of a volumetric flask in which the weight of bread is placed, cm³, V₃ – the volume of the water-bisulfite extract of bread taken on the titration, cm³; N – the concentration of iodine solution equal to 0.01 mol / dm³; W - mass fraction of moisture in bread, %.

Calculation of the nutritional value of products

"Nutritional value" characterizes the ability of bread to provide the physiological needs of the body in energy and basic nutrients. The integrated indicator of nutritional value is the

"integral acceleration", which shows the percentage of compliance of the content in 100 grams of bread of each component to the daily need of the human body in it. Integral acceleration (IA) is calculated by the formula 4:

$$IA = \frac{G_{100\text{gofbread}}^{\text{protein}} \times G_{\text{ofbread}}^{\text{perday}}}{G_{\text{perday}}^{\text{protein}} \times 100} \times 100 \quad (4)$$

Statistical analysis

The results were processed using methods of mathematical statistics using the programs Microsoft Excel 2010, Origin 8.0 and Fityc 0.9.8.

Results and discussion

The expert evaluation of the products has shown that in comparison with the control, when the enrichment of raw materials is introduced, the condition of the surface, the color of the crumb and crust, the taste and the flavor is improved, which is explained by the fact that the addition of protein in combination with sugar contributes to the more intensive reaction of melanoid formation and fermentation processes. The elasticity of the crumb is also improved, in particular due to the incorporation of corn oil.

The results of the ball assessment are summarized in the table (Table 1) and the profilograms are constructed (Figure 1).

Table 1

Average ball organoleptic score

Product name	Shape	Surface	Color of the crust	Condition of the crumb	Taste	Flavor
Fructose bread (Control)	5,0±0,3	4,7±0,4	4,9±0,3	4,4±0,3	5,0±0,3	4,8±0,3
«Bakery product 1»	4,8±0,3	4,9±0,3	4,8±0,3	4,8±0,3	4,8±0,3	4,8±0,3
«Bakery product 2»	4,8±0,3	4,8±0,3	4,9±0,3	4,7±0,3	5,0±0,3	5,0±0,3

The degree of preservation of freshness was determined by a penetrometer AP-4/1 (Table 2). Studies have shown that the general deformation of the crumb of «Bakery product 1» and «Bakery product 2» was less than in the control sample, which can be explained by the presence of food fibers in the structure of the crumb. These samples after 24 and 48 hours of storage had a better freshness by 3 and 9% and 2 and 8% respectively. In the process of storage, the percentage change in general deformation of the developed samples was less than in the control sample, which is the result of the introduction of raw materials, improves the elasticity of the crumb, has increased hydration ability and slows down the loss of moisture during storage.

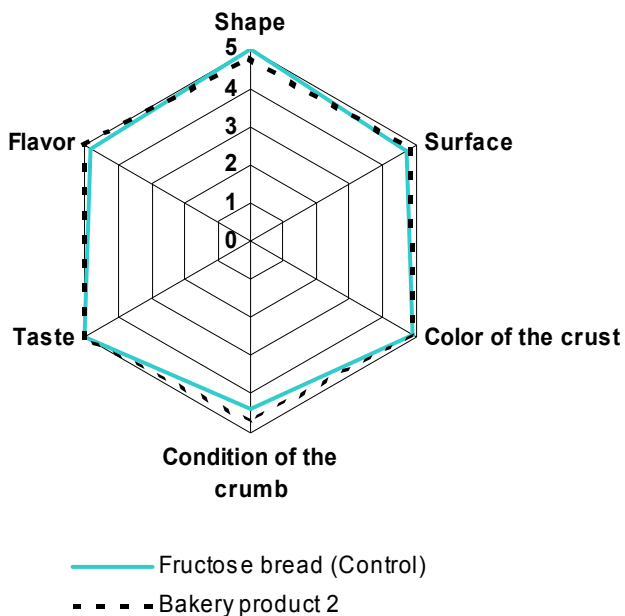
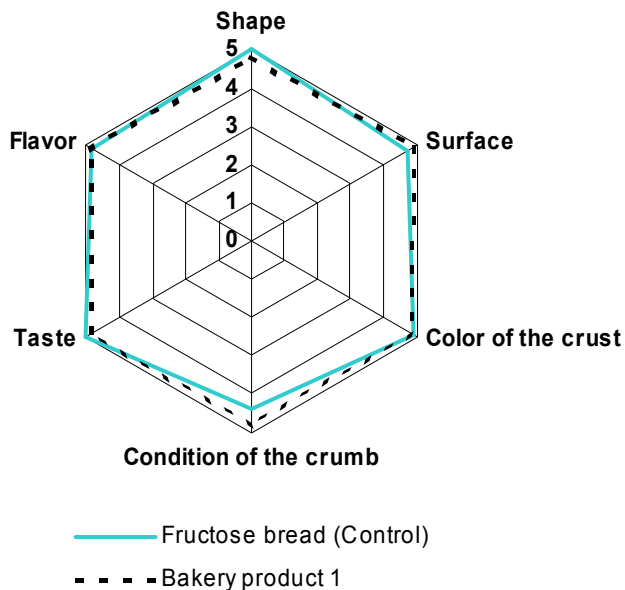


Figure 1. Profilograms of product quality indicators

Table 2

Indicators of deformation of the product's crumb

	Fructose bread (Control)	Bakery product 1	Bakery product 2
Deformation of the crumb, unit of the device			
– after 4 hours:			
general	66	59	57
– after 24 hours:			
general	48	45	43
Degree of preservation of freshness, %			
– after 48 hours			
general	36	38	36
Degree of preservation of freshness, %			
– after 48 hours	55	64	63

The detention of the drawing is confirmed by a decrease of cockiness by 30-67% after 24 hours and by 23-32% after 48 hours (Figure 2), and the increased water absorption capacity of the crumb (Table 3).

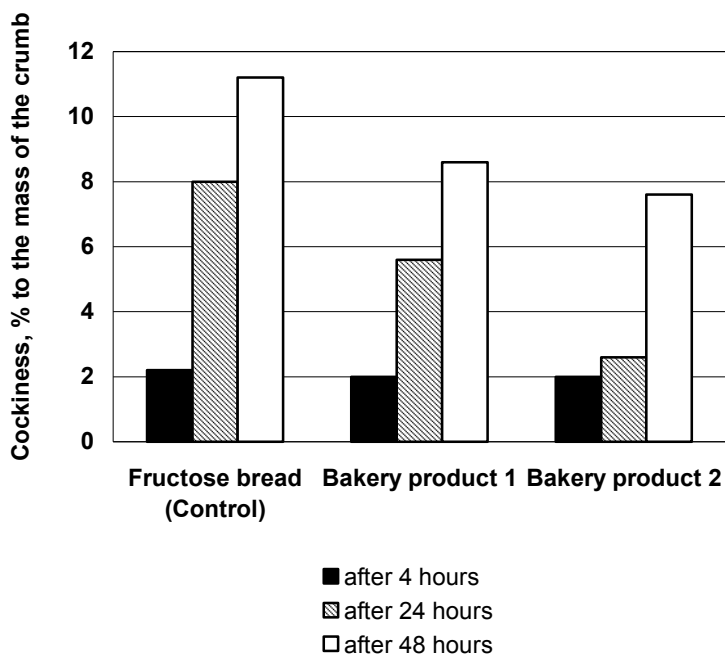


Figure 2. Cockiness of products during storage

Table 3

Water-absorbing capacity of crumb of the products,% on dry matter

Duration of storage, hours	Fructose bread (Control)	«Bakery product 1»	«Bakery product 2»
4	462	492	478
24	416	434	427
48	320	390	378

With the help of differential-thermal analysis, a determination of the forms of moisture binding in the bread crumb was made.

Derivatograms are shown on Figures 3, 4, 5.

The results of the analysis are in the Table 4.

Table 4

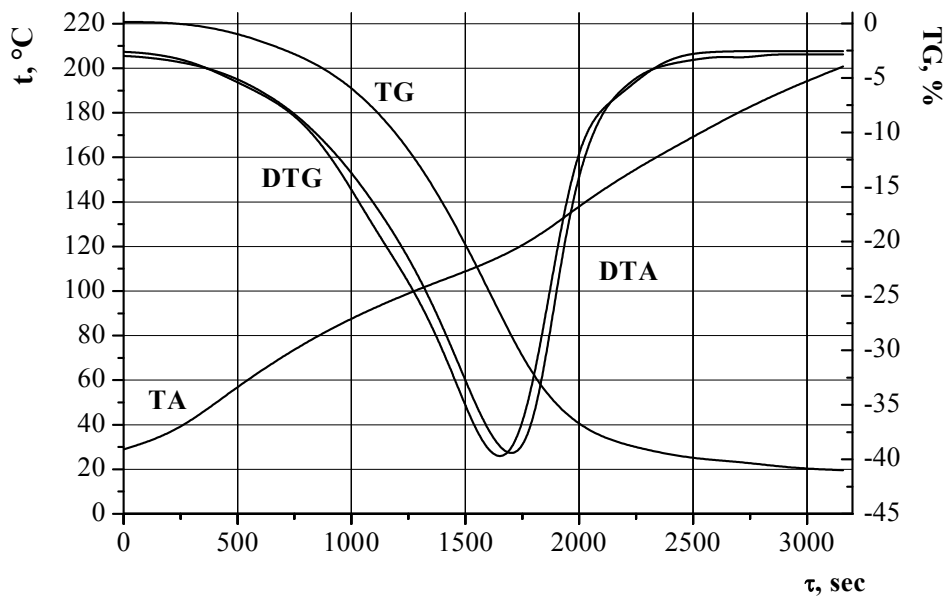
Loss of bound moisture by the samples

Samples	Duration of storage, hours	Mass fraction of moisture,% to the total volume		Reduced connected moisture content
		free	connected	
Fructose bread (Control)	4	72,0	28,0	3,9
	24	75,9	24,1	
«Bakery product 1»	4	69,2	30,8	1,4
	24	70,6	29,4	
«Bakery product 2»	4	68,8	32,2	2,0
	24	69,8	30,2	

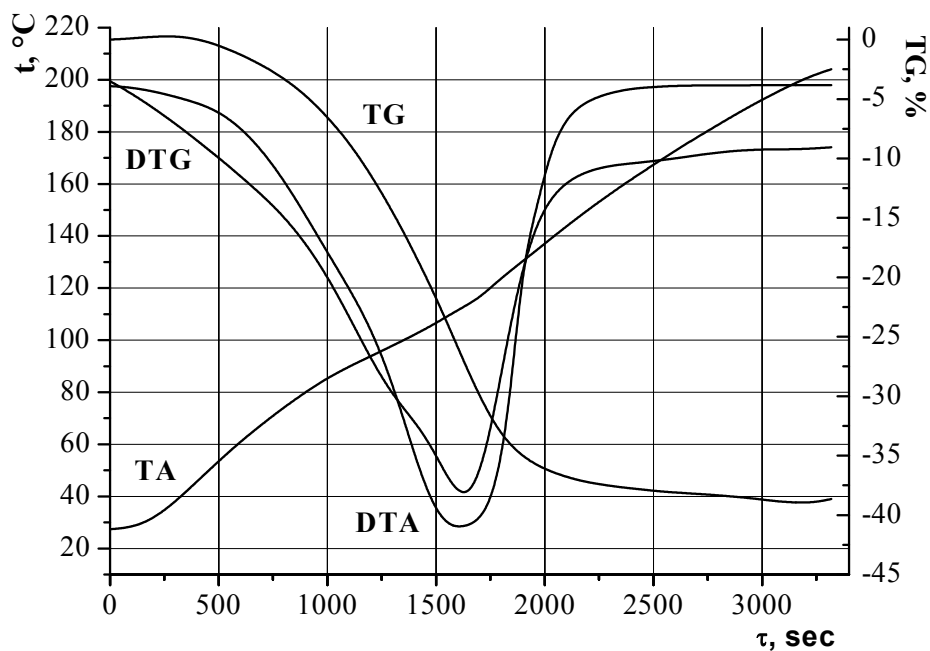
From the obtained derivatograms it is seen that during the evaporation of moisture for all samples, the peaks of the endothermic effect at certain specific temperatures are characteristic. All curves have similar nature, differing only by the size of temperature intervals corresponding to the evaporation of moisture with different levels of communication energy. The dependence of the higher content of the total amount of adsorption connected moisture with high communication energy in the samples «Bakery product 1» and «Bakery product 2» is seen compared with the control, which can be explained by the presence in the recipe of a greater quantity of products enriched with proteins and fibers with high hydrophilicity

As a result of the research, it was found that the storage of bread freshness correlates with a high content of connected moisture in it, which helps to slow down the processes of diffusion and bread crumbling.

An important component of the consumer value of products is taste and flavor. Their formation is conditioned by the chemical composition of the recipe components and observance of the technological process. It is believed that the main criterion that affects the formation of taste and flavor is the presence of carbonyl compounds formed during the baking process. Results of determining the content of bisulfite binding compounds are given in the Table 5.

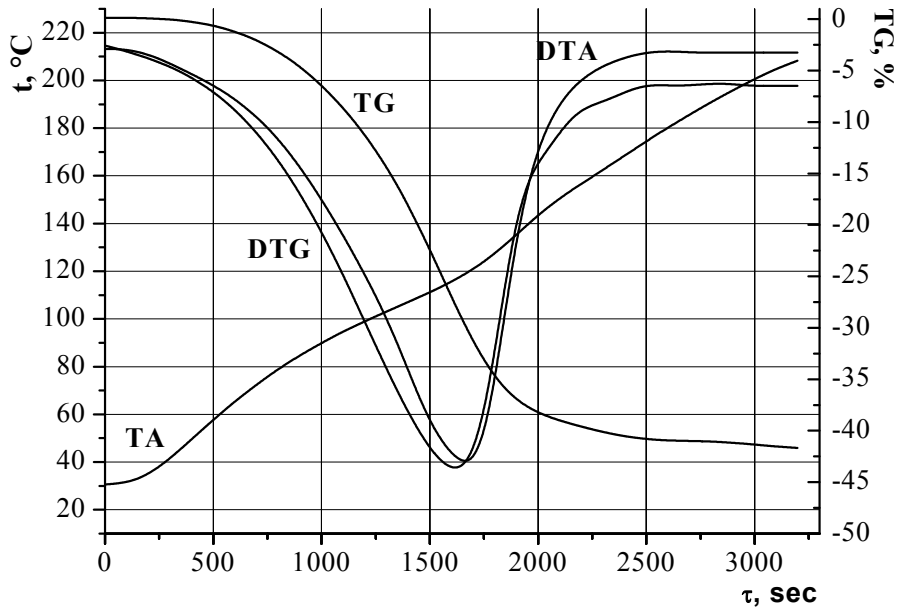


a

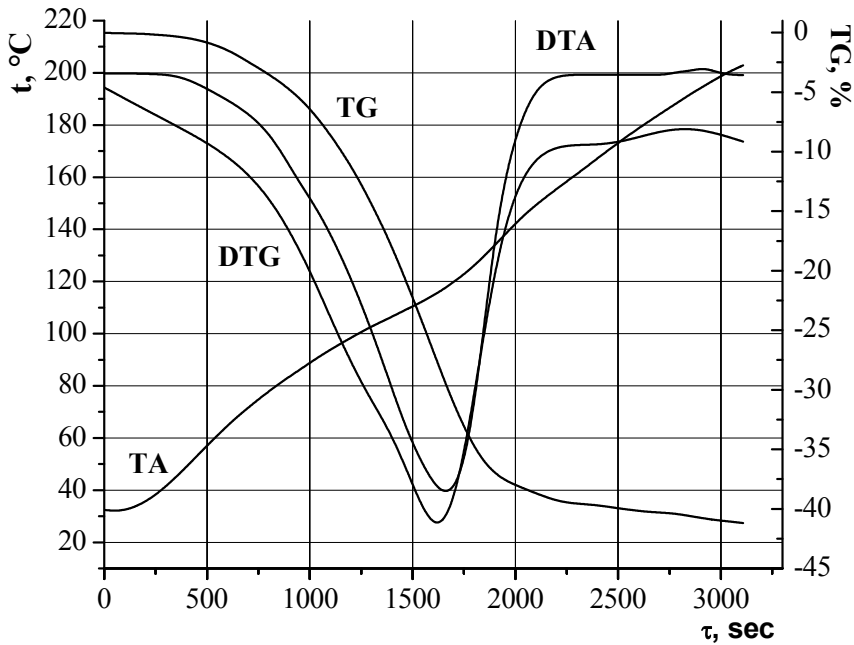


b

Figure 3. Derivatograms of thermolysis of bread crumb of Control sample:
a – after 4 hours, *b* – after 24 hours.

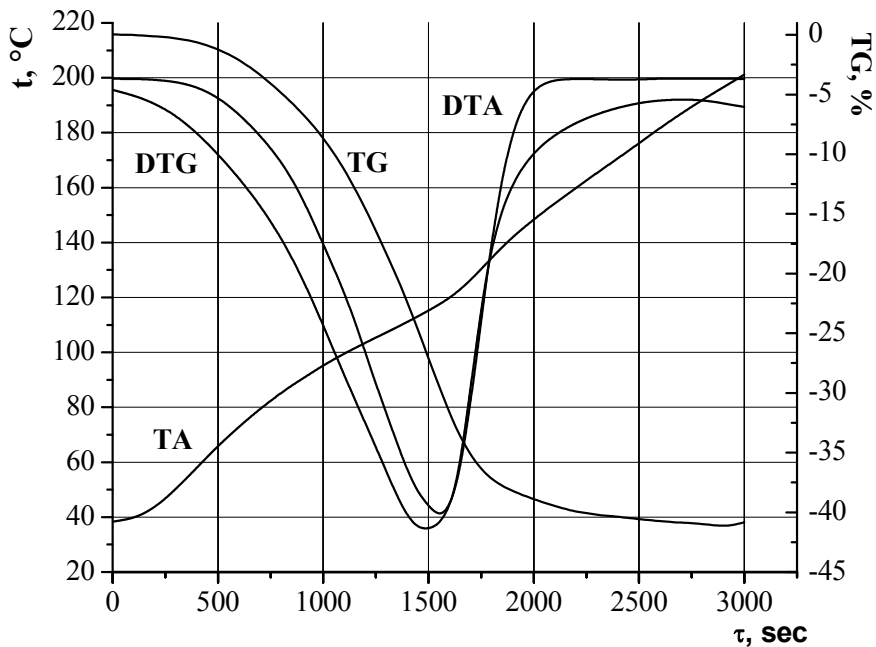


a

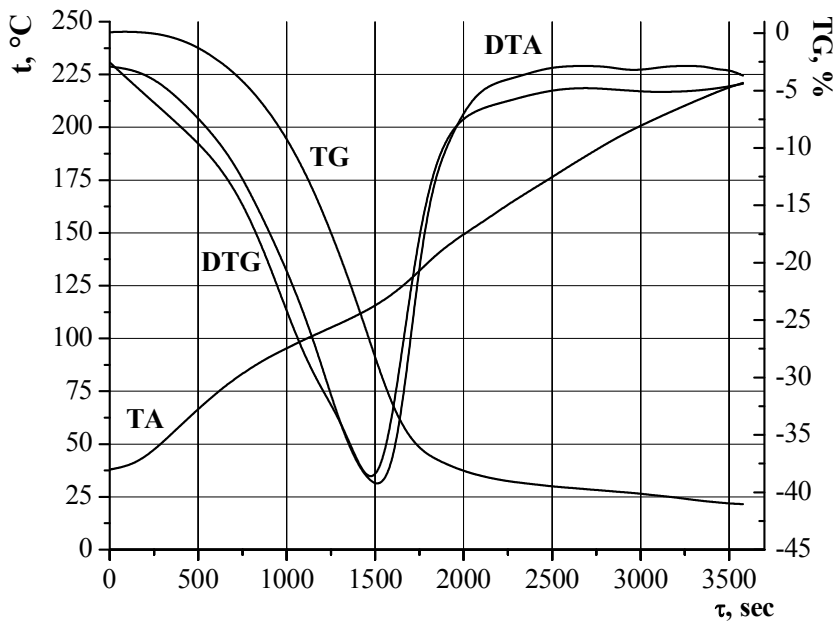


b

Figure 4. Derivatograms of thermolysis of bread crumb of «Bakery product 1»:
a – after 4 hours, *b* – after 24 hours.



a



b

Figure 5. Derivatograms of thermolysis of bread crumb of «Bakery product 2»:
a – after 4 hours, *b* – after 24 hours.

Table 5

Content of bisulfite binding agents, mg-eq/100 g of bread

Content of bisulfite binding agents, mg-eq/100 g of bread	Fructose bread (Control)	«Bakery product 1»	«Bakery product 2»
After 4 hours			
–in the crust	25,7	32,3	29,4
–in a crumb	5,3	6,4	6,1
After 24 hours			
–in the crust	22,8	26,4	24,2
–in a crumb	5,6	6,6	6,3
After 48 hours			
–in the crust	18,2	21,3	20,1
–in a crumb	4,9	5,9	5,6

Studies have shown that in the developed samples after 4 hours of storage the amount of aromatics is greater than the control: in the crust of «Bakery product 1» by 25,6%, in the crumb – by 20,7%, in «Bakery product 2» – in the crust by 14.4%, in the crumb – by 15%. In the process of storage, the products had less loss of bisulfite-binding agents.

The calculation of the nutritional value of products (Table 6) showed a significant increase of nutrient content in samples with additives.

Table 6

Nutritional value of products

Nutrient content in 100 g of products	Protein, g	Carbohydrates, g	Fat, g	Fiber, g	Mineral substances, mg			
					Mg	Ca	Zn	Fe
Fructose bread (Control)	6,4	44,8	0,7	0,7	0,01	0,014	0,006	0,01
«Bakery product 1»	7,7	30,2	1,4	1,6	7,8	11,1	0,4	0,6
«Bakery product 2»	7,8	31,8	1,5	1,8	8,0	11,7	0,4	0,6
Daily requirement for the 1 st group of work intensity at the age of 30-39 years	61	368	64	25	400	1200	17	15
Integral accelerator when consuming 100 g of bread, %								
Fructose bread (Control)	10,7	10,2	0,8	2,8	0,3	1,2	0,5	0,6
«Bakery product 1»	12,9	6,8	1,8	6,5	17,8	16,7	18,6	18,0
«Bakery product 2»	13,1	7,2	1,9	7,4	18,0	17,7	18,3	18,2

Conclusion

It is established that the products enriched with the ingredients of casein, artichoke powder, buckwheat fiber and calcium, zinc, magnesium and iron citrates, «Bakery product 1» and «Bakery product 2», have higher nutritional value than the control sample, which is confirmed by the percentage of daily nutrient requirement. The products have better quality characteristics and keep freshness longer during storage.

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Pro- and antioxidant activity of curcuminoids with lecithin in sunflower oil

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Abstract

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Introduction. Curcumin present as a major constituent amongst curcuminoids in turmeric has attracted significant attention due to wide range of biological and pharmaceutical activities. It reveals various therapeutic activities such as anti-inflammatory, nematocidal, anti-parasitic, antispasmodic and anticarcinogenic. Additionally, it is a powerful scavenger of reactive oxygen species. On the other hand, the pro-oxidant effect of curcumin has also been observed.

Materials and methods. The study has been carried out to evaluate the activity of curcuminoids in crude and refined sunflower oil containing synthetic antioxidant. The various blends of oil were prepared. The oxidative stability of oil blends was checked at 60 °C for 30 days at regular interval of 5 days according to the AOCS Official Methods by peroxide value (in meq/kg), *p*-anisidine value and total oxidation (Totox) value (in meq/kg).

Results and discussion. The tendency of curcumin to exhibit keto-enol tautomerism determines its physicochemical and antioxidant properties. It has been observed that curcuminoids showed noticeable dissimilar behavior in both oils. The hydrogen atom donation in case of curcumin is from the active methylene group, which exists only in keto form. The keto form predominates in neutral and acidic solutions whereas the enol form predominates in alkaline solution. In alkaline medium, curcumin undergoes degradation. The same theory is also applicable to other two curcuminoids, i.e., demethoxycurcumin and bisdemethoxycurcumin. Hence, it becomes crucial to maintain the curcuminoids in keto form to be used as antioxidant.

In crude sunflower oil, because of the presence of free fatty acids, curcuminoids did not undergo degradation imparting marginal antioxidant activity. Lecithin chelated metal ions present in oil, which promote oxidation of oil thereby inhibiting the autoxidation of oil. However, the synergistic activity of curcuminoids and lecithin revealed remarkable antioxidant activity.

In refined sunflower oil containing tertiary butylhydroquinone (TBHQ), curcuminoids showed pro-oxidant activity due to lack of acidic medium. Lecithin exhibited synergistic activity with TBHQ in refined sunflower oil. Nevertheless, the pro-oxidant effect of curcuminoids is not observed in presence of lecithin and TBHQ. Thus, the lecithin and TBHQ stabilized refined sunflower oil in presence of curcuminoids.

Conclusion. The structure-activity relationship plays an important role in determining the activity (antioxidant or pro-oxidant) of a particular compound. Thus, a constituent should exist in a proper structural form to be used as an antioxidant.

Introduction

Turmeric, the rhizome of plant *Curcuma longa* Linn has been widely used as a spice. Besides, it is used to colour food beverages like cheese, butter to increase its nutritive value [1] and in some medicinal preparations [2, 3]. The multiple traditional uses of turmeric in folk medicine have fostered research on the same. The dry rhizome of turmeric contains curcuminoids namely curcumin, demethoxycurcumin and bisdemethoxycurcumin [4]. Commercial preparations of curcuminoids usually contain approximately 77%, 17% and 3% of curcumin, demethoxycurcumin and bisdemethoxycurcumin respectively. Several studies in recent years have shown that curcumin has antioxidant, anti-inflammatory, antimicrobial, anti-bacterial, anti-parasitic, anti-mutagen and anticancer properties [5, 6]. It is believed that curcumin is a potent agent against many diseases such as anorexia, coughs, diabetes, hepatic disorders, rheumatism and Alzheimer disease [7–9]. Curcumin and avocado-soya bean unsaponifiables based antioxidant supplements are beneficial to get relief from knee osteoarthritis [10]. The other two curcuminoids namely demethoxycurcumin and bisdemethoxycurcumin also possess antioxidant activity [11]. The effectiveness of curcuminoids as an anti-depressive agent [12] and in wound healing [13] has also been proved. The safety of the *Curcuma longa* has been studied in various animal models [14, 15] and it is clear that turmeric is not toxic even at high doses in laboratory animals.

Curcumin has a strong antioxidant activity in food systems and in biological systems as well [16, 17]. Curcumin was proved to be considerably more effective than other spices in its ability to prevent lipid peroxidation. Its antioxidant effect was eight times more powerful than vitamin E [18] and it was significantly more effective in preventing lipid peroxide formation than the synthetic antioxidant, butylated hydroxytoluene (BHT) [19]. On the contrary, moderate pro-oxidant activity of curcumin has been observed in ghee [20].

Structurally, curcumin is 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione. It undergoes keto-enol tautomerism [21]. The tautomers are shown in Figure 1. Hydroxyl groups of the benzene rings, double bonds in the alkene part and the central β -diketone moiety are suggested to be likely responsible for the high beneficial activities of curcumin [22, 23]. The mode of action (i.e., either antioxidant or pro-oxidant) of curcumin depends upon the form (viz. keto or enol) in which it exists [24].

Sunflower oil being rich source of essential fatty acids is susceptible to autoxidation [25]. Hence, it cannot be stored without addition of antioxidant. In the view of the importance of curcumin, the objective of the study was to evaluate the activity of curcuminoids in crude and refined sunflower oil containing tertiary butylhydroquinone (TBHQ). The synergistic activity of curcuminoids with other natural antioxidants is illustrated [26, 27]. However, curcuminoids do not show remarkable synergistic effect in the presence of lipophobic antioxidant like ascorbic acid in water-in-oil emulsion [28]. The existence of other constituents in the substrate has a profound effect on the activity of the antioxidant [29]. The effect of natural constituents present in crude oil on the behavior of curcuminoids was investigated. Further, the mode of action of curcuminoids in presence of TBHQ alone in refined oil was examined. To our knowledge, this is the first report to investigate the effect of synthetic antioxidant on the activity of curcuminoids in refined sunflower oil. The study is extended further to investigate the effect of lecithin on the activity of curcuminoids in both oils. The outcome of the study was that the activity of curcuminoids differs in crude and refined sunflower oil containing TBHQ. In addition, the results led to the conclusion that the presence of other constituents had a remarkable effect on the activity of curcuminoids.

Materials and methods

Materials

Crude sunflower oil (CSFO) and refined sunflower oil (RSFO) without any synthetic antioxidant were received as gift samples from M/s Cargill India Pvt. Ltd., New Delhi. Curcuminoids powder was obtained from Kancor India Ltd., Angamaly South, India. The purity of curcuminoids was 96% with three components namely curcumin (59.3%), demethoxycurcumin (20.0%) and bisdemethoxycurcumin (16.7%) as analyzed by HPTLC (Desaga Sarstedt Gruppe, Applicator AS 30 and Densitometer CD 60) as per the previously mentioned method [30]. Soy lecithin was procured from M/s V.R. Chemicals, Mumbai. All other chemical reagents and solvents were obtained from s.d. fiNE-CHEM LiMiTEd, Mumbai.

Study of antioxidant activity

The various blends of oil containing curcuminoids (50 ppm), lecithin (1.5% w/v), TBHQ (150 ppm, 200 ppm) and their combinations were prepared. The oxidative stability of oil blends was checked according to the AOCS Official Methods [31] by Schaal Oven Test (Method Cg 5-97) at 60 °C for 30 days at regular interval of 5 days by peroxide value (in meq/kg) (PV, Method Cd 8-53), *p*-anisidine value (*p*-A.V., Method Cd 18-90) and total oxidation (Totox) value (in meq/kg) (Method Cg 3-91). All the experiments were carried out in triplicate and the values were expressed as arithmetic mean of the experiments along with standard deviation. The accelerated oxidative stability study of the oil blends is carried out to increase the rate of oxidation. At 60 °C, though the rate of oxidation is increased, the mechanism of oxidation is the same as that at ambient temperature.

The antioxidant activities of natural antioxidants were compared with the corresponding control samples under the same conditions. The relative antioxidant activities were compared using Oxidative Factor (OXF) for antioxidants based on mean peroxide value of triplicate experiments using following formula [32],

$$OFX = \frac{(PV_{final} - PV_{initial})_{antioxidant}}{(PV_{final} - PV_{initial})_{control}}$$

where PVs indicate the mean values of all triplicate determinations of the peroxide value.

Results and discussion

Jovanovic et al. [24] concluded that the two phenolic hydroxyl groups in curcumin are very weak hydrogen atom donors. The hydrogen atom donation in case of curcumin is from the active methylene group unlike other antioxidants which donate hydrogen atom from phenolic hydroxyl group to exhibit antioxidant activity. The active methylene group in curcumin exists only in keto form (Figure 1). In neutral and acidic solutions (from pH 3 to 7), the keto form predominates. In keto form, since methylene group is in-between two electron withdrawing carbonyl groups, the delocalization of the unpaired electrons on the oxygens of carbonyl groups takes place. This results in weakening of C-H bond of methylene group. The carbon radical so formed after donation of hydrogen atom gets

stabilized by resonance with neighboring carbonyl groups. Thus, a stabilized radical is formed, preventing the degradation of curcumin. Hence, curcumin exclusively acts as a hydrogen atom donor.

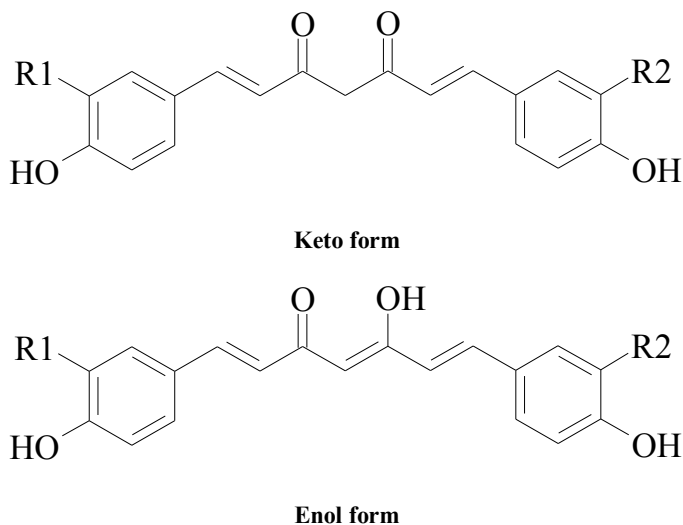


Figure 1. Tautomers of curcuminoids:

R1 = R2 = -OCH₃; Curcumin
 R1 = -H, R2 = -OCH₃; Demethoxycurcumin
 R1 = R2 = -H; Bisdemethoxycurcumin

The enol form of curcumin predominates above pH 8 and the active methylene group diminishes completely. In alkaline medium, curcumin is known to undergo degradation to form ferulic acid, feruloylmethane that further hydrolyzed to vanillin and acetone [33]. The formation of vanillin and ferulic acid takes place via peroxide formation [34]. Thus, the degradation of curcumin leads to increase in the peroxide value of the substrate [26].

The same theory is also applicable to other two curcuminoids, i.e., demethoxycurcumin and bisdemethoxycurcumin. Thus, it becomes necessary to maintain curcuminoids in keto form by providing reserved acidity in hydrophobic medium to utilize the antioxidant activity.

Effect of curcuminoids in synergism with lecithin on oxidative stability of CSFO

The crude vegetable oils extracted from oil bearing materials naturally contain free fatty acids formed during pretreatment and extraction processes [35]. The synergism between curcuminoids and lecithin was studied in crude oil (CSFO), i.e., in presence of tocopherols as natural antioxidants and free fatty acids those were anticipated to stabilize the curcuminoids by acting as an acidic buffer. The observations from Table 1 illustrate the synergism of curcuminoids and lecithin in CSFO that showed good antioxidant activity (Figure 2).

Table 1

Effect of curcuminoids and lecithin on oxidative stability of CSFO at 60 °C

Time (days)	CSFO	CSFO + 200 ppm TBHQ		CSFO + 50 ppm curcuminoids		CSFO + 1.5% lecithin		CSFO + 1.5% lecithin + 50 ppm curcuminoids	
	Totox [†]	OXF	Totox [†]	OXF	Totox [†]	OXF	Totox [†]	OXF	Totox [†]
5	41.2±1.4	0.42	24.9±1.0	0.63	41.7±1.5	0.42	18.9±0.9	0.69	25.1±0.4
10	57.4±1.2	0.28	27.1±1.3	0.74	51.2±1.7	0.45	32.0±1.4	0.42	30.7±0.7
15	80.7±1.5	0.26	30.2±1.1	0.78	64.8±2.1	0.58	50.9±1.8	0.39	38.8±0.9
20	106.8±1.6	0.29	38.9±1.8	0.81	88.3±1.9	0.66	74.1±1.5	0.42	51.9±1.1
25	124.2±1.9	0.28	44.7±1.5	0.83	104.0±2.2	0.71	89.6±2.1	0.46	60.6±0.9
30	138.1±2.3	0.28	49.4±1.7	0.84	116.5±2.8	0.74	102.0±2.5	0.49	67.6±1.3

[†] The Totox values (in meq/kg) given are means of three consecutive experiments ± standard deviations

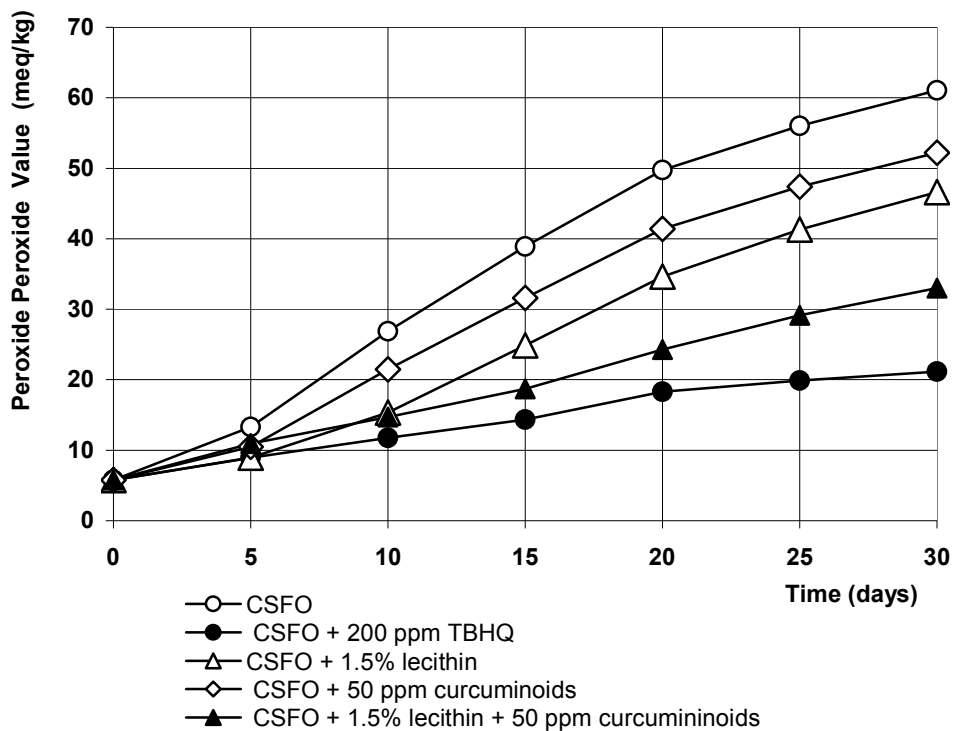


Figure 2. Effect of curcuminoids and lecithin on oxidative stability (peroxide formation) of CSFO at 60 °C

Generally, oil contains polyvalent metals ions caught during processing, which further promote autoxidation of oil on storage. Lecithin chelated these metal ions thereby inhibiting the formation of radicals and peroxides. Hence, CSFO in presence of lecithin gave lower peroxide value than CSFO. Lecithin being an emulsifier can additionally prevent the autoxidation of oil by its action as an oxygen barrier at oil/air interface. These effects inhibited the formation of radicals and peroxides due to metal ions, consequently reducing the peroxide formation at initial stage. However, the same effects were incapable to control autoxidation due to radicals formed at later stage.

Moreover, the free fatty acids present in CSFO (acid value, 3.4 mg KOH/g) stabilized curcuminoids, eventually imparting antioxidant effect. Hence, curcuminoids gave marginal antioxidant activity in CSFO. At the same time, the curcuminoids cannot terminate the activity of metal ions and peroxide formation was more than that of CSFO containing lecithin.

The synergistic activity of lecithin and curcuminoids gave good antioxidant activity, as lecithin promoted metal ion chelation and curcuminoids act as antioxidant. As a result, the autoxidation of oil was inhibited by two different ways. It was observed that this synergistic effect is less than TBHQ.

Effect of curcuminoids in synergism with lecithin on oxidative stability of RSFO in presence of TBHQ

The fatty acids from CSFO are removed in subsequent refining process. As discussed in our previous study, curcuminoids showed pro-oxidant effect in refined sunflower oil [26] due to absence of free fatty acids. The behaviour of curcuminoids in presence of lecithin in RSFO was evaluated. The acid value of RSFO is very low, i.e., 0.29 mg KOH/g. It can be seen from Table 2 that initially curcuminoids underwent degradation. However, lecithin scavenged radicals formed due to curcuminoids along with that generated by RSFO and continued to act as an antioxidant. As a result, the peroxide value was reduced below to the control after 20 days. Lecithin chelated metal ions by its usual phenomenon but the amount 1.5% was inadequate to scavenge free radicals generated by the combined process of autoxidation of oil as well as curcuminoids.

Table 2

Effect of curcuminoids and lecithin on oxidative stability of RSFO at 60 °C

Time (days)	RSFO	RSFO + 1.5% lecithin		RSFO + 1.5% lecithin + 50 ppm curcuminoids	
	Totox [†]	OXF	Totox [†]	OXF	Totox [†]
5	17.5±0.7	1.03	18.5±1.2	2.17	36.9±1.0
10	24.2±0.5	0.74	19.6±1.4	1.57	39.0±1.3
15	31.0±1.0	0.69	22.1±1.0	1.71	50.1±1.7
20	47.3±1.2	0.64	31.1±1.8	1.12	52.6±1.5
25	57.3±1.9	0.58	34.7±1.7	0.98	58.2±1.4
30	77.3±2.2	0.46	39.0±1.5	0.85	72.5±1.9

[†] The Totox values (in meq/kg) given are means of three consecutive experiments±standard deviations

The antioxidant effect of curcuminoids and lecithin was also studied in presence of TBHQ. The control sample was RSFO containing 150 ppm TBHQ in this case. Figure 3 reveals the pronounce pro-oxidant effect of curcuminoids in presence of TBHQ that was shown by higher totox values for curcuminoids as compared to control sample (Table 3). It signifies that, 150 ppm TBHQ was potentially insufficient to stabilize curcuminoids in RSFO. The combined activity of TBHQ and lecithin was found to be unaffected in presence of curcuminoids. In other words, curcuminoids did not show the pro-oxidant effect in presence of lecithin and TBHQ.

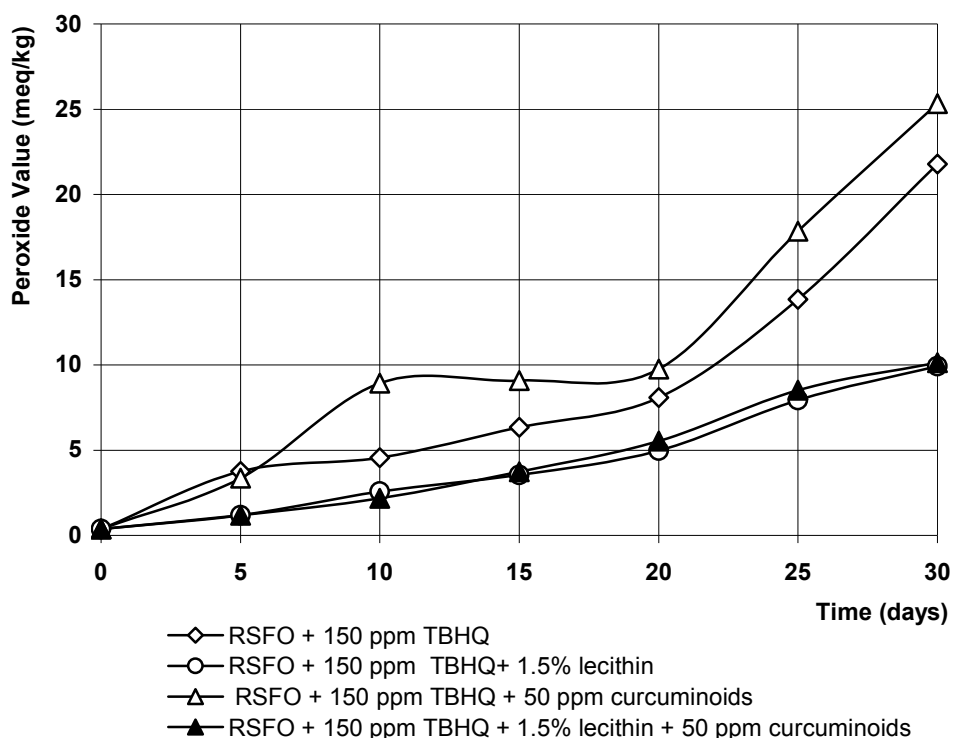


Figure 3. Effect of curcuminoids and lecithin with TBHQ on oxidative stability (peroxide formation) of RSFO at 60 °C

Lecithin showed synergistic antioxidant activity with TBHQ as shown with other phenolic antioxidants [36, 37]. It is quite possible that curcuminoids may undergo degradation in this blend as well. But the pro-oxidant effect of curcuminoids was not observed. This may be due to lecithin that chelated polyvalent metal ions and TBHQ that scavenged free radicals, generated by oxidation of oil and curcuminoids. Hence, the combined effect of lecithin and TBHQ stabilized RSFO even in presence of curcuminoids.

Table 3
Effect of curcuminoids and lecithin on oxidative stability of RSFO(T) at 60 °C

Time (days)	RSFO(T)	RSFO(T) + 50 ppm curcuminoids		RSFO(T)+ 1.5% lecithin		RSFO(T) + 1.5% lecithin + 50 ppm curcuminoids	
	Totox [†]	OXF	Totox [†]	OXF	Totox [†]	OXF	Totox [†]
5	10.8±0.2	0.89	15.7±0.7	0.24	5.5±0.8	0.24	3.9±0.4
10	13.7±0.4	2.05	21.1±1.2	0.52	7.5±0.7	0.43	6.5±0.6
15	17.1±0.3	1.46	23.9±1.0	0.53	9.9±1.1	0.56	9.6±0.7
20	21.2±0.5	1.22	25.5±1.5	0.60	12.6±0.7	0.67	13.3±1.4
25	34.1±0.9	1.30	41.8±2.2	0.56	18.2±1.4	0.60	19.3±2.2
30	50.2±1.1	1.17	56.9±1.7	0.45	22.1±2.4	0.46	22.7±2.7

[†] The Totox values (in meq/kg) given are means of three consecutive experiments±standard deviations

RSFO(T) is the refined sunflower oil with added 150 ppm TBHQ

Conclusion

The antioxidant or pro-oxidant effect of a compound depends upon its structure. This is particularly demonstrated in case of curcuminoids that showed contrast activity in keto and enol forms. Curcuminoids exhibited antioxidant activity provided they should remain in keto form. Curcuminoids showed antioxidant effect in crude oil due to the presence of free fatty acids that contributed to the stabilization of curcuminoids by maintaining them in keto form. In refined oil with TBHQ, curcuminoids were unable to maintain themselves in keto form exhibiting pro-oxidant effect due to the absence of free fatty acids. Curcuminoids showed synergistic antioxidant activity with lecithin in crude oil, which was not shown in refined oil even in presence of synthetic antioxidants like TBHQ. It can be concluded that it is crucial to maintain the proper form of a compound to utilize its antioxidant effect.

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Inhibition of microbiological processes in sucrose extraction

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Abstract

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Introduction. Due to the intensive development of microbiological processes in the diffusion installation there is an additional loss of sucrose as a result of decomposition, as well as deteriorating qualitative parameters of diffusion juice, which adversely affects all subsequent stages of sugar production.

Materials and methods. The objects of research were: diffusion juice; pure cultures of bacteria *Leuconostoc mesenteroides*, *Bacillus subtilis*, *Pseudomonas spp.*, *Escherichia coli*, which cause significant loss of sucrose in the production of sugar from sugar beet; a new generation of disinfectants.

Results and discussion. The greatest losses of sucrose in diffusion juice were caused by bacterias of the *Pseudomonas spp.* genus, because within 24 hours of incubation these samples of the diffusion juice, the content of sucrose decreased in 2 times. In samples of juice from *B. subtilis* and *E. coli*, a significant increase in nitrite was observed throughout the term of the incubation. In fact, the final content of nitrite in the samples after 24 h incubation increased 10-15 times. In the sample of juice from *L. mesenteroides* there was a significant increase in the level of lactic acid, compared with the initial value. After incubation at 37 °C for 2 h, the content of lactic acid was 10.63 mg/100 cm³, compared to the initial content of lactic acid – 3.07 mg/100 cm³. In the case of the development of slime-forming bacteria in diffusion juice, intensive accumulation of dextran is observed, which correlates with the increase of the number of cells of test culture *L. mesenteroides*.

Disinfectants on the basis of polyhexamethylenebiguanidine hydrochloride; quaternary ammonium compounds; dichloroisocyanuric acid sodium salt; peracetic acid and hydrogen peroxide showed high efficacy in most microorganisms that cause loss of sucrose in the process of its extraction from beetroot shavings and lead to a deterioration of the technological quality of intermediates beet sugar production. In addition, these means are also effective concerning slime-forming bacteria.

Conclusions. The investigated means are characterized by high bactericidal action against the microorganisms present in diffusion juice. These agents are also effective in suppressing the development of slime-forming bacteria.

Introduction

During extraction of sucrose from beetroot shavings, processes occur leading to the decomposition of sucrose due to the action of beet cellular invertase, acid catalysis and microorganism activity.

The activity of the enzyme invertase, which is part of the beet juice, may increase with the prolonged storage of root crops. During extraction of sucrose from beetroot shavings at a temperature of 70–75 °C, the enzyme is inhibited. Consequently, decomposition of sucrose under the influence of cellular invertase of beets can occur only at the initial stage of extraction. The issue of decomposition of sucrose as a result of inversion is devoted to a series of studies A.R. Sapronov and S.E. Harina [1]. According to their conclusions, decomposition of sucrose occurs as a result of auto-catalytic and consecutively reactions. The intensity of the autocatalytic reaction is influenced by the temperature and pH₂₀ of the medium.

Research of the influence of microbiological processes on sucrose loss during extraction is devoted to a large number of scientific works in Ukraine and abroad. It was established that, subject to the optimum regimen of the extraction process, the loss of sucrose from the abovementioned factors does not exceed 0.1% to the mass of beets. In the event of a violation of the technological process and the processing of beet affected by rot or mucous bacteriosis, the loss of sucrose from decomposition can reach 0.6–0.9% and above [2]. The microflora of diffusion juice is represented by bacteria, yeast and micelial fungi, the total amount of which in 1 centimeter of cubic juice ranges from tens of thousands to tens of millions. This is due to the technological quality and microbiological contamination of shavings and feed water entering the diffusion installing [3, 4].

Thus, microbiological processes cause the decomposition of sucrose with the formation of various metabolites, which leads to deterioration of the quality of white sugar. In particular, bacteria of the *Clostridium* genus are strong gas generators, which leads to increased foam ability of juice. During the active development of butyric bacteria there is formation of ammonia, acetone, acetic aldehyde, organic acids, which are the products of the decomposition of protein substances of diffusion juice [5, 6]. Accumulation of ammonia in juices inhibits the decomposition of amides on defecation, causing in juice of II saturation the alkalinity in the form of NH₄ON, which decreases during condensation at the evaporation station. Ammonia is a catalyst for increasing the color of the syrup boiling and subsequent crystallisation. When microbial decomposition of protein substances of sugar beet, amides are also formed, the main part of which in products of sugar production is glutamin and asparagine. Established [7], that the data of amino acids are involved in the processes of formation of melanodynes and increased the molasses forming coefficient.

Under the influence of denitrification microorganisms, in particular bacteria of *Bacillus*, *Pseudomonas* genus, sugar beet nitrates are transformed into nitrites [5], and then potassium imidosulfonate is formed during sulfitation. As a result of this conversion, the ash content of sugar increases [7].

Accumulation of organic acids (milk, oily, acetic) leads to acid hydrolysis of sucrose, increasing the content of calcium salts. In the case of microbiological decomposition of sucrose, lactic acid is up to 96% of the total content of organic acids. There is correlation dependence between the amount of decomposed sucrose and the lactic acid formed. The content of lactic acid in beet juice from conditioned raw materials is 1-3 mg per 100 g of juice. As a result of the microbiological damage of sugar beet, the content of lactic acid in beet juice can be increased to 10–12 mg per 100 g of juice and above. Accordingly, when processing beets of high quality and adhering to the technological regime of the extraction

process, the content of lactic acid in diffusion juice does not exceed 2-5 mg per 100 g of juice. When processing microbiologically damaged raw materials or non-compliance with the technological regime, the content of lactic acid is increased to 10-20 mg per 100 g of juice and above [8]. Therefore, it is recommended when calculating sucrose losses because of microbiological decomposition take into account the increase in the content of lactic acid in diffusion juice compared to beet juice [9, 10].

Due to the activity of bacteria of the *Leuconostoc* genus (*L. mesenteroides*, *L. dextranicum*) and spore-forming bacteria of the *Bacillus* genus (*B. betaevicosum*, *V. mesentericus*, *V. subtilis*), in the diffusion juice are formed polysaccharides of glucose and fructose – dextran and levan [11, 12]. These substances are well dissolved in water with the formation of viscous solutions. The negative influence of life products of slime-forming bacteria is manifested in: reducing the quality of intermediate products of sugar beet production; increase in sucrose losses in production (due to increased content of sucrose in molasses); deterioration of filtration properties of juices in the process of purification; distortion of the indexes of sucrose content in beets at the polarimetric method of determination and, accordingly, purity of cell and diffusion juices [11, 13–15].

The greatest effect of suppression of vital activity of microorganisms can be achieved by maintaining a temperature of about 75 °C throughout the extraction process. However, from a technological point of view, such a temperature regime leads to an increase in the content of soluble pectin substances in diffusion juice, which negatively affects the filtration process and leads to deterioration of the quality of the purified juice. Therefore, at the sugar factories, in order to inhibit microbiological processes, disinfectants are introduced at the extraction stage [8].

Accordingly, our research objectives was to study the microbiological and acid decomposition of sucrose and investigate the effectiveness of a new generation of disinfectants on inhibiting the activity of microorganisms which cause significant loss of sucrose in the production of sugar from sugar beet.

Materials and methods

As for the objects of research, we selected pure cultures of bacteria *Bacillus subtilis*, *Pseudomonas spp.*, *Escherihia coli* and slime-forming bacteria *Leuconostoc mesenteroides* [16], which cause significant loss of sucrose in the production of sugar from sugar beet [8, 15, 17].

The research applied the use of laboratory diffusion juice of average technological quality and factory diffusion juice with additionally introduced culture *L. mesenteroides*.

In accordance with the current requirements [18], which put forward to for disinfectants, chemical compounds used as active substances should be characterized by a wide range of biocidal action, maintain their activity for a long time, should not have a negative impact on the quality of products, according to the parameters of acute Toxicity belongs to the 3rd–4th grade of moderately hazardous substances. Taking into account the above-mentioned factors, the following disinfectants were selected for research: on the basis of polyhexamethylenebiguanidine hydrochloride – "Antykam® CID-LEUCO 20"; quaternary ammonium compounds – "XSG des 3"; dichloroisocyanuric acid sodium salt – "XSG des 4"; peracetic acid and hydrogen peroxide – "XSG des 5".

Determination the influence of microbiological processes on the accumulation of metabolism products in diffusion juice

In samples sterile diffusion juice made a certain number of vegetative cells of a certain type of bacteria (*Leuconostoc mesenteroides*, *Bacillus subtilis*, *Pseudomonas spp.*, *Escherichia coli*). Incubation was performed at 37 °C for 24 hours. After 2, 5 and 24 hours indicator determined by the change in pH, purity, the content of lactic acid, nitrites, dextran, microorganisms and compared with control values of the original diffusion juice. Determination of lactic acid, nitrites and dextran was carried out by colorimetric method [13, 19]. The pH value of the medium was monitored using a pH meter. The total number of microorganisms was determined by sowing on the medium of MIA (meat infusion agar) and MIA + 10% sucrose.

Determination of the effectiveness of disinfectants activity

For research, disinfectants were used with the following expenditures: "Antykam® CID-LEUCO 20" – 0.002%; "XSG Des 3" – 0,0006%; "XSG Des 4" – 0.002%; "XSG Des 5" – 0.004%, which were added to the initial diffusion juice. The factory diffusion juice with additionally introduced culture *L. mesenteroides* was used for research. The samples were thermostated at 37 ° C. for 24 hours. Thermostatic the sample of diffusion juice without disinfectants was also performed. Microbiological examination of the output diffusion juice and juices with the means was carried out after 30 minutes. Determination was conducted by seeding the samples using the Koch method for dense nutrient media: MIA – for determining the total content of microorganisms QMAFAnM – Quantity of Mesophilic Aerobic and Facultative Anaerobic Microorganisms), MIA + 10% sucrose – for the determination of slime-forming bacteria; indicator beetroot agar – for acid-forming bacteria; wort agar – for micelial fungi and yeast.

After counting the colonies grown on the appropriate nutrient medium, the effect of disinfection calculated according to the formula:

$$E_d = \frac{(B_1 - B_2)}{B_1} \cdot 100$$

where B_1 is the initial content of microorganisms in 1 g (cm^3) of the product; B_2 – the content of microorganisms in 1 g (cm^3) of the product after appropriate treatment.

Determination of microbiological contamination of diffusion juice by spontaneous fermentation. The laboratory diffusion juice of average technological quality was used for research. Disinfectants were used with the following expenditures: "Antykam® CID-LEUCO 20" – 0.002%; "XSG Des 3" – 0,0006%; "XSG Des 4" – 0.002%; "XSG Des 5" – 0.004%, which were added to the initial diffusion juice. The samples were thermostated at 37 ° C. for 24 hours. Thermostatic the sample of diffusion juice without disinfectants was also performed. In the samples at the beginning of the experiment and at certain intervals, the value of pH indicator of the juice was measured. On the basis of the obtained indicators, the control of microbiological processes in diffusion juice was carried out and conclusions were made about the intensity of microorganisms in it.

Results and discussion

An important task for extraction of sucrose is to minimize losses due to decomposition. We consider the microbiological and acid decomposition of sucrose. In addition, comparative studies of the effectiveness of modern disinfectants at the sucrose extraction stage have been carried out.

Determination the influence of microbiological processes on the accumulation of metabolism products in diffusion juice

The purpose of this study was to determine the dependence of the growth of metabolism products of microorganisms in diffusion juice on the temperature, duration of the process and the nature of the contaminating microflora.

Table 1 shows the results of studies using pure cultures *L. mesenteroides*, *B. subtilis*, *Pseudomonas spp.*, *E. coli*.

Table 1
Incubation of diffusion juice with clean cultures of bacteria

Technological indices of diffusion juice	pH value	Mass fraction of dry substances, %	Mass fraction of sucrose, %	Cleanliness, %	Lactic acid content, mg/ 100 cm ³	Nitrite content, mg/dm ³
Output juice (sterile)	6,6	10,3	8,25	80	3,07	2,38
2 hours later						
<i>L. mesenteroides</i>	6,0	10,2	8,0	78,4	6,69	2,46
<i>B. subtilis</i>	6,02	10,3	8,2	79,6	3,13	3,6
<i>Pseudomonas sp.</i>	5,99	10,2	7,6	74,5	3,2	3,74
<i>E. coli</i>	6,06	10,3	8,1	78,6	3,45	3,48
5 hours later						
<i>L. mesenteroides</i>	5,8	10,2	7,8	76,5	7,29	2,8
<i>B. subtilis</i>	6,14	10,3	7,9	76,7	3,18	8,06
<i>Pseudomonas sp.</i>	6,03	10,0	7,1	69,6	4,42	7,59
<i>E. coli</i>	5,9	10,3	7,4	71,8	3,6	20,3
24 hours later						
<i>L. mesenteroides</i>	5,36	10,4	6,7	64	10,63	2,92
<i>B. subtilis</i>	6,22	10,0	7,0	70	3,21	27,08
<i>Pseudomonas sp.</i>	6,21	10,3	4,5	43,7	9,14	36,1
<i>E. coli</i>	5,48	10,4	6,9	66,3	6,08	43,76

On the basis of the analysis of the results of the conducted studies, there was a decrease in the content of sucrose and the purity of the diffusion juice in all the analyzed samples. It

has been established that the greatest losses of sucrose in diffusion juice are caused by bacteria of the *Pseudomonas spp.* genus. So, after incubation these samples of diffusion juice for 24 hours, the sucrose content decreased 2-fold. In samples of juice from *B. subtilis* and *E. coli*, a significant increase in nitrite was observed throughout the term of the incubation. In the sample juice from *L. mesenteroides* after incubation at 37 °C for 2 h, the content of lactic acid increased by 50%, after 18 h. – by 60%, and after one day – by 3.5 times and was 10.63 mg / 100 cm³ compared with the initial content of lactic acid – 3.07 mg / 100 cm³.

The most dangerous type of microbial damage to sugar beets is mucous bacteriosis. As a result of affection of roots in beet juice, dextran is formed, which causes not only direct loss of sucrose, but also creates significant problems in production. The most common species among the slime-forming bacteria found in sugar factories is *Leuconostoc mesenteroides*. The formation of dextran by the bacteria of the *Leuconostoc mesenteroides* genus occurs as a result of the decomposition of sucrose, similar to the enzymatic inversion, except that glucose is polymerized in dextran, and fructose is used to feed bacteria [11].

We have established the dependence (Figure 1) accumulation of dextran at incubation a diffusion juice samples infected with *L. mesenteroides* culture.

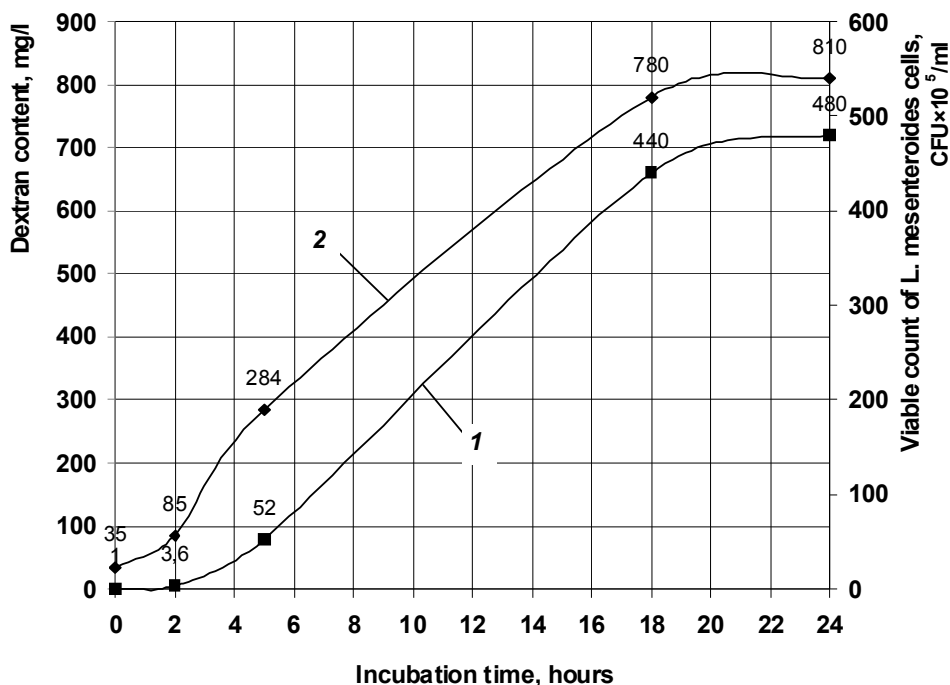


Figure 1. Accumulation of dextran at incubation of diffusion juice samples infected with *L. mesenteroides*:

1 – Viable count of *L. mesenteroides* cells; 2 – Dextran content.

* Note: the initial content of *L. mesenteroides* cells is 1 × 10⁵ CFU/cm³

It should be noted that at incubation samples of diffusion juice, the number of test cultures cell increased by almost two orders of magnitude compared with the initial content and amounted to 4.8×10^7 CFU/cm³ after 24 hours of cultivation, and the content of dextran in 24 hours increased 20 times compared with initial meaning.

According to the conducted studies, it can be concluded that with significant infection of diffusion juice in the event of untimely response and failure to comply with appropriate disinfection measures increases the amount of unaccounted loss of sucrose due to the livelihoods of microorganisms. In addition, products of microbial metabolism accumulate, which also cause sucrose loss in the subsequent stages of production.

Determination of the effectiveness of disinfectants activity

Consequently, in the process of extraction, undesired processes of decomposition of sucrose are possible. In this case, the most effective way of preventing is the use of modern disinfectants. Among the wide range of modern disinfectants we have chosen to study the means on the basis of active substances that have found the most widely used in the sugar industry of Ukraine.

Intensive development of microorganisms and, consequently, decomposition of sucrose occurs in the processing of bad quality beet and in the event of significant infection of the diffusion juice. Therefore, the factory diffusion juice with additionally introduced culture *L. mesenteroides* was used for research.

The results of experimental studies of the microflora of diffusion juice during the use of disinfectants are given in table 2, indicate that the selected means have a high bactericidal effect on the microorganisms present in the diffusion juice.

Table 2
Microbiological parameters of diffusion juice when administering disinfectants

Indicators	Control diffusion juice	Investigated disinfectants			
		Antykam	XSG des 3	XSG des 4	XSG des 5
		Expense of means, % by weight of juice			
		0,002	0,002	0,0006	0,004
QMAFAnM, CFU $\times 10^8$ / cm ³	6,0	1,05	0,5	0,6	0,7
The effect of disinfection, %	-	82,6	91,6	90,0	88,3
The content of slime-forming bacteria, CFU $\times 10^7$ / cm ³	61,2	12	4,6	6,0	2,3
The effect of disinfection, %	-	80,4	92,5	90,2	96,2
The content of acid-forming bacteria, CFU $\times 10^7$ / cm ³	98	21	12	3	4
The effect of disinfection, %	-	78,6	87,7	96,9	95,9
Content of mold fungi and yeast, CFU $\times 10^6$ / cm ³	8,6	1,5	1,0	0,8	4,8
The effect of disinfection, %	-	82,5	88,4	90,6	41,2

Determination of microbiological contamination of diffusion juice by spontaneous fermentation

One of the indirect methods for determining the microbiological contamination of diffusion juice is the method of spontaneous fermentation. It should also be noted that along with microbial decomposition of sucrose there is a decomposition of sucrose due to acid catalysis. Since disinfectants are different in terms of the chemical nature of the substance, it is interesting to research their effect on the technological quality of diffusion juice. To this end, has been carried out the determination of the change in the meaning of pH₂₀ of diffusion juice by introducing of different expenditure of disinfectants and thermostating of diffusion juice at 37°C for 24 hours.

Changing the value of pH₂₀ of diffusion juice at incubation treated with disinfectants is given in Table 3.

Table 3
Dynamics of change of pH₂₀ at incubation of diffusion juice treated with disinfectants

Duration of incubation, hour	Control diffusion juice	Investigated disinfectants			
		Antykam	XSG des 3	XSG des 4	XSG des 5
		Expense of means,% by weight of juice			
		0,002	0,002	0,0006	0,004
Immediately after entering, 0 hours	6,40	6,28	6,31	6,30	6,02
1 hour	5,89	6,00	6,01	6,25	6,01
2 hours	5,70	5,91	5,93	6,17	5,76
6 hours	5,30	5,60	5,32	6,08	5,40
24 hours	3,60	4,90	3,75	5,90	4,16

The results of the studies presented in tables 2-3 show an intensive course of microbiological processes in the control sample of diffusion juice (QMAFAnM – 6.0×10^8 CFU / cm³), resulting in a decrease in the pH of the juice for 24 hours incubation at 37 °C from 6.4 to 3.6 units.

At the same time, in the case of the use of the tool "XSG Des 4" for the expenses of 0,0006% to the mass of the product, the development of microbiological processes is significantly suppressed, as evidenced by the meanings of pH of the juice during its incubation at 37 °C and a duration of 24 hours, as well the effect of disinfecting diffusion juice on different groups of microorganisms.

It should be noted that the meanings of pH of the diffusion juice samples with the means "XSG Des 5" has decreased immediately after its introduction. This is due to the chemical nature of the active substance of the product (peroxyethane acid) and, consequently, the low meaning of pH of the working solutions of the means.

Therefore, when choosing a disinfectant, the meaning of pH of the working solutions should be taken into account, as well as the change of the pH of the diffusion juice after the application of the disinfectant.

Conclusions

As a result of experimental studies, it has been established that the development of microbiological processes at the stage of extraction of sucrose from beetroot shavings causes significant loss of sucrose.

Researches have shown that in the case of the development of slime-forming bacteria in diffusion juice there is an intense accumulation of dextran, which correlates with an increase in the number of cells of the test culture *L. mesenteroides*.

The results of the research show that the means of "XSG des 3", "XSG des 4", "XSG des 5", "Antykam® CID-LEUCO 20" have high efficiency in relation to the majority microorganisms that cause loss of sucrose in the process of its extraction from beetroot shavings and lead to a deterioration of the technological quality of intermediate products of sugar beet production.

It can be concluded that it is expedient to use the means of "XSG Des 4" and "Antykam® CID-LEUCO 20" for processing of nourishing water and a juice-shavings (juicer) mixture in order to disinfect them and prevent the development of microbiological processes. At that, the range of concentrations of working solutions for root crop processing is: for the means on the basis of active chlorine ("XSG des 4") 0,02–0,006%, based on polyhexamethylenebiguanidine hydrochloride (Antykam® CID-LEUCO 20") – 0,1–0,2%.

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Comparative studies on the quality of sandesh from cow milk chhana with soy-milk chhana addition

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Abstract

Keywords:

Milk
Sandesh
Cow
Soy
Chhana
Quality

Introduction. Sandesh is a popular chhana based sweetmeat of Bangladesh. The present study was carried out to compare the quality of Sandesh made from Cow-milk Chhana and along with addition of different level of Soy-milk Chhana.

Materials and methods. Four different types of Sandesh, namely S₁ (from 100% cow milk chhana), S₂ (75% cow milk chhana +25% soy milk chhana), S₃ (25% cow milk chhana + 75% soy-milk chhana) and S₄ (100% soy-milk chhana) were processed in the Laboratory of the Department of Food Processing and Engineering, Chittagong Veterinary and Animal Sciences University. Prepared sandesh samples were analyzed for moisture, protein, fat, ash, carbohydrate content, % acidity and sensory properties. The acceptability of Sandesh samples were studied by a taste panel consisting of 15 panelists.

Results and discussions. Results indicated that the moisture content were 22.53±0.12, 22.95±0.20, 23.54±0.22 and 25.44±0.17% respectively; protein content 21.87±0.32, 23.02±0.17, 25.92±0.42 and 29.62±0.23%; fat content 20.44±0.05, 19.02±0.03, 17.00±0.05 and 16.42±0.10%; ash content 0.88±0.04, 1.39±0.03, 1.53±0.04 and 1.95±0.02%; acidity 0.05, 0.033, 0.023 and 0.22% and carbohydrate content 34.28±0.22, 33.62±0.16, 32.01±0.59 and 27.15±0.31% respectively. On the basis of sensory evaluation of colour, flavor, texture and overall acceptability, Sandesh made from fresh cow milk chhana ensure highest acceptability and liked very much. Sandesh made with 75% Cow-milk Chhana and 25% Soy-milk Chhana (S₂) was also liked moderately and other types (S₃ and S₄) were not acceptable.

Conclusions. Soy-milk Chhana can be used as a replacement of Cow-milk Chhana in preparation of Sandesh.

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Introduction

Soybean (*Glycine max*) is a new prospective oil crop in Bangladesh. It is regarded as an ideal food for the people of Bangladesh as it contains high quantity of protein and superior quantity of edible oil. Most of the people of our country can't afford to get protein-enriched food like fish, meat, egg, milk etc. due to their high cost. So, to supplement protein at low cost, soybean should be cultivated in more areas in our country. Soybean cultivation is highly concentrated geographically, with only four countries - USA, Brazil, Argentina and China - accounting for almost 90 % of world output [1].

Soybean accounts for approximately 50% of the total production of oil seed crop in the world [1]. Soybean are not consumed directly, but are processed into a large number of variety of popular products. The most of popular soybean products are Temphe (fermented soybeans), Tahu or Tofu (soybean curd), Taoge (soybean sprouts), Kecap (soy-sauce), Tauco (fermented mixture) which are usually consumed as side dishes with rice. Other popular soybean products are yaba, soy-milk and sere.

Soybeans are an excellent and cheap source of calories and quality protein. They contain 35–40% protein and 18–20% fats [2] and can therefore be useful in combating protein-calorie malnutrition in the poorer strata of the population. Regarding this soy-milk (prepared from soybean) can be used as a replacement for milk to meet the deficiency of whole milk.

Milk is one of the most important commodities entering trade and required in everyday life as an article of food. The basic public health and economic considerations require that consumers should be provided with pure milk, free from pathogenic bacteria. To maintain quality standards, control operations have to be performed at all stages of the production of milk which include maintenance of sanitary conditions of byres; cleanliness of utensils and of the milking machines, if used; and care during storage and handling. Any kind of adulteration at the producing or supplying centre, by carriers or by middlemen, has to be prevented. The need for having uniform methods for assessing the quality of milk at the time of purchase or sale is, therefore, obvious. Milk is widely used in the preparation of sweetmeats. The sweetmeats made from milk are delicious, wholesome, nutritious and very popular items in Bangladesh. From birth to death in each sphere of life, milk sweetmeats have occupied a significant place in our society. On occasions like birthdays, marriages, funeral ceremonies, religious festivals and guest entertainment, everywhere sweetmeats are inevitable.

The importance of sweetmeats in this subcontinent has been recognized since five thousand years ago [3]. It is reported that about 10% of the total milk production in Bangladesh is used for the preparation of chhana and finally for sweetmeat milk. In India, 40% of total milk is used for chhana which is mainly used for sandesh preparation [4]. In Bangladesh, there are some areas where sweetmeats and very much famous e.g. 'monda' of Muktagacha (Mymensingh), 'Chomachom' of Porabari (Tangail), 'Resomalai' of Comilla, Kachhagolla of Natore, 'Dahi' of Bogra etc. But there is no such specific area, which is famous for sandesh. Sandesh, the highest priced sweetmeat, is widely manufactured throughout the country and in every area there are some sweetmeat shops which are particularly famous for this grand item.

Sandesh, a chhana based sweetmeat, is very popular in Bangladesh because of its high palatability. It is also popular in West Bengal and some parts of Assam, Tripura, Orissa, Myanmar, Bihar, and some parts of India. The demand for sandesh is steadily growing [5].

Sandesh is usually prepared from cow's milk because it produces a soft body with fine and uniform grain size product which are considered defects in soft grade sandesh. Although cow milk is considered highly suitable for chhana making [6], but a few reports

indicates that modification of buffalo milk for chhana production yields acceptable quality sandesh [7,8].

Sandesh is a kind sweetmeat, which is prepared by heating the mixture of freshly, prepare chhana and ground sugar on a slow fire. Varieties of sandesh are available in the market which may be grossly classified into three main groups such as-first soft grade, second hard grade and third high moisture grade depending upon their physical qualities and chemical composition. In India, about 4 percent of the total milk is used for chhana preparation [4]. Mostly cow milk is used to obtain good quality chhana and its subsequent based sweetmeats. This has limited the availability of cow for fluid consumption.

Sweetmeat, specially, sandesh is one of the most important pleasant and charming foods to most of the people of the country. Sweetmeats are extensively used, chiefly along with other foods due to their good flavour and high food value. They are also easily digested. However, sandesh is a chhana based sweetmeat, it is very vital to health because of its fairly high protein and fat content, minerals, specially, calcium and phosphorus and also fat soluble vitamins particularly, vitamin A and D content. Not only in our country but also in this subcontinent, the importance of sweetmeat has been recognized since five thousand years ago [3]. Limited works in connection with quality of laboratory made sandesh from cow's milk was done in different areas of Mymensingh, Jessore, Khulna and Satkhira districts and also different districts of Bangladesh. Under the above circumstances the present investigation was planned with preparation of Sandesh from fresh cow's milk Chhana and along with addition of different level of Soy-milk Chhana, compare the quality of prepared Sandesh on the basis of proximate and organoleptic properties.

Materials and methods

The experiment was conducted in the laboratory of the Department of Food Processing and Engineering, Chittagong Veterinary and Animal Sciences University, Chittagong.

Preparation of sandesh

For making chhana, cow milk samples were collected from dairy farm located in Chittagong city, Bangladesh.

Preparation of soy-milk

Fresh soybean seeds were collected from local markets. The method used by Kapoor, et al (1977) was modified slightly for making soy-milk [9].

Socking of soybean seeds. For preparation of soy-milk, 2000 gm of fresh and clean soybean seeds were soaked overnight in 0.5 percent sodium bicarbonate to make the husk soft and also to remove bitterness.

Removal of husk. After socking overnight outer coating of the seeds (husk) were removed physically by means of pressure applied by two hands. After removing all husks, the collected seeds were washed in fresh and clean cold water.

Preparation of soy-milk. One litre (1000 ml) of clean water was added with the washed soybean seeds and about 2–3 gm of cardamom was also added to remove the beany flavour present in soybean seeds. The mixture was grinded in a grinder for about thirty to forty minutes. After satisfactory grinding the residue of soy-milk was removed by

filtering with a fine muslin cloth and the soy-milk was collected in a beaker. At the first time about 2 liter of soy-milk was obtained.

Chhana making

Chhana was prepared by boiling both cow milk and soy-milk separately into stainless steel pan for about ten minutes and was cooled down slightly and as coagulant whey was added at a temperature of 70° C. Lumps of casein were formed as soon as the whey was added to the boiled milk, which is generally known as chhana. The content was then allowed to stay for few minutes for complete coagulation of chhana. About 5 to 10 minutes after coagulation, contents were gradually poured into a coarse muslin cloth with four corners raised to allow free drainage of whey. When the transfer of whey was completed the four corners of the cloth were tied together drainage of whey. The coagulum was then carefully removed and weighed.

Four different types of sandesh were prepared by different combination of cow milk and soy-milk their combinations are shown below.

Table 1

Ingredients of Sandesh

*Sample Type	Cow milk chhana (gm)	Soy-milk chhana (gm)	Sugar (gm)
S ₁	500	-	175
S ₂	375	125	175
S ₃	125	375	175
S ₄	-	500	175

*Sample Type S₁ (Only cow milk chhana)

*Sample Type S₂ (Cow milk chhana: Soya milk chhana=3:1)

*Sample Type S₃ (Cow milk chhana: Soy milk chhana =1:3)

*Sample Type S₄ (Only cow milk chhana)

Freshly made chhana was broken into bits. Sugar (35% by wt of total chhana was mixed into it and was kneaded. Then chhana was taken into an iron pan. The mixture is baked by slow heating with continuous stirring and then scraping with the help of a specially made flat type light wooden ladle, until pat formation stage appeared. After sufficient cooling at room temperature, it was then worked into desired size and shape. No flavour of colour was added so that making of the original colour and flavour could be avoided. Sandesh were kept in clean polythene bag and preserved in the refrigerator at 4 °C.

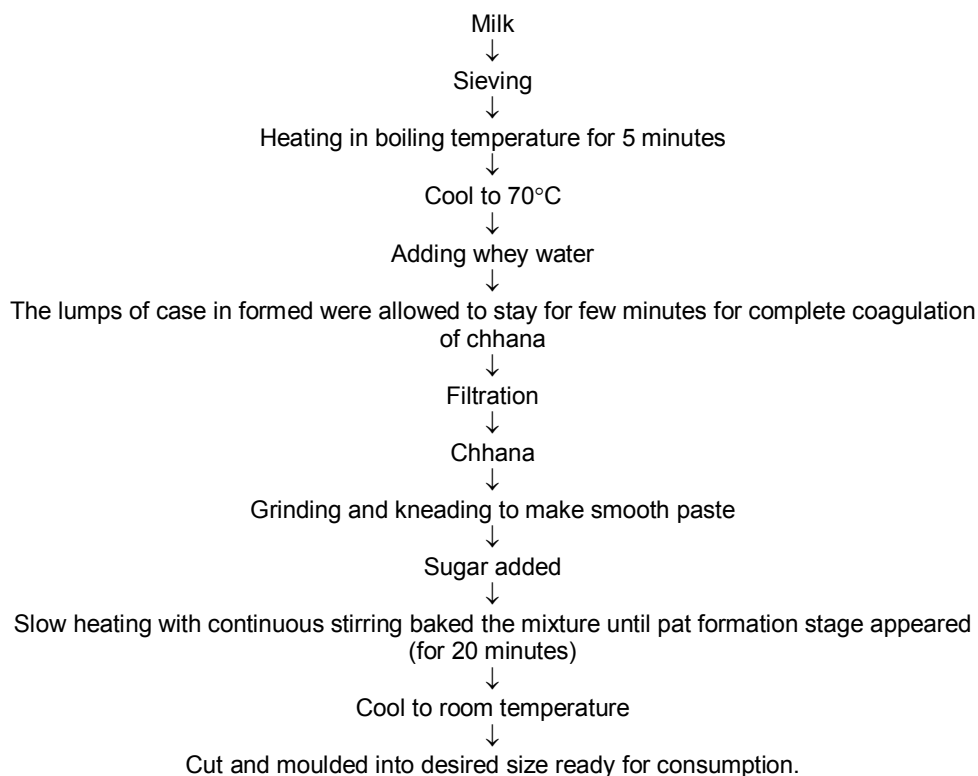


Figure 1. Schematic diagram for sandesh preparation

Chemical Analysis

Proximate composition (Moisture, Protein, Fat, Ash and Carbohydrate).

Moisture, Protein, Fat and Ash of prepared sandesh samples were analysed in triplicate following standard procedures [10]: Moisture content by drying in an oven at 105°C for 24 h; Crude protein content (Nx6.25) by the Kjeldahl method using an Auto Kjeldahl System, Lipid by ether extraction and Ash by incineration in a muffle furnace at 600°C for 6 h. Carbohydrate content were calculated by difference method i.e., %Carbohydrate = 100-(%Moisture + %Protein + %Fat + %Ash)

Acidity. 5 g sample was taken and blended, homogenized in a blender with distilled water and carefully transfer to a 250ml beaker. The mixture was boiled for 1hr periodically adding water to replace the loss by evaporation. Cooled and transferred to a 100ml volumetric flask. Then volume was made to 100ml and filtered. 30ml filtered liquid was titrated against 0.1N NaOH using phenolphthalein as an indicator. The titration was done in triplicate and titratable acidity was calculated from the following relationship Ranganna (1994) [11].

$$\% \text{Acidity} = \frac{\text{Eq. wt of lactic acid} \times \text{Normality of NaOH} \times \text{Volume} \times T.V}{1000 \times \text{wt of sample} \times \text{ml of extract taken for estimation}} \times 100.$$

Sensory evaluation. The consumer acceptability of developed products was evaluated by a testing panel. The panelists were untrained and selected from the students, teachers and employees of the Department of Food Processing and Engineering, Chittagong Veterinary and Animal Sciences University, Chittagong. The panelists (15) were asked to assign appropriate score to each product tested on a 1 to 9 point hedonic scale for characteristic colour, flavour, sweetness and overall acceptability of various mixed samples. The scale was arranged such that; 9 = Like extremely, 8 = Like very uch, 7 = Like moderately, 6 = Like highly, 5 = Neither like nor dislike, 4 = Dislike slightly, 3 = Dislike moderately, 2 = Dislike very much, and 1 = Dislike extremely. The results were evaluated by Analysis of Variance and Duncan's New Multiple Range Test procedure of the statistically analysis system [12].

Results and discussions

Four different types of sandesh were prepared in the laboratory with different combinations of cow milk chhana and soy-milk chhana. The prepared sandesh sample types were designated as S₁ (100% cow milk chhana), S₂ (75% cow milk chhana+25 % soy-milk chhana), S₃ (25% cow milk chhana + 75% soy-milk chhana), S₄ (100% cow milk chhana).

Chemical composition analysis of sandesh

Moisture content. The moisture content were 22.53±0.12, 22.95±0.20, 23.54±0.22 and 25.44±0.17% in S₁, S₂, S₃, and S₄ type sandesh respectively (Table 2). It is observed that S₁, type sandesh had the lowest moisture content and it was gradually increased in in S₁, S₂, S₃, S₄, type sandesh. The differences in moisture might be due to differences in level of fat in these four-type sandesh on one hand and due to the presence of varied proportions of soy-milk chhana solids in chhana on the other hand. This could be attributed due to greater binding capacity of soy solids specially protein [13,14,15]. De and Ray (1954) also reported that capacity of chhana to retain moisture is essentially is the function of milk protein which did increase with greater levels of soy-milk in milk [6]. Sarker (1975) reported that acceptable quality of sandesh contain 234.00 gm/kg moisture [16]. The moisture content of the prepared sandesh was in same range as described by Poonia (2015) [24].

Protein. The protein percentage of S₁, S₂, S₃ and S₄ types of sandesh were 21.87±0.32, 23.02±0.17, 25.92±0.42 and 29.62±0.23% respectively. It was observed that increase of soy-milk chhana enhanced the protein percentage of sandesh. This might be due to the higher percentage of protein in soy-milk chhana than in cow milk chhana which cause increase in protein percentage in sandesh. Jailkhani and Sukumar (1980) observed 170.03 gm/kg protein in a better quality sandesh [17] and protein content of prepared sandesh were identical to Poonia (2015) [24].

Fat content. The fat in S₁, S₂, S₃ and S₄ types of sandesh were 20.44±0.05, 19.02±0.03, 17.00±0.05 and 16.42±0.10% respectively. It was observed that S₁ type sandesh had highest percentage of fat and S₄ type of sandesh had the lowest percentage of fat. Enhancing the proportion of soy-milk chhana in the mixture affected the fat content of sandesh adversely. Generally soy-milk chhana contains low level of fat.

Ash content. The ash content of in S₁, S₂, S₃ and S₄, types of sandesh were 0.88±0.04, 1.39±0.03, 1.53±0.04 and 1.95±0.02% respectively. It was shown that the different types of sandesh have the similar ash content and those were in same range described by Poonia (2015) [24]. Katra and Bhargava, (1994) reported that soy-milk contains 0.73 percent ash which is similar to average ash content of milk [18]. Jailkhani and sukumar (1980) reported better quality sandesh contain 16.6g/ kg ash [19].

Carbohydrate content. The carbohydrate content of S₁, S₂, S₃ and S₄ types of sandesh were 34.28±0.22, 33.62±0.16, 32.01±0.59 and 27.15±0.31% respectively. There was no significant difference among the carbohydrate content of different sandesh sample. The carbohydrate content of milk is usually 4.9 gm/100gm and for soy-milk, it is 3.2gm/100gm [20]. So it was usual that sandesh containing higher percentage of soy chhana would have lower percentage of total carbohydrate content because of lower carbohydrate content in soy-milk. Acceptable quality sandesh contain 16.6 gm/kg of carbohydrate [21].

Acidity. The percentage of acidity of S₁, S₂, S₃ and S₄ types of sandesh were 0.05, 0.033, 0.023 and 0.022 respectively. In respect of the acidity content types S₁ had lowest percentage of acidity and S₄ the highest. Our result agreed with the result of Jeoun et al (1995) [22]. So, increased acidity of S₁, S₂, S₃ and S₄ samples were due to addition of soy-milk chhana with them.

Table 2

Chemical compositions of sandesh product

Sample Type	Moisture content (%)	Ash (%)	Protein (%)	Fat (%)	Acidity (%)	Carbohydrate(%)
S ₁	22.53±0.12	0.88±0.04	21.8±0.32	20.44±0.05	0.05	34.28±0.22
S ₂	22.95±0.20	1.39±0.03	23.0±0.17	19.02±0.03	0.033	33.62±0.16
S ₃	23.54±0.22	1.53±0.04	25.9±0.42	17.00±0.05	0.023	32.01±0.59
S ₄	25.44±0.17	1.95±0.02	29.0±0.23	16.42±0.10	0.022	27.15±0.31

*Sample S₁ (only cow milk chhana)

*Sample S₂ (only cow milk chhana: Soy-milk chhana =3:1)

*Sample S₃ (cow milk chhana: Soy-milk chhana =1:3)

*Sample S₄ (only soy- milk chhana)

Sensory evaluation of the products

The mean score for colour, flavour, texture and overall acceptability of the sample are evaluated and the mean score of their responses are presented in Table 3. A two-way analysis of variance (ANOVA) was carried out and results revealed that there was

significant ($P < 0.01$) differences in colour acceptability among the prepared sandesh samples, since the calculated F-value was greater than tabulated F-value so the colour of control (Sample S_1) sandesh was most preferred and also sample S_1 and sample S_2 had on significant difference for colour. Sample S_3 and S_4 are not equally acceptable. The colour of the samples S_1 and S_2 were significantly better than samples S_3 and S_4 . Highly preference of colour sample- S_1 among the sample S_2 , S_3 and S_4 .

In case of flavour preference among the prepared sandesh sample, two-way ANOVA shown that significantly ($P < 0.01$) affected flavour acceptability since the calculated F-value was greater than the tabulated F-value. The results (Table 3) showed that the flavour of the control (Sample S_1) was most preferred and significantly different than the other samples. The flavor of the sample S_1 was highly preferred among the sample S_2 , S_3 and S_4 . In case of texture preference among the samples, a two-way ANOVA showed that significantly ($P < 0.01$) affected texture acceptability since the calculated F-Value was greater than the tabulated F-value. The results (Table 3) showed that the texture of the control (Sample S_1) was most preferred and significantly different than other sample. As shown in Table 3 the sample S_2 and S_3 had on significant deference. Highly preference of texture of sample S_1 than the sample S_2 , S_3 and S_4 . In case of texture preference among the sample, a two-way ANOVA showed that significantly ($P < 0.01$) affected texture acceptability since the calculated F-Value was greater than the tabulated F-value. The results (table-3) showed that the texture of the control (Sample S_1) was most preferred and significantly different than other sample. As shown in Table 3 the samples S_2 and S_3 had no significant difference. S_1 was highly preferred than other sample types S_2 , S_3 and S_4 in terms of texture quality. Interrelationship was found among textural parameters and composition in all samples of sandesh as described by Khamrui and Solanki (2010) [23].

It is apparent from the results of ANOVA that there was significant ($P < 0.01$) difference in overall acceptability among l the prepared sandesh samples, since the calculated F-value was greater than the tabulated F-value. The result (Table 3) showed that the overall acceptability of the control (Sample S_1) was most preferred. Sample S_3 and Sample S_4 had no significant difference. Lastly highly preference overall acceptability Sample S_1 among the samples-

Table 3

Mean sensory scores of Sandesh samples

Sandesh Types	Sensory attributes			
	Colour	Flavour	Texture	Overall Acceptability
Sample S_1	8.533 ^a	8.067 ^a	6.933 ^a	7.200 ^a
Sample S_2	7.867 ^a	6.800 ^b	5.867 ^b	5.800 ^b
Sample S_3	7.000 ^b	6.000 ^c	5.333 ^b	5.600 ^{bc}
Sample S_4	6.200 ^c	5.133 ^d	4.267 ^c	4.933 ^c
L.S.D	0.6875	0.6896	0.8997	0.7955

Means with same superscripts with in a column are not significantly different at $P < 0.01$.

Conclusions

Different types of sandesh named S₁ (from 100% cow milk chhana), S₂ (75% cow milk chhana +25% soy milk chhana), S₃ (25% cow milk chhana + 75% soy-milk chhana) and S₄ (100% soy-milk chhana) were prepared to compare the quality. Results indicated that moisture content in four types of sandesh were approximately 22.53±0.12, 22.95±0.20, 23.54±0.22 and 25.44±0.17% respectively; protein content 21.87±0.32, 23.02±0.17, 25.92±0.42 and 29.62±0.23%; fat content 20.44±0.05, 19.02±0.03, 17.00±0.05 and 16.42±0.10%; ash content 0.88±0.04, 1.39±0.03, 1.53±0.04 and 1.95±0.02%; acidity 0.05, 0.033, 0.023 and 0.022% and carbohydrate content 34.28±0.22, 33.62±0.16, 32.01±0.59 and 27.15±0.31%. Statistical analysis on the response of taste panel on the sensory properties of sandesh revealed that the colour, flavour, texture and overall acceptability of different sandesh were significantly affected. The overall acceptability of sample type S₁ was found to be more acceptable than those of sample S₂, S₃ and S₄. Sandesh with 75% cow milk chhana and 25% Soy-milk Chhana (S₂) was also liked moderately and other types (S₃ and S₄) were not acceptable in terms of organoleptic properties but have good nutritive quality. Addition of flavor substitute will enhance the organoleptic properties of Soy-milk Chhana and it can be used as a replacement of Cow-milk Chhana in preparation of Sandesh.

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Mathematical modeling of Pickering emulsions stabilization process by solid nanoparticles

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Abstract

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Introduction. The aim of this work is to predict and study the conditions for the stabilization of food and cosmetic emulsions with the Pickering effect establishing the possibility of mathematical modeling of conditions for the most effective stabilization of emulsions.

Materials and methods. It was studied a model emulsions with injected solid nanoparticles based on water and triglycerides of carboxylic acids such as Glyceryl tributyrate (C4), Glyceryl tricaprlylate (C6), and Glyceryl trioleate, linseed oil (a mixture of triglycerides of acids: 9–11% of palmitic and stearic, 13–29% of oleic, 15–30% of linoleic, 44–61% of linolenic acids) and their ethyl esters with a similar composition, and perfume oil. Calculations of surface tension and stability for the model systems of food and cosmetic emulsions were carried out by means of MathCAD-2000 software by Binks method.

Results and discussion. It was calculated free energy values of a spherical nanoparticle (in $k_B T$ units, $T = 298$ K) which occupies position at the water / oil interface (tributyryn, tricaprlylin, triolein, linseed oil and their ethyl esters, perfume oil). The stability of a particle is characterized by the energy barrier, from the side of one of the liquids. In connection with the fact that the energy wells are parabolas, it was collected information on the magnitude of the barriers and the position of the minimum when the particle is moved from the minimum with the z_m coordinate into water ($z = -1$) and into oil ($z = 1$). The best energy well parameters of this solid emulsifier were about 2830 (in linseed oil and in their ethers), 4010 (perfume oil), 400 (triolein) and 150 $k_B T$ (tributyryn). It was shown that a nanoparticle consisting of 50% hydrophilic silica possesses the best stabilizing properties.

Conclusions. The principal possibility of theoretical prediction of the conditions for the stabilization of food and cosmetic emulsions by the Pickering effect is shown. Stabilizing particles, which corresponds to optimal selection of the nanoparticle material, are consisting of 50% hydrophilic silica.

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Introduction

Stabilization of emulsions by means of solid particles has been known for almost a century (so-called Pickering emulsion) [1], but the idea of improving the stability of emulsions by developments in nanotechnology has arisen only recently [2]. Emulsions are heterogeneous systems consisting of mutually insoluble, finely dispersed liquids. In the food, pharmaceutical and cosmetic industries emulsions are intended for internal, external or parenteral use.

Solid nanoparticles of insoluble substances are a special class of stabilizers for disperse systems, primarily emulsions and foams. Solid stabilizers are clay, coal, silica, glass, oxides, hydroxides and insoluble salts of many metals [3].

The problem of increasing the shelf life of emulsions requires the involvement of new knowledge and approaches, including mathematical modeling of physicochemical processes. Experimental confirmation of the Pickering stabilization's processes of emulsions is a rather complicated procedure, which also indicates to the necessity of conducting of model calculations for the searching the optimal material of a solid emulsifier.

Thus it was chosen food and cosmetic emulsions model with injected solid nanoparticles of different substances as the object of the study, which are already used as food additives (it has record in Codex Alimentarius). The subject of the study is the conditions for the Pickering stabilization of emulsions by solid nanoparticles.

The aim of this work is to predict and study the conditions for the stabilization of food and cosmetic emulsions with the Pickering effect establishing the possibility of mathematical modeling of conditions for the most effective stabilization of emulsions. Hence it was put such tasks in this work:

- to investigate the literature data about promising disperse food and cosmetic objects, nanodisperse solid materials for the Pickering stabilization effect;
- to choose the necessary techniques for theoretical study of the Pickering effect and mathematical modelling of the stabilization process;
- to compile a model of surface energy calculations of the stabilizing nanoparticle by means of MathCAD-2000 software and to make the necessary calculations;
- to make conclusions regarding to the optimal choice of stabilizing food additive depending of the emulsion's type.

Materials and methods

Objects of our study were model food and cosmetic emulsions with injected solid nanoparticles of various substances, which have the ability to Pickering stabilization and are used as food additives, are emulsions based on water and triglycerides of carboxylic acids such as Glyceryl tributyrate (C₄), Glyceryl tricaprlylate (C₆), and Glyceryl trioleate, linseed oil (a mixture of triglycerides of acids: 9–11% of palmitic and stearic, 13–29% of oleic, 15–30% of linoleic, 44–61% of linolenic acid [4]) and their ethyl esters with a similar composition (trade name - Linaetholum), and perfume oil [5]. Subjects of our study were investigation of stabilizing effects of nanoparticles in above mentioned emulsions and ways for its theoretical prediction.

Perfume oil by chemical composition is a mixture of hydrocarbons, which are produced by deep purification of spindle oil obtained during petroleum distillation. It is colorless transparent liquid without odor and taste with a density of 0.875–0.880 g/cm³. It

boils at a temperature of about 360 °C, insoluble in water and alcohol, but soluble in all organic solvents, easily fuses with waxes and fats, immiscible and stable against air, alkalis and acids. It is widely used in cosmetics for the manufacture of Vaseline [6].

Solid stabilizing nanoparticles are carbon (E153), paraffin (E905x) and silica (E551) with varying degrees of hydrophilicity.

Further in our work, “liquid 1” corresponds to triglycerides of carboxylic acids C₄, C₆ or oleic acid, or triglycerides or ethyl esters of fatty acids of linseed oil or perfume oil; “Liquid 2” is water; “Solid phase” (particle) – SiO₂, paraffin or carbon. The spherical particles with a radius of 12 nm, which corresponds to the average particle size in the AEROSIL® 200 product (Evonik Industries AG) were considered.

The procedure of calculating of the energy of nanoparticles, which are located on the surface between two liquids, are given in ref. [2]. The unknown values of the surface tension values were calculated in accordance with the procedure shown in [7]. Calculations of surface tension at the surface of two phases for the model systems of food and cosmetic emulsions, which used in the work, were carried out by means of the software MathCAD-2000 [6] according ref. [2].

Results and discussion

When someone perform free energy calculations of a system consisting of a particle placed on the surface between two liquids which formed an emulsion, it is necessary to distinguish between large and small particles. In the case of significant weight of the particles, the stabilizing properties of the particle are reduced due to action of external forces which move out particle from liquid-liquid interface where it was stabilized. For small nanoparticles this effect can be neglected. All kinds of interactions between stabilizing nanoparticles are also neglecting for simplicity. The double electric layer at the solid nanoparticle-liquid interface in this model is also not taken into account.

The stable position of the solid spherical particle at the interface of two phases is determined by the equilibrium edge angle θ_{ow} (Figure 1). To estimate the efficiency of the binding energy, it is usually compared with the kinetic energy of the Brownian motion ($3k_B T/2$, where k_B – the Boltzmann constant, the temperature T in Kelvin). Calculations of free energy will be carried out in temperature units according to equations 1-2.

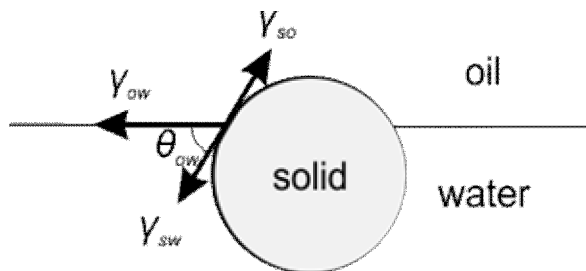


Figure 1. Schematic representation of a solid particle at the interface of emulsion phases [2].

$$z_0 = \frac{z}{R}; S_T = 4\pi R^2; A_T = \pi R^2 \quad (1)$$

$$E_{P1} = \gamma_{P1} S_T \frac{(1+z_0)}{2}; E_{P2} = \gamma_{P2} S_T \frac{(1+z_0)}{2} \quad (2)$$

$$E_0 = \frac{E_{P1} + E_{P2} + E_{12}}{k_B T} = \frac{\pi R^2 \gamma_{12}}{k_B T} \left(z_0^2 + \frac{2(\gamma_{P1} - \gamma_{P2})}{\gamma_{12}} z_0 + \frac{2(\gamma_{P1} + \gamma_{P2})}{\gamma_{12}} \right) \quad (3)$$

where R is the radius of the nanoparticle, z is the distance from the interface of the liquids to the center of the particle, $z_0 = z/R$ is the dimensionless distance, σ_{P1} , σ_{P2} and σ_{12} are a surface tension between solid particle-liquid 1, particle-liquid 2 and liquid 1-liquid 2, respectively.

In order to calculate the free energy of solid particle shown in Figure 1, it is necessary to know the interfacial tension between solid particle–water and solid particle–oil (σ_{P2} and σ_{P1} , respectively). These values are unknown from the experiments, but they can be calculated if the surface tension of water, oil and solid particles at the boundary with air is known. In this case, this surface tension is represented as the sum of dispersed and polar components (γ^d and γ^p , respectively). For water, the polar and dispersed parts are taken from the literature [2]. The formulas 4–7, by which the surface tension values were calculated, can be written as follow:

$$\gamma_{SO} - \gamma_{SW} = \gamma_{OW} \cos \theta_{OW} \quad (4)$$

$$\gamma = \gamma^d + \gamma^p \quad (5)$$

$$\gamma_{SW} = \gamma_S + \gamma_W - 2\sqrt{\gamma_S^d \gamma_W^d} - 2\sqrt{\gamma_S^p \gamma_W^p} \quad (6)$$

$$\gamma_{SO} = \gamma_S + \gamma_O - 2\sqrt{\gamma_S^d \gamma_O^d} - 2\sqrt{\gamma_S^p \gamma_O^p} \quad (7)$$

where indices denote S – “solid particle”, W – “water” and O – “oil”. The values of γ^d and γ^p for calculations were taken from reference data [2, 7, 9].

In a number of experiments, a correlation was observed between the value of the edge angle θ_{ow} of solid emulsifiers and the type, dispersion and stability of the emulsions. Hydrophilic particles with a corner angle $\theta_{ow} < 90^\circ$ (for example, metal oxides, silica) form direct emulsions or foams, and hydrophobic particles with an angle $\theta_{ow} > 90^\circ$ (for example, coal, graphite) form inverse emulsions.

The calculated values of free energy of a spherical nanoparticle (in $k_B T$ units, $T = 298$ K) which is located at the interface between water and perfume oil are shown in Figure 2, water and glyceryl trioleate are shown in Figure 3, and Table 1 demonstrates the parameters that were used to calculate this system. Carbon and silica nanoparticles with different degrees of hydrophilicity were chosen as stabilizing impurities. The horizontal axis in Figure 2 is the dimensionless quantity z equal to the distance from the center of the particle to the liquids interface divided by the radius of the particle (z , Eq. 1). If the center of the spherical particle is at the interface, then $z = 0$, if the particle is completely immersed in the water that is on the left, then $z = -1$, and vice versa, if the particle passes into the oil, then $z = 1$.

The values of the parameters of surface tension coefficients, which were calculated by theoretical formulas, are shown in Table 1.

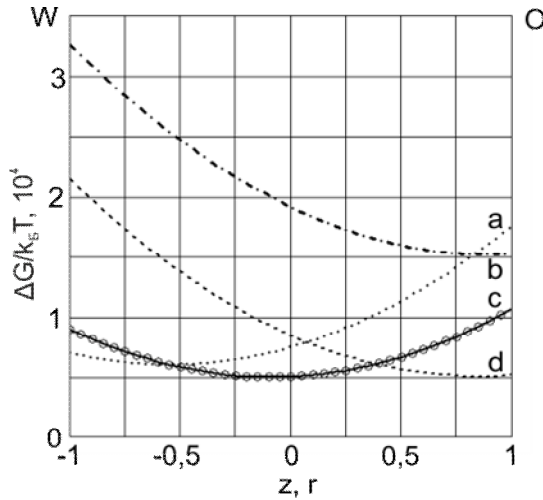


Figure 2. Schematic representation of a quadratic energy well at the perfume oil-water interface $E(z)$ for spherical particles ($R = 12$ nm) of hydrophilic silica (a), carbon (b); 50% hydrophilic (c), and hydrophobic (d) silica (W is water on the left side, O is perfume oil on the right, and the interface boundary in the middle is $z = 0$); z is the ratio of the position of the center of the particle to its radius.

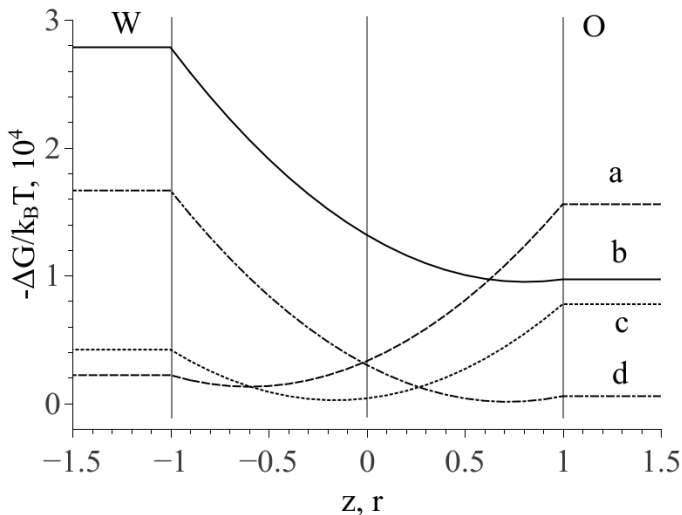


Figure 3. Schematic representation of a quadratic energy well for spherical particles ($R = 12$ nm) of hydrophilic silica (a), carbon (b); 50% hydrophilic (c), and hydrophobic (d) silica at oil (O is glycerin trioleate) – water (W) interface. Other notation is similar to Figure 2.

Table 1

Surface tension values at the interface between liquid 1-liquid 2, liquid 1-solid, and liquid 2-solid phases and parameters for the calculations

Substance	γ^d , mJ/m ²	γ^p , mJ/m ²	γ , mJ/m ²	Reference	γ_{x-y} calculated, mJ/m ²	
Water	21.5	50.4	71.9	[2]	-	-
Perfume oil (O1)	29.9*	0.3*	30.2	[5]	γ_{O1-W}	43.8
Ethyl esters of fatty acids of linseed oil (O2)	30.0	0.5*	30.5	[4]	γ_{O2-W}	41.4*
Glyceryl trioleate (O3)	28.1	0.0	28.1	[9]	γ_{O3-W}	50.8*
Carbon	375.0	56.0	431.0	[7]	γ_{W-C}	63.3*
					γ_{O1-C}	23.7*
					γ_{O2-C}	23.9*
					γ_{O3-C}	22.0*
Hydrophilic silica SiO ₂ (1)	42.0	34.0	76.0	[2]	$\gamma_{W-SiO2(1)}$	5.0*
					$\gamma_{O1-SiO2(1)}$	29.1*
					$\gamma_{O2-SiO2(1)}$	27.1*
					$\gamma_{O3-SiO2(1)}$	35.4*
50% hydrophilic silica SiO ₂ (2)	32.0	17.5	49.5	[2]	$\gamma_{W-SiO2(2)}$	9.5*
					$\gamma_{O1-SiO2(2)}$	13.4*
					$\gamma_{O2-SiO2(2)}$	12.0*
					$\gamma_{O3-SiO2(2)}$	17.6*
Hydrophobic silica SiO ₂ (3)	22.0	0.9	22.9	[2]	$\gamma_{W-SiO2(3)}$	37.8*
					$\gamma_{O1-SiO2(3)}$	0.8
					$\gamma_{O2-SiO2(3)}$	0.7
					$\gamma_{O2-SiO2(3)}$	1.3*

*surface tension values that were calculated by formulas (4-7)

Calculated data of the quadratic energy well for emulsions based on linseed oil fatty acid esters are demonstrated in Figure 4.

It was shown in Figure 4 that a nanoparticle consisting of 50% hydrophilic silica possesses the best stabilizing properties. The minimum of energy is near the liquids interface with a slight shift toward the water. The stability of a particle is characterized by the energy barrier, from the side of one of the liquids. If the energy barrier is of the same order as the energy of the Brownian motion, the particle will pass without difficulty from the interphase boundary to the liquid volume and stabilization will not occur.

Parameters which were taken to calculate the system consisting of ethyl esters of linseed oil acids with same particles that were selected for the previous calculations, are shown in Table 2. The asterisk shows the theoretically calculated parameters. According to Figure 4, the optimal choices for the material of nanoparticles corresponds to the dependence (c), for which the stabilizing particles at the interface between the phases of the esters of linseed acids – water are formed by 50% hydrophilic silica.

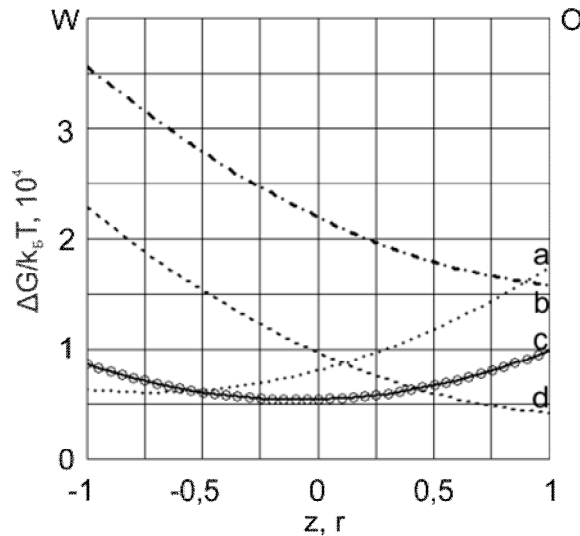


Figure 4. Schematic representation of the quadratic energy well $E(z)$ at the linseed acids esters (O) - water (W) interface for spherical particles of hydrophilic silica (a), carbon particles (b); 50% hydrophilic (c) and hydrophobic (d) silica.

Due to the fact that the parameters of the esters of acids of linseed oil and perfume oil are quite similar, the absence of qualitative changes in the graphs have occurred. Nanoparticles of 50% hydrophilic silica were stabilized near the phase interface with a small displacement of the particle toward the water and had the same. best stabilizing properties.

Let us analyze the obtained data for the paraffin. The surface tension of solid-air (mJ/m^2) for non-polar hydrophobic paraffin is $\gamma_s = \gamma_s^d = 23.9, \gamma_s^p = 0$ [10]. We will change the system, choosing triglycerides of carboxylic acids C_4 and C_6 as the oil. The experimental values of the parameters are given in [10]; calculated and reference data are summarized in Table 2. Quadratic energy wells for triglycerides of carboxylic acids are shown in Figure 5. In this case the oil, which the emulsion consists, was varied. Paraffin particles best stabilize the Glyceryl tributyrate. As can be seen from Figure 5, the particles stabilize water-in-oil emulsion, because they show a high hydrophobicity.

Table 2
Surface tension (mJ/m^2) for triglycerides on the phases' interface with air [10] and the calculated values of surface tension at the oil-water (γ_{ow}), paraffin-water (γ_{sw}) and paraffin-oil (γ_{so}) systems

Triglyceride (oil)	γ_o^p	γ_o^d	γ_{ow}	γ_{ow}	γ_{sw}	γ_{so}
Tributyrate (C_4)	27.7	2.8	30.5	29.8*	26.4*	2.9*
Tricaprylate (C_6)	25.9	3.3	29.2	28.1*	26.4*	3.3*

*Values of surface tension calculated by formulas (4-7).

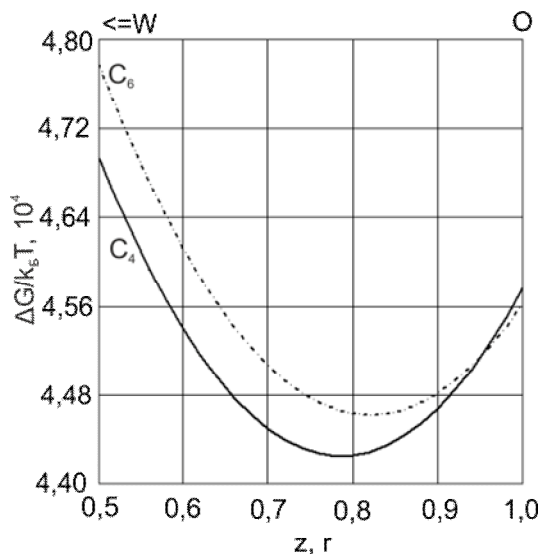


Figure 5. Quadratic energy well for nonpolar hydrophobic paraffin nanoparticles, which stabilizing emulsions of triglycerides of carboxylic acids: tributyrate (C_4) and tricaprlyate (C_6). Water is the left edge, triglycerides is the right edge, the liquids interface is in the middle ($z = 0$).

Table 3
Energy barriers for the transfer of the selected emulsifier particle to the bulk phase of the oil (ΔE_{SO}) and to the water (ΔE_{SW}), in $k_B T$ units*

Triglyceride (oil)	z_m	ΔE_{SO}	ΔE_{SW}	ΔE_{min}
50% hydrophilic silica				
Glycerol trioleate	-0.2	750	400	400
Perfume oil	-0.09	5690	4010	4010
Linseed acids esters	-0.08	3920	2830	2830
Carbon				
Glycerol trioleate	0.80	200	1840	200
Perfume oil	0.90	40	1750	40
Linseed acids esters	1.29	-	-	-
Paraffin				
Tributyrate (C_4)	0.79	150	1040	150
Tricaprylate (C_6)	0.81	100	1020	100

*optimal compositions from the point of view of the Pickering stabilization are selected in bold

In connection with the fact that the energy wells are parabolas, information on the magnitude of the barriers and the position of the minimum can be represented in the form of Table 3. Energy barrier values ΔE_{SO} and ΔE_{SW} are presented in Table 3 in $k_B T$ units when the particle is moved from the minimum with the z_m coordinate into water ($z = -1$) and

into oil ($z = 1$). Thus, a sufficiently strong stabilizing effect is generally observed for the triglycerides which chosen by us for model calculations.

Stabilizing particles, which corresponds to optimal selection of the nanoparticle material, are consisting of 50% hydrophilic silica. The best energy well parameters of this solid emulsifier make about 2830 (in linseed oil and in their ethers), 4010 (perfume oil), 400 (triolein) and $150 k_B T$ (tributylin). In our opinion, ΔE_{min} can be general parameter of nanoparticles ability to be stabilized at O / W interface of an emulsion (Table 3). The more ΔE_{min} value the higher is the stability. Therefore, the best nanomaterial is again 50% hydrophilic silica and perfume oil / water interface with 50% hydrophilic silica represents the most stable emulsion.

Conclusions

The principal possibility of theoretical prediction of the conditions for the stabilization of food and cosmetic emulsions by the Pickering effect is shown. The parameters of the system are calculated which indicate the most effective composition of the emulsions: the position of the particle relative to the interface of the liquids, the energy barriers corresponding to the transfer of the particle from the energy minimum position, if this energy minimum is in the boundary layer between oil and water. One of the conditions for the stabilization of emulsions by solid nanoparticles is the existence of an energy stabilizing "well" due to the difference in the surface tension of the interacting phases.

The appearance of the Pickering effect is confirmed by calculations for a number of model oil-water systems, consisting of linseed oil and its ethyl esters, perfume oil, triglycerides of carboxylic C_4 , C_6 and oleic acids, and water. In the case of solid nanoparticles, paraffin, activated carbon, hydrophilic, hydrophobic silica and 50% hydrophobized silica were chosen.

The parameters of the systems that indicate the type of stable emulsion are calculated (the positions of the particle relative to the interface of the liquids, the value of the energy barriers which corresponding to the transfer of the particle from the energy minimum position [if this minimum lies in the boundary layer] into the bulk oil or water phase) and their most effective compositions were chosen.

Stabilizing particles, which corresponds to optimal selection of the nanoparticle material, are consisting of 50% hydrophilic silica. The best energy well parameters of this solid emulsifier make about 2830 (in linseed oil and in their ethers), 4010 (perfume oil), 400 (triolein) and $150 k_B T$ (tributylin). In our opinion, ΔE_{min} can be general parameter of nanoparticles ability to be stabilized at O / W interface of an emulsion. The more ΔE_{min} value the higher is the stability. Therefore, the best nanomaterial is again 50% hydrophilic silica and perfume oil / water interface with 50% hydrophilic silica represents the most stable emulsion.

The chosen systems modelled for stabilization of emulsions by nanoparticles are close to real food and cosmetic objects and were limited first of all experimental or theoretical data available. For the best of our knowledge, 50% hydrophilic silica exhibits the optimal parameters and the further work on experimental confirmation of effects considered is to be planned. The prospective direction of the further researches could be the study of other oxides with partially hydrophilic surface.

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Determination of moisture connection forms of protein-herbal clots

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Abstract

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Introduction. The interest is research by the moisture bonding forms in the modified milk-protein concentrates, especially, in protein-herbal clots (PHC) which are obtained by thermo acid coagulation of milk proteins.

Materials and methods. Protein-herbal clot (control) and protein-cereal mixture on its basis with rice extrudate.

Determination of moisture content was carried out by thermogravimetric method. Research of the moisture content of various forms of bonding in protein-herbal clots and mixtures based on rice extrudate – protein-cereal mixture was carried out on a derivative of the Paulik-Erdey Q-1000 system in the temperature range of 20–250 °C at a heating rate of samples of 1000 mg – 2.5 °C per minute.

Results and discussion. The removal of the main part of the moisture (free) from the specimen PHC without rice extrudate occurs faster – for 6.0–6.5 min, and with the addition of rice extrudate – slower and this figure is within 7.5–8.0 min

Extrudate's hydrophilic substances interact with PHC moisture due to the formation of H-bound polyasociates with the participation of water molecules and H-bound functional groups of hydrophilic substances. Hydrophobic groups are aggregated at the expense of dispersion forces.

The interaction of the rice extrudate with the milk proteins, after coagulation, leads to the formation of conglomerates that do not differ in the strength of the bonds, but are quite sufficient to bind the free moisture contained in the PHC in the form of whey.

For examples of protein-herbal clots, protein-cereal mix and the mixtures based on its and rice extrudate are characterized by the presence of four critical temperatures (T_I 49–58 °C, T_{II} 91–98 °C, T_{III} 131 °C, T_{IV} 179–186 °C), which removes moisture of different types, differing in the strength of the bond. As a result the temperature rises from T_I 49–58 °C to T_{II} 91–98 °C. All free (mechanically bound) moisture, which appears as a result compaction of protein-grain mixture's structure, is removed and is in layers between the protein-herbal base and rice extrudate.

Conclusions. The results are confirmed the expediency of adding rice extrudate to the protein-herbal clots for the free moisture binding which will provide steel quality indicators in protein-herbal clots.

Introduction

The quality of dairy raw materials, the conditions and the storage of finished products, the prescription composition features and technological operations are factors affecting on production volumes and product-line expansion.

The priority direction of research in the milk processing industry is extension of the storage at low temperatures of milk-protein concentrates (MPC) obtained by different methods with a limited storage. At a temperature from 4 to 8 °C in MPC slowly continues to evolve the extraneous microflora resistant to acidic environment. There is a process of syneresis conditioned by low water-retaining capacity of milk protein [1]. The most common ways of extending storage life are: the use of stabilizers and preservatives; thermisation of fermented products; creation of aseptic conditions for production; freezing, drying; storage in an atmosphere of gases, etc. [2, 3]. *Among them, a special place is taken by the methods of refrigerated processing: cooling and freezing. In the case for prolonged storage of dairy products the advantage is given to the latter one.* [4, 5].

During the storage water in foods plays an important role in maintaining texture, structure and storage stability. The total moisture indicates the quantity and characterizes its relation to chemical, biochemical and microbiological changes in milk-protein products. The ratio of free and bound moisture plays an important role in ensuring stability of MPC during the storage. Chemically bound water in the form of hydroxyl ions or crystalline hydrates is the strongest and can be removed from the MPC only due to chemical interaction or high temperatures. Physical-chemically bound water is divided into adsorption-bound and osmotically absorbed. Adsorption-bound water is contained by a force field on the external and internal micelles surface of casein-calcium phosphate complex (CCPC). Due the large internal surface, milk proteins have free superficial energy thanks to which adsorption binding of water happens. Adsorption heat is allocated at adsorption binding of the first monomolecular layer of water with proteins. Moreover, there is volume compression; herewith volume of hydrated protein appears to be less than the volumes sum of the protein itself and the absorbed water.

Mainly, osmotically absorbed water binds with milk proteins and keeps them firmly. When gel is formed, part of the water is absorbed inside the CCPC and is contained as in a semi-permeable capsule. The other part of the osmotically absorbed water penetrates inside the gel of CCPC through the cell walls from the environment due to osmosis. Concentration of dissolved fraction of substances is greater inside the CCPC gel than in the external.

The physically and mechanically bound water is contained in indefinite ratios and is usually freely secreted from MPC by drying or pressing. Physically and mechanically bound water can be divided into bounded by macro- and micro-capillaries with an average radius greater than 10^5 cm and less than 10^5 cm accordingly. Capillary moisture can be considered as free, because it moves in the capillaries of MPC in the form of milk whey.

The analysis of existing technologies of milk – protein concentrates has shown that the properties' stabilization is achieved through the use of technological ingredients most often. The use of stabilizers, thickeners, emulsifiers, etc. ensures the formation of necessary structure and stability in the technological flow. The lack of scientifically grounded storage recommendations of modified MPC dictates the necessity conducting additional researches. The introduction of cereal products processed in different ways, including extruding, for the bonding of free moisture in dairy products is actual. Cereal extrudates contain in large quantities easily digestible polysaccharides, proteins, food fibers (cellulose, hemicellulose, lignin, fiber), vitamins, minerals and others.

The interest is research by the moisture bonding forms in the modified MPC, especially, in protein-herbal clots (PHC) which are obtained by thermo acid coagulation of milk proteins. As coagulant is used sorrel (*Rumex*) which belongs to the genus of one-, two- and perennial herbaceous plants of buckwheat family, the order of polygonales [6, 7].

In the received protein-herbal clot is a small amount of compounds with pronounced colloidal properties – nondenaturing milk proteins which are capable of absorbing large quantities of water during swelling. Adding extruded cereal products which include high molecular weight carbohydrates – starch, pectin and other substances will contribute the bonding of free water. Swelling speed and maximum absorption of water depend on the nature of colloids, their individual hydrophilicity, concentration, the presence of various substances. As you know, extruding of cereals provides a change in the properties of starch macromolecules – decreasing of the crystalline phase by 52–62%, destruction of starch polysaccharides and the formation of dextrin the number of which increases in 7–18 times. [8]. Changes of starch complex in the extrusion process are accompanied by gelatinization with the formation of high concentration starch pastes; thermal and mechanical destruction of polysaccharide chains, consequence of which is increase of water-soluble substances.

During the hydrothermal processing of grain raw materials the amount of water-soluble proteins is decreases by 20–30%, but salt-, meadow-, and alcohol-soluble – increases. Decrease solubility can be explained by non-covalent interactions between polypeptide chains and other constituents, the formation of new amide and disulphide bonds due to exchange reactions and the additional formation of cystine from cysteine.

Moisture-thermal processing and mechanical influence cause a partial structural deployment of the protein with the break of some weak ties. The thermal motion of peptide chains causes the discontinuity of hydrogen bonds between the chains, and the connections between the hydrophobic groups begin to "melt". Simultaneously with the structural deployment of proteins, their aggregation is also taking place.

The amount of proteins' low-molecular fraction decreases and the amount of high-molecular fraction increases as a result of extrusion processing. This is explained by the fact that as a result of denaturation is formation of disulfide bonds from sulfhydryl groups. The intermolecular interaction of reactive protein groups contributes to the emergence of a significant amount of covalent, hydrogen and other forms of communication electrostatic origin and leads to the formation of sufficiently stable high-molecular protein substances.

Obviously, the changes caused by these processes will find a reflection in the formation of physico-chemical indicators of protein-herbal clots (PHC) with the adding extrudate.

The reaction course and the integral group characteristics of the obtained protein-herbal clots should be explored by the method of differential thermal analysis and thermogravimetric method. The study of the swelling mechanism, the bonds' identification that arise in the interaction of carbohydrate extrudates with PHC moisture were conducted by using the above method.

The aim of research is to determine the moisture bonding forms in protein-herbal clots and mixtures based on them with rice extrudate.

Materials and methods

Materials

Objects of research – protein-herbal clot (control) and protein-cereal mixture on its basis with rice extrudate (RE), with the following chemical composition (Figure 1) [9].

Total protein content 7.0%, including, %	Total of the main components in rice extrudate, %
Albumin – 7.8	Carbohydrates – 63.1
Globulin – 8.4	Starch – 73.7
Prolamin – 5.7	Cellulose – 9.0
Glutelin – 54.8	Water – 14.0
Insoluble residue – 20.8	Ash – 4.6

Fig. 1. Composition of rice extrudate

Method of obtaining protein-herbal clot

For thermo acid coagulation, juice with dry solids weight ratio 3,8% is obtained from the leaves of Rumex and introduce in the prepared milk under appropriate regimes. Aerial part is sorted, inspected from contaminations and mechanical impurities, washed, dried and crushed to a homogeneous state for 2–3 minutes on the DEX DHB-572 device with a power of 750 W. Rumex juice is introduced into the milk heated to a temperature of 93–95 °C in the amount of 7–8%, moderately mix up and kept for 3–5 min before clot formation. The complex effect of high temperatures and acid coagulant on milk proteins leads to fullest coagulation. Coagulation process is fixed visually for intense formation of a strong protein clot and whey detachment.

The research is directed at determining the moisture bonding forms in the protein-cereal mixture (PCM) on basis of protein-herbal clot obtained for the modes by thermo acid coagulation of milk proteins with Rumex juice. The obtained PHC has the following quality indicators: moisture mass fraction at the level (64±2)%, titrated acidity (80±1) °T, color – light pistachio, non-uniform, consistency – soft, mastic, to a degree dense, taste – milk-protein, cheesy, without foreign smells, with a slight herbal flavor. Introduction interest of rice extrudate in the PHC is 3%.

Thermogravimetric method

Determination of moisture content in protein-herbal clots (PHC) and mixtures based on rice extrudate – protein- cereal mixture (PCM) was carried out by thermogravimetric method on the laboratory electronic moisture meters ADGS 50 (production of the company "Axis"). This method is to determine the mass of the test sample before and after it is dried by heating to a temperature not higher than 160 °C. Moisture scales are general purpose laboratory weights of grade 3 of precision with a built-in drying device and have the following characteristics: the largest / the smallest weighing limit is 50 / 0.02 g; discreteness of reading of mass values – 0,5 mg; limit of permissible error of determination of mass – 0,5 mg; RMS deviation of no more than 0.16 mg; the limit of the permissible error of determination of moisture content – 0,3%.

The moisture meter is equipped with an RS-232C interface, which allows information on the results of weighing and determining the moisture content to be printed on the printer or on a computer.

The evaporation of the moisture from the sample during heating leads to a decrease in its mass, which allows, based on the mass measurement data, to calculate the content in the sample of moisture which was before the process of drying the sample.

Determination of moisture content in the same specimen can be realized with the same accuracy at significantly different values of the drying temperature of the sample (the difference will be solely in the time of the procedure).

Moisture scales consist of laboratory weights and a device for drying the samples (hereinafter – a dryer). The principle of determining the moisture content with a weight-moisturizer is to automatically measure the mass before, during and after drying of the prototype (BTS and BZS with rice eczema) with a drying agent. The results of weighing determine the moisture content of the sample that was in it before the start of the drying procedure. The moisture content calculation is carried out automatically by the moisture meter according to the pre-selected formula (1), which is displayed on the moisture meter indicator. The automatic termination of the drying procedure takes place provided that the difference between several consecutive measurements of the sample mass is not more than 20 mg.

$$W = \frac{m_0 - m}{m_0} \times 100\% \quad (1)$$

The moisture content display on the humidity indicator allows you to monitor the moisture evaporation process and, if necessary, correct the drying parameters.

Differential-thermal analysis

Research of the moisture content of various forms of bonding in protein-herbal clots (PHC) and mixtures based on rice extrudate – protein-cereal mixture (PCM) was carried out on a derivative of the Paulik-Erdey Q-1000 system in the temperature range of 20–250 °C at a heating rate of samples of 1000 mg – 2.5 °C per minute. The sensitivity of thermogravimetric analysis (TG) was 2,5 mv/mg, and the differential-thermogravimetric research (DTG) – 2,5 mv·s/mg, the sensitivity of differential-thermal analysis (DTA) – 200 mv·g/j.

This device is an automatic installation for complex thermal analysis: differential-thermal and thermogravimetric. The temperature and differential weight loss curves can be received actually in one format. The essence of method is experimental samples (PHC and PCM with rice extrudate) samples weighing 1000 mg are placed in the working volume of device and heated at a constant rate 2.5 °C / min in the temperature range 20–250 °C. At this, the sample temperature (curve TA) is measured and the temperature difference (DTA curve) is continuously recorded using a differential thermocouple. In parallel with the temperature measurement, the PCM is weighed. During the heating, moisture is removed and this leads to PCM weight decrease. The change in samples' mass (TG curve) and the mass difference of PCM (DTG curve) during the heating is recorded in parallel with the curves TA and DTA. Four charts are recorded on thermogram: TA, DTA, TG, and DTG.

The change in samples' mass of PHC and PCM (TG), differential rate of mass change (DTG), heat conductivity (DTA), temperature (T) were fixed during the heating process. The differential rate of mass change which characterizes the different rate of its loss throughout the experiment, was calculated by the formula (2):

$$DTG = \frac{\Delta m}{\Delta t} = \frac{m_1 - m_0}{t_1 - t_0} \quad (2)$$

where, t_0 – initial heating time of the sample; t_1 – duration of sample heating at a certain temperature; m_0 – primary mass of the sample; m_1 – the sample mass at a certain time t_1 .

Results and discussion

The thermoanalytical method was used in the study of the forms of bonding of moisture in the protein-herbal clots and protein-cereals mixtures based on it using laboratory electronic scales-moisture and derivative. This is traditional in the research of chemical reactions and physical transformations under thermal activity in multicomponent systems between individual compounds. Thermal processes are always accompanied by a change in the internal heat content of the system.

According to the disperse systems classification, the protein-herbal clot has a thixotropic structure of the coagulation type in which the particles are held by intermolecular forces. The presence of liquid (whey) causes less structure strength which gives it plasticity and elasticity. The thicker layers the less structure strength. Synaeresis and thixotropy are characteristic for coagulation structures. Milk whey contains on average 95,8–92,6% moisture, which is a dispersion medium for swelling and partial dissolution of rice extrudate. Moisture is bound in a protein-herbal clot by physical-mechanical and physical-chemical bonds. Moisture affects the structural and mechanical properties of mixture and the technological parameters during prolonged storage.

When a protein-herbal base with RE is combined, moisture bonding forms are redistributed – increase in the amount of bound water that does not freeze at low temperatures does not dissolve the electrolytes, has twice the density that a free water density. This is due to bonds that arise when combined with carbohydrate and protein complexes of RE with whey.

The dynamics of evaporation of moisture from the prototype were fixed on electronic scales-moisture. The results are presented in Figure 2.

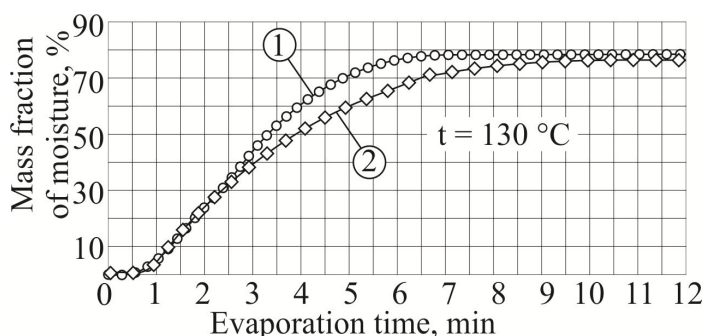


Figure 2. Dynamics of evaporation of moisture from protein-grass clusters:
1 – without extrudate rice (control), 2 – with rice extrudate.

According to the results of the measurements, the removal of the main part of the moisture (free) from the specimen PHC without rice extrudate occurs faster – for 6.0–6.5 min, and with the addition of rice extrudate – slower and this figure is within 7.5–8.0 min. Extrudate's hydrophilic substances interact with PHC moisture due to the formation of H-bound polyasociates with the participation of water molecules and H-bound functional groups of hydrophilic substances. The molecules of hydrophobic groups become more orderly as evidenced by decreasing entropy. Hydrophobic groups are aggregated at the expense of dispersion forces.

In the case of milk proteins, when the acid & heat coagulation occurs, irreversible deposition reactions with loss of primitive properties occur. This is accompanied by the deployment of polypeptide chains of proteins that have been folded in the native protein molecule. As a result of such transformations of chains (with the destruction of tertiary and secondary structures), hydrophobic groups "emerge" on the surface of protein molecules. In this casein and whey proteins lose solubility, aggregation and fall in the precipitate.

The interaction of the rice extrudate with the milk proteins, after coagulation, leads to the formation of conglomerates that do not differ in the strength of the bonds, but are quite sufficient to bind the free moisture contained in the PHC in the form of whey.

Research results of protein-cereal mixture with EP is presented in the form of derivatograms in Figure 3.

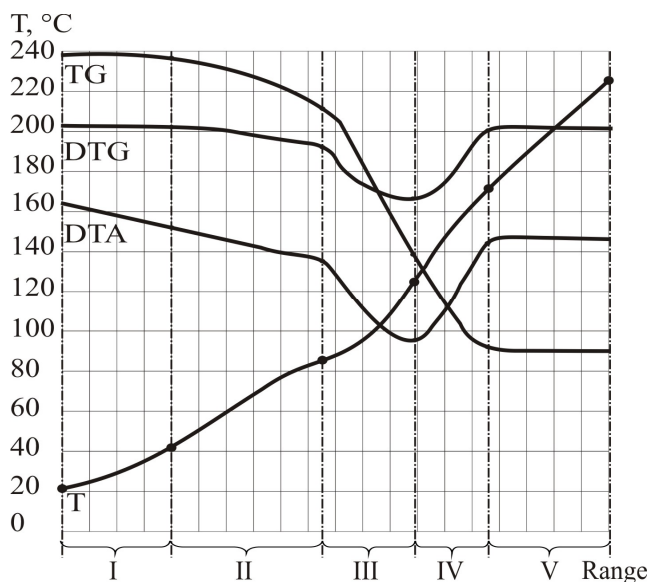


Figure 3. Derivatogram of PCM on the protein-herbal clot basis with rice extrudate: where TA – temperature curve, DTA – differential-thermal analysis curve of enthalpy, DTG – differential-thermal analysis curve of weight loss, TG – mass loss curve.

The curve fixes the changes in the temperature of research samples and the thermogravimetric curves of TG show a change in mass as the temperature function. The curves of the differential-thermogravimetric DTG research and the differential-thermal DTA analysis characterize the rate of moisture mass evaporation and the heat content change in protein-cereal mixture with RE.

The analysis of obtained derivatograms allows to reveal some regularities for PHC and PCM samples. Characteristic is presence four critical temperatures which the moisture various types, differing in the bonding strength, is removed.

DTA and DTG curves go to the negative side. Moisture evaporation from the surface of protein-cereal mixtures at a slight speed is in I and II ranges on all curves. The heat content

increases more intensively in I range on the DTA curve (to a value T_I 49–58 °C) than in II range on the same curve. This is due not only to the increase in temperature (as in the entire area OT_{II}), but also due to an increase in the water heat capacity to the maximum value. Areas I and II range are characterized by increasing speed of mass transfer (II range, DTG curve) and heat content. As a result the temperature rises from T_I 49–58 °C to T_{II} 91–98 °C. All free (mechanically bound) moisture, which appears as a result compaction of protein-grain mixture's structure, is removed and is in layers between the protein-herbal base and rice extrudate.

The nature of the DTA and DTG curves makes it possible to assert that the process is endothermic. The maxima of these curves coincide. This means at these temperatures there are changes that are not related to chemical or physical transformations – the rupture of physical-mechanical and physical-chemical moisture bonds.

After reaching the phase transformation temperature to 131 °C, the mass reduction process (DTG curve, III range) is intensified, under which removal the capillary (free) liquid and vapor phase from the bioscience occurs.

The heat content is predicted to fall due to the intense moisture mass evaporation as evidenced by the DTA course curve in the III range. The rate reduction of moisture removal due to the completion the molar removal residues vapor phase of capillary moisture from the protein-cereal mixture is observed on the TG and DTG curves in the IV range.

In the same period evaporation of the physical-mechanical capillary-bound liquid phase the temperature in cells of PCM with RE spatial structure, formed as a result of the formation connecting bridges between the PHC protein globules and the RE carbohydrate complex, rises from T_{III} from 131 °C to T_{IV} 179–186 °C and pressure inside the structure reaches strength limit. An increase in the evaporation rate of the internal liquid phase, by the formed capillary-structural channels, occurs on this site. The DTA curve in the IV range determines in this respect a rate decrease in enthalpy increase. There are thermal processes characterizing the removal of moisture which are bound by PCM adsorption centers. They can be hydrophilic groups that are on the PHC protein globules surface and in carbohydrate RE macromolecules. When the samples reached a temperature to 179–186 °C, the removal of all of the physical-mechanical bound intracellular moisture is complete and the rate of weight reduction sharply falls.

As evidenced by the IV range of the DTG curve.

At temperatures above 189 °C (V range) begin the decomposition processes of organic and mineral components – pyrolysis, i.e. chemically bound moisture is evaporated.

Designing the DTG curve minimum for the TG curve (mass loss curve), the amount of free and bound moisture was determined. For PHC and PCM with RE the amount of bonded and free moisture is respectively: 27,08% and 71,26%; 33,65% and 68,32%. Taking into account the research results, we can conclude the addition of rice extrudate to PHC can increase the amount of bound moisture by 36,07% compared to the control.

Conclusions

1. The moisture bonding forms in protein-cereal mixtures with rice extrudate on the basis of protein-herbal clot has investigated by thermogravimetric method and differential-thermal analysis.
2. The amount of bonded moisture PCM samples with EP is 33.65% which is 36.07% higher than in PHC. The results are confirmed the expediency of adding rice extrudate to the free moisture binding which will provide steel quality indicators in protein-herbal clots.

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Pressure and temperature influence on the friction coefficient of granular polymeric materials on the metal surfaces

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Abstract

Keywords:

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Extruder
Friction

Introduction. The research is carried out to determine the friction coefficients (FR) of granulated polymeric material on a metal surface, in particular, to describe the principles of their movement in the feeding zone of a screw extruder.

Materials and methods. To study the movement of polymer granules in the channel of an extruder the four types of granules are used: high density polyethylene (PE), ethylene-vinyl acetate copolymer (EVA), polystyrene (PS) and polyvinylchloride (PVC). The FR are defined using a plane-parallel model of the extrusion process.

Results and discussion. Analysis of the results showed a general decrease of FR with the increasing pressure, but upon the reaching the maximum values at almost all curves is a transition through a minimum, after which values of FR begin to rise.

For the PE the FR decreases from 0.35 to 0.26 in a load 200 Pa and from 0.23 to 0.17 in 2000–2200 Pa, with the increasing of a channel depth from 7 to 23 mm. For the EVA the FR increases from 0.15 to 0.44 in 200 Pa and from 0.15 to 0.17 in 1900–2100 Pa. For the PS the FR changes from 0.6 in 200 Pa to 0.3 in 2100 Pa and doesn't depend on the changes a channel depth. For the PVC the FR increases from 0.3 to 0.7 in 200 Pa and from 0.22 to 0.43 in 1900–2100 Pa.

With the increasing of a temperature of a working surface to 90 °C the FR of the PE becomes independent on the changes a channel depth and acquires medium values to 0.3 in 200 Pa and to 0.2 in 2100 Pa. For the EVA in 80 °C the FR for each depth increases and reaches values from 0.25 to 0.4 in 200 Pa and from 0.19 to 0.23 in 1600–1700 Pa. For the PS in 100 °C the FR decreases to 0.5 in 200 Pa and to 0.2 in 2100 Pa. For the PVC the FR doesn't depend on the heating of the working surface.

The difference between the described dependencies for four researched types of polymer is explained by the different mechanical properties of investigated polymers, including the values of strength, FR and deformation at different temperatures.

Conclusions. The obtained results allow to improve the process of extrusion, increase its productivity and reduce its energy consumption by increasing the accuracy of calculations.

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Introduction

Analysis of scientific papers

In most of the existing research papers, polymer materials are performed using the continuous samples, ignoring the interaction between the individual particles. This is especially true for studies of the friction coefficients (FR) of polymeric materials on the metal surface, for example on the working bodies of the extruder.

For example, the authors of [1] suggests a general nature depending on the FR on the normal load and the temperature for the most known polymeric materials. They write that during the friction of polymers, the contact is partially elastic and partially plastic with the predominance of an elastic component at low loads and the predominance of the plastic component when increasing loads, and the dependence of the FR on the temperature varies depending on the change in the hardness, the viscosity and the other physical and mechanical properties of the polymers.

The paper [2] also shows the study of the dynamic FR for some polyethylene resins and shows its dependence on the surface temperature, the pressure and the velocity.

The authors [3] carried out the investigations to determine the static and dynamic coefficients friction of the polyethylene of low pressure for different temperatures. The conducted research shows that the static FR reaches the values are similar to the values of the dynamic FR.

The paper [4] describes the relationship between the temperature, the load and the velocity dependence on the FR for various types of polymer materials and noted that the FR of all polymers are very sensitive to the state of the metal surface that is in contact with the polymers during experiments.

And although the works for granular polymers exist, for example, the authors [5] found the effect of the pressure, the temperature and the velocity of polypropylene pellets on the FR between them and the metal surface and the impact on friction the form of granules, but the uniform regularities for the different types of granules are not revealed and in each case it is necessary to conduct the separate researches.

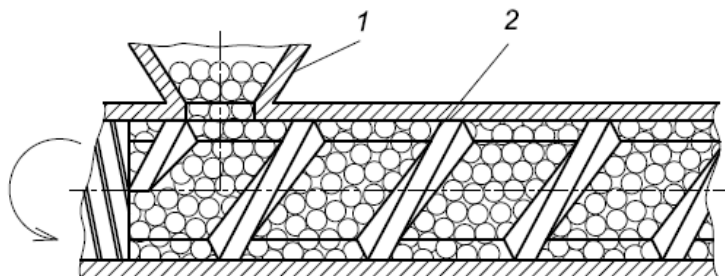
Also, the studies using the granular polymer were carried out by authors [6], showed the effect of the selected granulometric properties on the main parameters of extrusion and found that the process is the most effective when using the granules which length is close to the diameter of the granule, but the study was conducted only for the plasticized polyvinylchloride.

Practical tasks

The production field of plastic products is one of the most important fields of the industry. Polymer materials are widely used for the manufacture of such products as the polymeric films of various designation, the bags for packaging and the other products, constantly increases demand for finished products of polymeric materials from construction, transport, agriculture, medicine and other branches of the economy.

The significant increasing of polymeric materials manufacturing, the range of which is being constantly expanded, requires the creation of highly resource- and energy-efficient equipment for their processing. The most efficient equipment for processing of polymeric raw materials is the extrusion unit, among which the most commonly used is the screw extruders [7–9]. The productivity of the extrusion process is primarily determined by the productivity of the feeding zone of the screw extruder, where the polymeric materials often come in the form of bulk granular materials and enter through a hopper 1 (Figure 1) in the

extruder channel, where they are in the solid form and transported by a helical surface of a screw 2 along the surface of the cylinder by the friction forces.



**Figure 1. The movement of the material in the channel of a screw:
1 – hopper; 2 – helical surface of a screw**

The friction between the recycled material, the cylinder and the screw plays a basic role as a means for moving and heating of the material. The friction also considerably influences the wear intensity of the working bodies, because material way and movement speed depends on it [10–11].

The successful design and calculations of the new equipment is largely depends on the accuracy of values and the correlation of friction forces that act on the contact borders of the material with a cylinder and a screw, which in combination with other parameters define the design of the screw, the pressure and the temperature mode of processing. The most important parameters of the operational modes of friction include the impact of the load and the temperature.

In the area of material feeding in the screw extruder the polymer is often in the form of solid granules, which can slide, roll one by one and be deformed and so on, which affects the movement of the material relatively to the working bodies of an extruder. Thus, the study of the movement of the exactly granulated polymeric materials in the area of material feeding of the screw extruder is the actual task.

The purposes of the research are the experimental determination of the FR of granulated polymeric material on a metal surface, the definition of dependency of FR on the load and the temperature, and the changes of the defined dependencies on the changes of geometrical dimensions of the working bodies of the extruder and the analysis of polymer granules movement in a feeding zone of the screw extruder.

Materials and methods

Materials

Figure 2 shows the photos of the using granules of polymers as follows:

- a – high density polyethylene (PE) Marlex HHM 5502BN [12];
- b – ethylene-vinyl acetate copolymer (EVA) 11104-030 [13];
- c – polystyrene (PS) Denka Styrol MW-1-301 [14];
- d – polyvinylchloride (PVC) SorVyl G 2171/9005 11/01 [15].

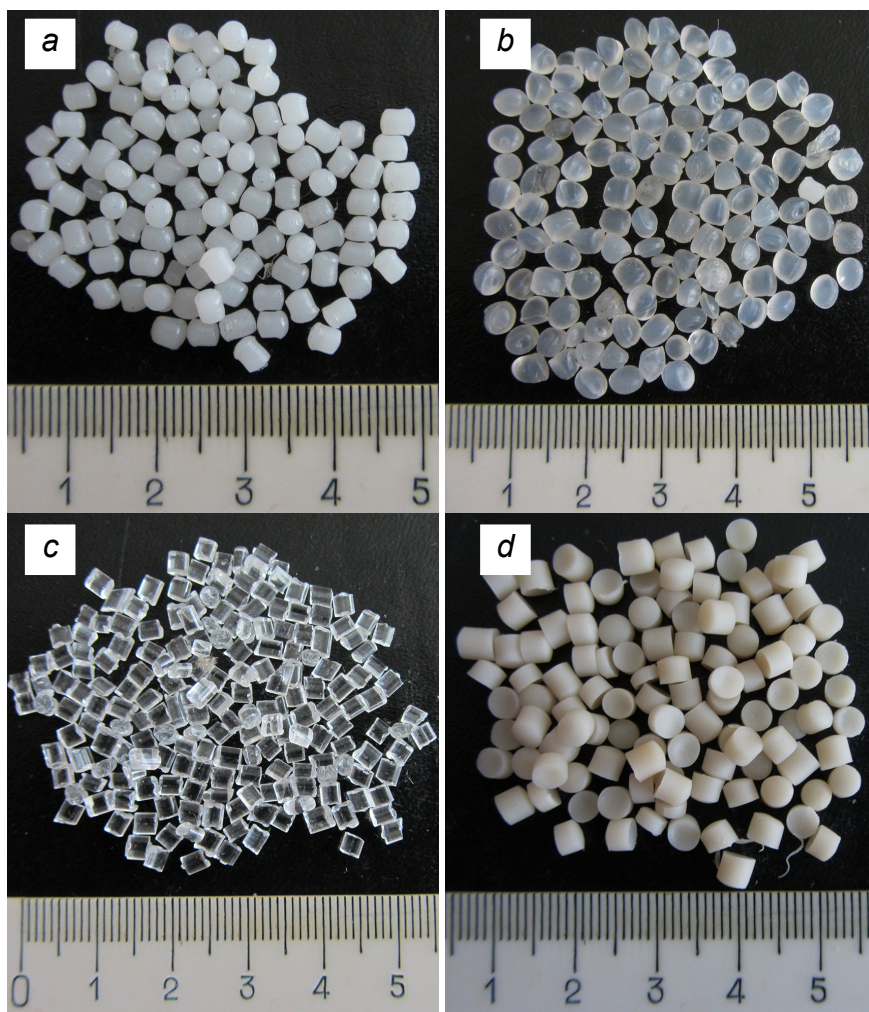


Figure 2. The photographs polymeric granules that were used during the experiments (explanation in the text)

Methods

The article presents the experimental dependences obtained from the research of polymeric granules in the extruder channel using a plane-parallel model of the extrusion process. Thus helical channel of the extruder, which is formed by the screw threading and cylinder, conditionally deployed in the plane (Figure 3) and we assume the following: the channel curvature is ignored, the screw surface is considered to be immobile and the deployed surface of the cylinder is deemed to be moving at a speed that is equal to the circular speed of the screw [16–17].

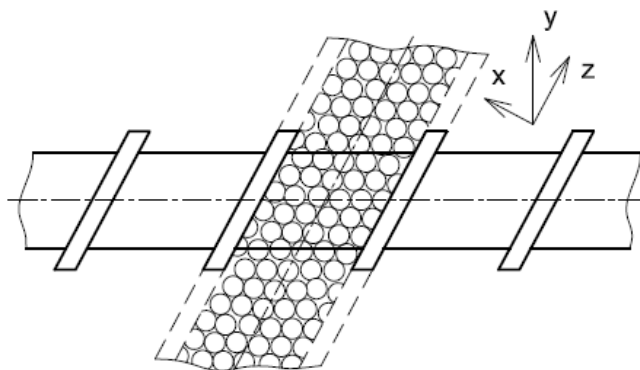


Figure 3. The scheme of the plane-parallel sweep of helical channel of the extruder

Experiment

The process is described in the Cartesian coordinate system where the x -axis is directed perpendicular to the spiral ridge, the y -axis directed by height of the channel and the z -axis directed along the deployed channel (Figure 3). The scheme of the experiment is shown in Figure 4.

In the steel box 1 that simulates a sweep of the screw surface are poured the polymeric granules until the box is completely filled. Further the filled box 1 flips in a way that granules found on the flat metal surface 2, which simulates the internal surface of the cylinder case. Number of granules in the box was sufficient that between her and immobile surface the certain gap in the form of the granules layer has remained.

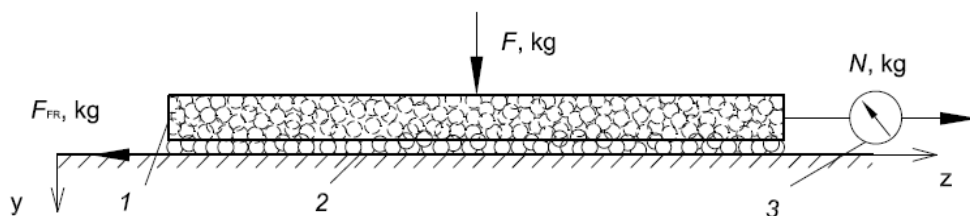


Figure 4. The scheme of the experiment: box (1); immobile metallic surface (2); dynamometer (3)

After that, the box 1 loaded the force F . Next given the movement to the box 1 to surface 2 into the z -axis direction, while the dynamometer 3 fixed the value of the applied force N . Dynamometer is connected with box using a flexible rope. The research was carried out using three boxes of height $H = 7, 15$ and 23 mm, which correspond to the screw extruder channel depth. Ratio of the box length to the width is no less than five to reduce the impact on friction for the end surfaces.

The coefficient of the polymeric granules friction on the metal surface K_{FR} calculated by the formula (1) for the different load values F . To display the dependencies between the load and FR, the pressure P (Pa) is additionally calculated by the formula (2).

$$K_{FR} = \frac{N}{F}; \quad (1)$$

$$P = \frac{F}{S}, \quad (2)$$

where S is the area on where the force F acts, that the area of the box bottom, m^2 .

Results and discussions

General analysis

In Figure 5–8 shows the approximating curves which show the relationship between the calculated FR of polymer material on a metal surface K_{FR} and pressure P , by heating working surface to the temperature t . Heating temperature of the working surface is determined experimentally and for the every polymer separately as the maximum possible value for the feeding zone.

The curves built by using the linear or polynomial approximation while the average value of the approximation reliability is not lower than 0.9 for the all curves.

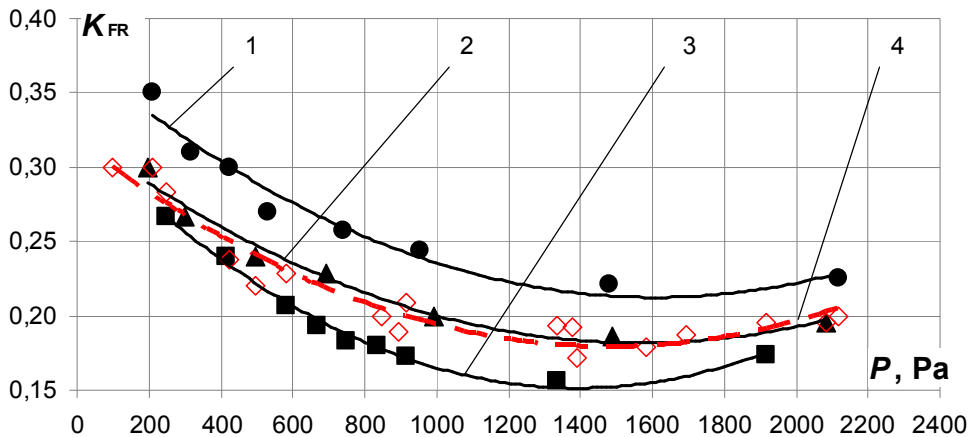


Figure 5. The dependence of the FR of PE on load at different values of channel depths H by heating the work surface:

- 1 – $H = 7$ mm, $t = 20$ °C;
- 2 – $H = 15$ mm, $t = 20$ °C;
- 3 – $H = 23$ mm, $t = 20$ °C;
- 4 – $H = 7, 15, 23$ mm, $t = 90$ °C

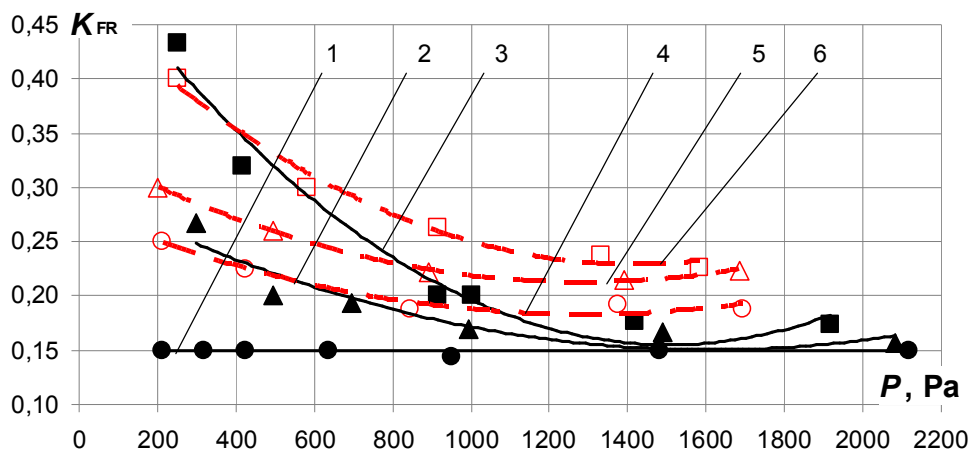


Figure 6. The dependence of the FR of EVA on load at different values of channel depths H by heating the work surface:
 1 – $H = 7$ mm, $t = 20$ °C;
 2 – $H = 15$ mm, $t = 20$ °C;
 3 – $H = 23$ mm, $t = 20$ °C;
 4 – $H = 7$ mm, $t = 80$ °C;
 5 – $H = 15$ mm, $t = 80$ °C;
 6 – $H = 23$ mm, $t = 80$ °C

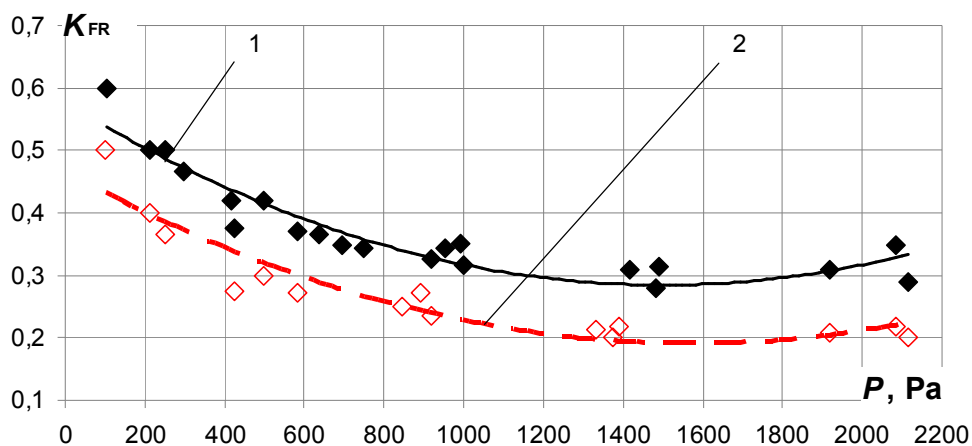


Figure 7. The dependence of the FR of PS on load at different values of channel depths H by heating the work surface:
 1 – $H = 7, 15, 23$ mm, $t = 20$ °C;
 2 – $H = 7, 15, 23$ mm, $t = 100$ °C

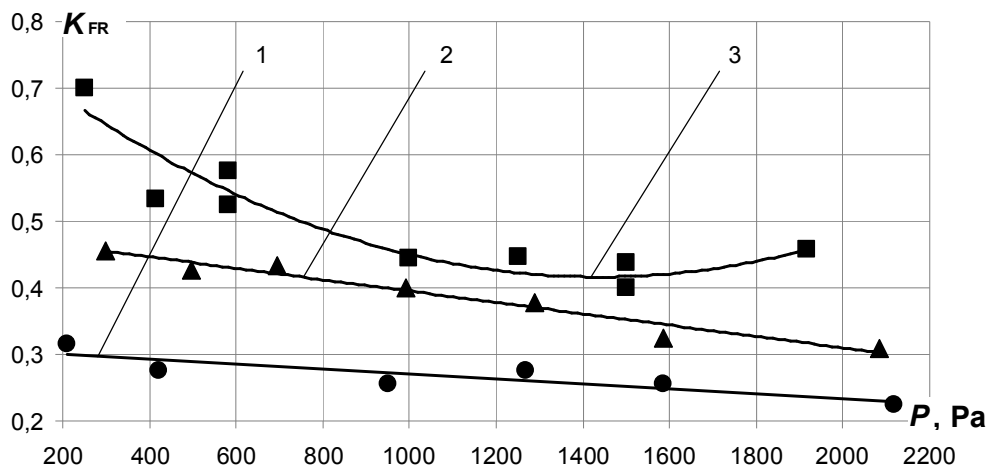


Figure 8. The dependence of the FR of PVC on load at different values of channel depths H by heating the work surface:
 1 – $H = 7$ mm, $t = 20, 90$ °C;
 2 – $H = 15$ mm, $t = 20, 90$ °C;
 3 – $H = 23$ mm, $t = 20, 90$ °C

The listed graphs showed a general decrease of FR dependence on the pressure with the reducing of the channel depth. In the case of approaching the researched loads to the maximum values at almost all curves is a transition through a minimum, that is, the FR begin to rise with the increasing of the load after the certain pressure values. Obviously, this is due to the fact that the granules layer behaves like a solid body after the certain pressure values, for which the dependence of FR on the load generally has the form of the curve with a minimum [1].

High density polyethylene (PE)

The PE granules (Figure 2, *a*) have a rounded shape and is the little-deformed therefore during the movement they can slide with the rotation relative to each other. Thus, in the case of increasing the granules layer thickness H the sliding friction is partly changed to the rolling friction and the FR decreases from 0.35 to 0.26 in a load 200 Pa and from 0.23 to 0.17 in 2000–2200 Pa, with the increasing of a channel depth from 7 to 23 mm (Figure 5).

With the increasing of a temperature of a working surface to 90 °C the value of FR for PE becomes independent on the changes a channel depth and acquires medium values to 0.3 in 200 Pa and to 0.2 in 2100 Pa with saving the character of dependence.

Ethylene-vinyl acetate copolymer (EVA)

For the EVA, the FR increases from 0.15 to 0.44 in 200 PA and from 0.15 to 0.17 in 1900–2100 Pa with the increasing of a channel depth (Figure 6), because though its granules have a rounded form (Figure 2, *b*), like as the PE granules, and have the ability to slide with the rotation relative to each other, but there are deformed and as a result have the interaction with each other, so when the granule layer thickness H is small they are partially

rotated and while increasing the granule layer thickness they are compressed and move as one.

When heating surface of a working surface to 80 °C the value of FR for EVA increases for each depth increases and reaches values from 0.25 to 0.4 in 200 Pa and from 0.19 to 0.23 in 1600–1700 Pa, at the same time when reaching of maximum load values the minimum of the curves for the 80 °C is less expressed than for the 20 °C.

Polystyrene (PS)

The FR of PS (Figure 7) changes from 0.6 in 200 Pa to 0.3 in 2100 Pa and doesn't depend on the changes a channel depth, the graph shows the one approximating curve from measurements for three depth values H . This can be explained by the fact that its granules are not spherical form, but flattened cylinders form with sharp edges (Figure 2, *c*), and they hardly deformed, therefore the rotation and compression almost doesn't happen and the granules layer behaves like a solid (as a single unit) during the movement even for the small loads.

When the PS granules are being moved on the surface heated to a temperature of 100 °C, the values of FR is decreases to 0.5 in 200 Pa and to 0.2 in 2100 Pa and the character of dependence is the similar to the non-heated surface.

Polyvinylchloride (PVC)

The dependence of the FR of PVC granules (Figure 8) is similar to the graph for the EVA, increases from 0.3 to 0.7 in 200 Pa and from 0.22 to 0.43 in 1900–2100 Pa, however, thanks to another form of granules, the flattened cylinders form (Figure 2, *d*), and less deformity PVC granules are rotated at a larger the granule layer thickness H and even at the maximum (of the investigated) granule layer thickness are compressed and move as one.

The FR for PVC doesn't depend on the heating of the working surface, on the Figure 8 shows the common points for the temperatures $t = 20$ and 90 °C.

Explanation

The difference between the described dependencies is explained by the different mechanical properties, including the values of strength, FR and deformation at different temperatures, which confirmed by many existing research.

Conclusions

As a result of the research, the FR of granulated polymeric material on the metal surface for the four types of polymer: high density polyethylene, ethylene-vinyl acetate copolymer, polystyrene and polyvinylchloride were determined. Dependences of FR on the load and the temperature and the changes of the defined dependencies on the changes of geometrical dimensions of the working bodies of the extruder are obtained. The values obtained using a scheme of the plane-parallel sweep of helical channel of the extruder.

The obtained results allow to improve the process of extrusion, increase its productivity and reduce its energy consumption by increasing the accuracy of calculations.

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Thermodynamic analysis of systems anaerobic fermentation

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Abstract

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Introduction. The article deals with the use of peculiarities of processes of micro-biological and thermodynamic transformations in digestible media, which are combined by the principles of minimizing of energy potentials and targeting to the most probable states.

Materials and methods. The research methods are based on the study of the peculiarities of material and energy transformations in the wadding cycles due to entropy transformations in biological systems.

Results and discussion. The course of technologies of anaerobic and aerobic fermentation is a local component of the general carbon cycle, in which there are entropy transformations and losses in the form of thermal energy. The self-sufficiency and irreversibility of the processes of preparation of sugar-containing environments and the fermentation process itself is a reflection of the laws of thermodynamics, on the basis of which the system of utilization of fermentation heat is proposed.

The technologies of anaerobic and aerobic fermentation are those that have the potential of non-traditional energy sources, the use of which is possible on the theoretical basis of heat pumps. According to R. Clausius, the course of natural processes is self-destructive and it concerns chemical and biochemical reactions. This provision relates to technical systems that supply natural self-sustaining phenomena and processes, in which, among others, the natural properties of yeast- sugar mites are realized. The thermodynamic evaluation of biological systems in the form of the characteristics of the seams of the parts of the entropy change and the energy transformations of the nutritional components with the participation of ATP and ADP and the free energy of Gibbs, shows that saturation of the culture medium with carbon dioxide creates obstacles in the path of endogenous processes of the synthesis of ethyl alcohol and carbon dioxide. The scheme of utilization of secondary energy resources of fermentation processes is proposed, taking into account that the potential of fermentation heat is almost twice the heat of distillation.

Conclusions. The amount of heat of fermentation is sufficient for the distillation process with parallel connection of these processes, and the magnitude and speed of generation of free Gibbs energy in culture media is related to the dynamics of growth of its entropy.

Introduction

Solving the problems of energy supply of modern technologies is carried out on the ways of searching for non-traditional energy sources with the creation of new systems and simultaneously at the expense of secondary energy resources. In the latter case, the technical possibilities of recovery and regeneration of energy-material flows, including those on the basis of closed energy circuits, are created. Understanding that the entire biological world of the Earth exists in the ocean of energy always pushes humanity to seek opportunities for its redistribution. So in 1852, William Thomson Lord Kelvin proposed to use a heat sink for heating facilities on the basis of refrigerating cycles. Since then, extensive use of heat pumps in various forms began, including air conditioners of various applications [1, 2, 7]. The theoretical basis of the converters of low potential energy sources on a high potential relates to the Carnot inverse cycle and the Rankine's cycle for wet pairs in accordance with the laws of thermodynamics. Particularly useful heat pumps are in cases of their dual purpose, when using cooling and simultaneously heating different environments. One of the possible cases of such use may be the temperature stabilization of the sorted ethanol environments and the heat supply of the masonry or distillation columns. It is known that the production of one moth of sugar in anaerobic conditions is accompanied by the allocation of 169 kJ of thermal energy, which, in the first place, is lost in modern technologies, and, secondly, requires additional material and energy costs. In connection with this, the necessity for in-depth study of the thermodynamics of thermal processes in the collections of fermentation and distillation technologies and the creation of closed circuits is inevitable.

Materials and methods

The research methods are based on the study of the peculiarities of material and energy transformations in the wadding cycles due to entropy transformations in biological systems. The basis of the research was the well-known laws of technologies, approximating to the provisions of thermodynamics and phenomenological considerations.

Result and discussion

According to Rudolf Clausius, natural processes in their movements are self-inflating. Sometimes they are called "non-compensated" [3, 4, 15]. It is known that in steady-state equilibrium in mechanical systems, the equilibrium is equivalent to the minimum of the potential energy. It is natural to assume that the chemical processes under the self-flow flow are directed towards the reduction of the internal energy of the system. At the same time, the principle of orientation of processes to the most reliable state takes place, which corresponds to the most unordered form of particle distribution. The combination of these two principles is accompanied by heat conduction, re-creation of work into heat, diffusion processes. However, in the opposite direction, their course "by itself" without compensation is impossible. Irreversible processes are possible, but they do not have the course "by themselves". In every direct circular carrier-free process, the transformation of heat into work is offset by the simultaneous self-governing process of transferring part of the summed heat from the heat transfer to the heat-receiving device.

Any unscrupulous process occurs only after its accompaniment by the self-governing process. The second Clausius integral has the form:

$$\oint \delta Q / T \leq 0 \quad (1)$$

where the sign "equals" refers to the reverse processes, and the sign "less" - to non-inverse.

Entropy is a state function, therefore, the change in entropy for both inverse and irreversible processes will be the same. For every process $ds \geq \delta Q / T$, where δQ is the amount of perceived heat, $s = \int \delta Q / T + s_0$, where the integration state s_0 can not be determined within the framework of the first and second laws of thermodynamics. Of course, values s_0 are chosen arbitrarily, focusing on practical needs. All smooth processes, which proceed from the states less likely to be more probable, are irreversible and associated with an increase of entropy. The general laws of the course of processes in inanimate and biological systems are based on the first and second laws of thermodynamics, but in the first case the first section of the classical (equilibrium) thermodynamics is used, and in the second, the thermodynamics of irreversible processes (non-equilibrium) is used. Biological systems are open-ended, irreversible and non-equilibrium, and their transition from one state to another is impossible without the additional inflow of energy from the outside and the basic notion about them is the stationary state of the system. In stationary states, gradients of parameters are supported.

In accordance with the second law of thermodynamics, the change in entropy ds is greater than or equal to the absorbed system of elementary reduced heat:

$$ds \geq \frac{\delta Q}{T} \quad (2)$$

For an isolated system ($\delta Q = 0$) we have $ds \geq 0$. In the inverse (equilibrium) processes, the entropy is unchanged (the sign is "equal"), in irreversible it increases to maximum (sign "more"). This corresponds to the Clausius criterion and the isolated system is directed toward achieving a finite equilibrium with maximum entropy.

Thus, the second law of thermodynamics indicates the direction of the processes in the system. Even in the case of unexpected fluctuations, which led to a decrease in entropy, the subsequent flow of processes will lead the system to maximum entropy [3].

For the functioning of the biological system there are three possible cases:

- the level of organization of the system decreases;
- remains unchanged;
- grows.

At first sight it seems that the last two cases are related to the violations of the second law of thermodynamics. However, there is the development of living systems that are open, and the exchange of matter and energy with the environment takes place. In this case, the general change in the entropy ds in them occurs as a result of the development of irreversible processes with the release of heat δQ_e , as well as due to the external influx δQ_i from the outside:

$$ds = \frac{\delta Q_e}{T} + \frac{\delta Q_i}{T} = d_e s + d_i s \quad (3)$$

For reverse processes $d_i s = 0$, and for irreversible ones $d_i s > 0$.

In an isolated system we also have $d_e s = 0$, then:

$$d_i s \geq 0 \quad (4)$$

By the differentiation of expression (3) we obtain:

$$\frac{ds}{dt} = \frac{d_e s}{dt} + \frac{d_i s}{dt} \quad (35)$$

Thus, the rate of change of the entropy of an open system is equal to the sum of the rates of entropy change due to interactions with the external environment and due to the change of entropy in the irreversible process of the system. Component $d_i s/dt > 0$ because of its correspondence to an irreversible process, but the component $d_e s/dt$ may be less than zero. The overall result for the system is possible in three combinations:

$$1. \quad \frac{ds}{dt} > 0, \text{ if } \frac{d_e s}{dt} > 0 \text{ and if } \frac{d_e s}{dt} < 0 \text{ and } \left| \frac{d_e s}{dt} \right| < \frac{d_i s}{dt}; \quad (6)$$

$$2. \quad \frac{ds}{dt} < 0, \text{ if } \frac{d_e s}{dt} < 0 \text{ and } \left| \frac{d_e s}{dt} \right| > \frac{d_i s}{dt}; \quad (7)$$

$$3. \quad \frac{ds}{dt} = 0, \text{ if } \frac{d_e s}{dt} < 0 \text{ and } \left| \frac{d_e s}{dt} \right| = \frac{d_i s}{dt}; \quad (8)$$

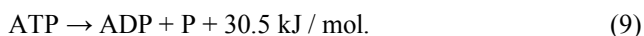
In the first case ($ds/dt > 0$), the degree of ordering of the system decreases. The second case corresponds to an increase in the order of order, and in the third case the stationary state of the system is achieved.

The above three cases are present in colloquia of carbon, water, oxygen and resorted to biotic and abiotic components. A special role is played by the process with decreasing entropy. Total energy metabolism of living organisms is associated with plant organisms that synthesize hydrocarbons from H_2O and CO_2 . The oxidation of the latter in the processes of breathing of living organisms and microorganisms in the conditions of anaerobic and aerobic fermentation is accompanied by the release of energy, which ensures their livelihoods. Synthesis of hydrocarbons takes place in an environment of the atmosphere with the presence of elements of the lithosphere, the energy field of sunlight and the natural catalyst - grains of chlorophyll. At the same time, in the synthesized hydrocarbons, the energy potential is fixed in the form of chemical energy, and the Earth with its plant and biological world is a part of the system on a planetary scale. Thus, the implementation of systems with stabilized entropy or decreasing entropy requires an external or internal energy source.

Taking into account the "equality" of different types of energy sources, we turn to the estimation of culture environments of fermentation technologies. Their formation is grounded on the use of aqueous solutions of nutritional components (mainly - sugars) and

yeast cultures. At the same time, the dissolution of sugars and yeast can be carried out at the level of self-destructive irreversible processes. In accordance with the meaning of the second law of thermodynamics, all real natural processes are irreversible, and the reciprocal processes are only their finite idealized cases [4]. Thus, the realization of any real process requires energy compensation for irreversible changes that arise in the system and in the culture environment.

The processes of fermentation with the aggregate of mass and energy exchange with the formation of CO_2 and $\text{C}_2\text{H}_5\text{OH}$ are also self-destructive and irreversible in the system "environment + microorganisms". The carrier of concentrated chemical energy is glucose, the oxidation of which liberates energy. The intermediate points of conservation of energy are chemical compounds in which electrons move to higher levels with energy consumption. When they return to previous energy levels, energy is released. The only natural compound - adenosinetriphosphate (ATP) stores a unit of energy and this unit of chemical energy can be converted into other forms of energy. It contains ATP of purine base (adenine), sugar with 5 carbon atoms (ribose) and three phosphoric acid residues. The connection between the external and the middle atom of phosphorus is particularly advantageous in energy terms. At its discontinuity there occurs to the emergence of adenosetidophosphate (ADP), phosphate, and there is an energy release of 30.5 kJ per mole of ATP:



Approximately the same amount of energy is required for the transition from ADP to ATP, and ATP plays the role of an "energy storage" and a direct carrier of energy for all processes in cells that occur with energy expenditure or its release. At the same time, the transfer of energy is constantly and the accumulation of "energy bomb" becomes impossible. If the intake of glucose or other substances ceases, then there is no energy and the cell dies.

In yeast cells, the cytoplasm pyruvate synthesized in the mitochondria (cell power stations), where it is transformed into oxygen and water with a release of 38 ATP / mole of glucose in the presence of oxygen, occurs. Therefore, in the presence of oxygen, yeast immediately pass to more energetically more desirable breathing.

The transformation of glucose into alcohol in the mode of anaerobic fermentation is accompanied by the difference in the free energy of Gibbs:

$$\Delta G = 2870 - 2640 = 230 \text{ kJ / mole.} \quad (10)$$

For alcohol fermentation, chemical energy is stored in the form of two molecules of ATP and the cells consume only

$$2 \cdot 30.5 = 61 \text{ kJ / mole of glucose,} \quad (11)$$

And the balance of 169 kJ / mol of glucose is transformed into heat. Under the conditions of isobaric-isothermal process, the change in Gibbs energy is determined by dependence:

$$\Delta G = \Delta H - T\Delta S, \quad (12)$$

where ΔH – the change of the enthalpy of the medium.

Thus, in the processes of anaerobic and aerobic fermentation, the Clausius theory is fully reflected with the direction of biochemical reactions and thermodynamic transformations in accordance with the principles of minimizing the energy potential of the system and the most probable state. The magnitude and velocity of Gibbs free energy directly determine the dynamics of the entropy change, as indicated by condition (12) and in the absence of forced stabilization the temperature of the culture medium would increase and eventually the fermentation process would stop with the subsequent lethal effect. So for the fermentation in each m³ of the environment 160 kg of glucose for the entire cycle of anaerobic process, the amount of heat energy that should stand out should be:

$$Q_i = \frac{160 \cdot 169}{0,18} = 150222,2 \text{ KJ} \quad (13)$$

with an equivalent increase in temperature by

$$\Delta t = \frac{Q_i}{cm} = \frac{150222,2}{4,19 \cdot 1000} = 35,85 \text{ }^\circ\text{C}. \quad (14)$$

Under the condition that the nominal temperature of the medium is maintained at about 30 ... 32 ° C, compulsory cooling becomes obligatory. Aerobic fermentation is close to 1 million kJ per approximate to the above initial conditions.

If the consequent increase in entropy is due to the increase in temperature is simply enough neutralized by cooling the culture medium, the result of biochemical reactions in the form of synthesis of C₂N₅ON and CO₂ in modern anaerobic technologies with significant increase in the osmotic pressure is not subject to neutralization. Due to the absence of ethyl alcohol in the atmosphere, aerobic technology does not have such a disadvantage, and the increasing biological mass of microorganisms does not participate in the creation of osmotic pressure.

Returning to the effects of the processes of anaerobic fermentation, we emphasize that the saturation of the liquid phase with carbon dioxide in its quantitative characteristics is limited in accordance with Henry's law. However, although this limitation also applies to the osmotic pressure of dissolved CO₂, there is another barrier to mass exchange on the surface of the phase separation "medium - microorganisms". The state of saturation of the liquid phase on CO₂ complicates the release of cells from the synthesized gas in them, whereas the solubility of alcohol has no limitations. Reduction and stabilization of the concentrations of alcohol in environments is possible, for example, by the partial pressure reduction at reduced pressures, which uses the biological warming of the casting. In this case, the synthesized in 1 m³ of heat energy for the heat-vaporization of alcohol kJ / kg should be sufficient to obtain C₂N₅ON in the theoretical count in the amount:

$$m_{cn} = \frac{Q_i}{r_{cn}} = 164,9 \text{ kg}, \quad (15)$$

which is almost twice the yield of alcohol.

The named energy-material relations lead to the conclusion about the possibility of a complete distillation process due to the transformed heat of fermentation using thermal transformers.

The system of fermentation and distillation of wort in the production of ethanol (Figure 1) is provided to the use, it is shown in the scheme consisting of a crusher 1 grain, a mixer 2 grinding and water, a thermo-enzymatic treatment unit 3, a solvent-refilling unit 4, a pump 5, a fermenter 6 with a cooling shirt 7, which are connected to each other, the bragging column 8, the cooling circuit 9 of the fermentation apparatus, the heat pump 10 in the composition of the evaporator 11, the compressor 12, the condenser 13, the regulating valve 14 and the pumps 15, the heating circuit 16 of the bragging column.

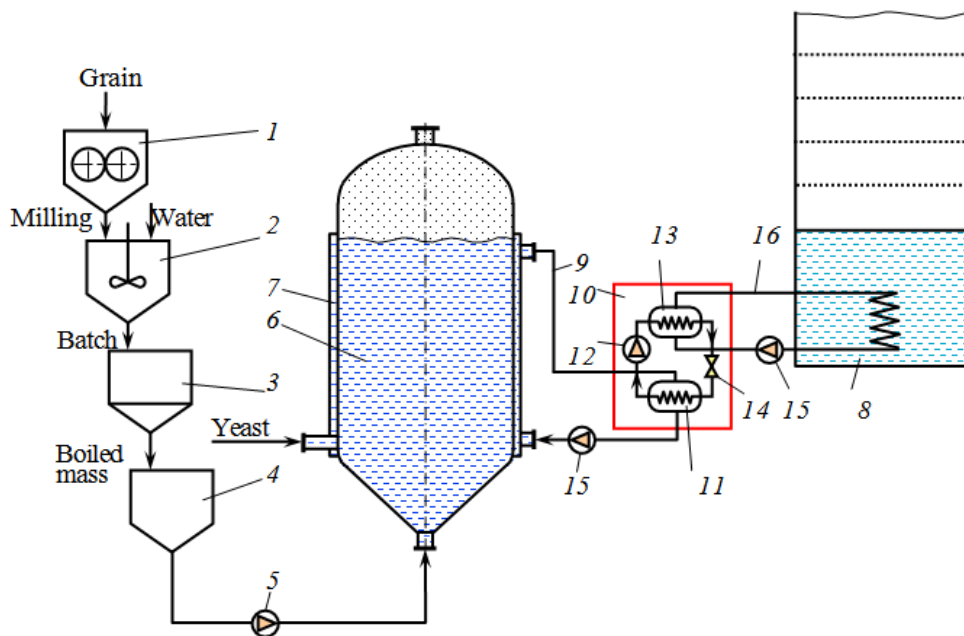


Figure 1. The scheme of the system of processing and distillation of the wort in the production of ethanol

The proposed system works in the following way. Recycled grain-weight mass is fed to a crusher, from which the milling enters the mixer, where the batch is prepared with water and enzymes. The latter is transmitted to the syrup, from which, after sacrifice, it enters the wart apparatus. The heat of digestion is diverted from the environment at the expense of the cooling shirt, stabilizing the temperature at the nominal value. The technical support of this process involves cooling the operating agent of the circuit 9 in the evaporator 11 of the heat pump.

The closed circuit 9 allows to create a cyclic process in which, in accordance with the 1st and 2nd laws of thermodynamics, there are processes of heating and cooling with the temperature-thermal circulation amplified by the pump 15. Under these conditions, a closed contour eliminates the loss of the working agent, which role can be performed by water. In addition, the thermodynamic deficiency of the covered heat exchange systems is reduced, which is associated with an increase in internal energy losses due to the final difference in the temperature of the heat carrier, and the possibility of adjusting the temperature

fluctuations in the evaporator is achieved as a driving factor of transferring the heat. The evaporator formed in the vapor phase of the energy carrier of the heat pump is compressed by the compressor 12 with an increase in its temperature to 105 ... 110 °C and transmitted to a condenser 13, where it condenses with the transfer of thermal current to the heating circuit of the turbine distillation column 16. Condensed heat-soak of the heat pump in the control valve is transformed with lowering the pressure and temperature and returns to the evaporator with subsequent transformations in the cycle. The heating circuit 16 of the medium of the refractory column ensures the formation of a steam in the alcohol mixture and the operation of the column in distillation. The result of such a transformation of the low-potential flow of heat of fermentation, which in modern schemes is accompanied by additional energy-consuming costs, is the complete recovery of secondary energy resources by utilizing the dual possibilities of heat pumps to obtain the source streams for the thermal stabilization of the cooling of fermented environments and for the heat-and-power supply of distillation processes. These advantages reveal the perspectives of the use of heat pumps in such systems, although the thermodynamic deficiencies include the presence of four heat transfer surfaces in the proposed system and the process of expanding the refrigerant in the throttle. At the same time there is a loss of pressure due to mechanical friction. Although there is no work in the process of expanding the working agent, and the throttle does not affect the amount of heat generated in the condenser, however, the amount of heat that is perceived in the evaporator at a constant temperature decreases. As a result, the interaction of the flow of the refrigerant with the throttle makes the process non-reversible and this feature is not excluded.

Conclusions

1. A quantitative indicator of the biological heat of fermentation is sufficient to ensure distillation of the parallel combination and execution of these processes.
2. The allocation of thermal energy in digestible media is the result of entropy losses of chemical energy in the form of free Gibbs energy.
3. The magnitude and rate of generating free energy of Gibbs in culture media is directly related to the dynamics of change in its entropy.
4. Technical support for the use of biological heat of fermentation for distillation processes is possible due to the use of thermal transformer grids in the form of closed energy circuits.

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Non-uniform fluidization in auto-oscillating mode

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Abstract

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Introduction. The objective of this work is mathematical modeling of non-uniform fluidization in an auto-oscillating hydrodynamic mode, which will improve the efficiency of heat and mass transfer along processes of dehydration and granulation by creating an intensive directed mixing of granular material.

Materials and methods. The granular material contained in the granulator chamber, equipped with a special gas distributing device in the lower part and a guiding insert in the upper. Determinations of porosity and pressure drop in a fluidized bed with video recording of the process were carried out using specialized equipment.

Results and discussion. Is implemented the non-uniform fluidization in an auto-oscillating mode with the application of an original gas distributing device with a coefficient of a cross-section coefficient $\varphi=4.9\%$, and an improved granulator chamber. Is provided an intensive macro mixing of granular material with an equivalent diameter of $D_e=3.97$ mm and a density $\rho_s=1450$ kg/m³ with relation of the nominal pressure drop to height of a fluidized bed $\Delta P_{bed}/H_0 \geq 8500$ Pa/m with a pulsating frequency $f=1.67$ Hz. Non-uniform fluidization in an auto-oscillating mode provides a granulation coefficient $\psi \geq 90\%$, and the average specific load of the bed surface of granular material by moisture $a_f=0.8-0.9$ kg_{moist.}/(m²·h). Mathematical model was chosen and on the basis of experimental researches was modified. The developed mathematical model with taking into account heterogeneity made possible to determine the conditions of realization a process in which up to 25% of the mass of a fluidized bed is in the active phase outside the bed with a frequency $f=1.67$ Hz. The mathematical model with an accuracy of 94.1% confirms the results of experimental study.

Conclusions. The hydrodynamics in granulator chamber without formation of stagnant zones was realized. The modified mathematical model made possible to determine the intensity of an active pulsating and a volume circulating mixing, that will significantly increase the stability of kinetics of granule formation in dehydration of composite liquid systems.

Introduction

By previous studies [1-6] was found that stability of a difficult dehydration and granulation process in a fluidized bed with in the presence of phase transitions is determined by the method of interaction of the coolant (gas fluidizing agent) with solid particles [5, 7]. This is especially true for obtaining granular organic-mineral fertilizers with given properties [1-6].

The purpose of the article is modeling of an auto-oscillating mode of fluidization in chamber of a fluidized-bed apparatus.

Analysis of a literature

In order to intensify the transfer processes in apparatuses with a fluidized bed in works [8-11] proposed applying the pulsating feed of coolant during working with heat-resistant materials. In particular, [8] the pulsating mode of coolant feeding to a fluidized bed is performed by using a mechanical pulsator. Realization of this method depends on reliability of mechanical pulsator in medium of high-temperature coolant, and this system does not work in auto-oscillating mode.

The method of creating non-uniform fluidization is proposed by authors [6, 7] by applying of an original gas distributing device (GDD) [2]. Such construction of GDP with the constructive changes of chamber of an apparatus [2] provides realization of a jet-pulsating non-uniform mode of fluidization, which under certain conditions transfers into auto-oscillatory mode.

Experimentally [6-7] found that non-uniform auto-oscillating mode of fluidization when obtaining humic-mineral fertilizers allows increasing in 1.63 times values of the average specific load of the bed surface of granular material by moisture (a_f) in comparison with the traditional bubbling mode of fluidization.

The total surface of granular material determines the minimum height of fixed bed H_0 in apparatus in carrying out processes of dehydration and granulation of liquid heterogeneous systems in fluidized bed. The ratio of gas torch height y_f to $H_0 - y_f/H_0 < 0.5$ causes an implementation of the usual bubble mode of fluidization [12].

Small gas bubbles chaotically pass through a fluidized bed of granular material, bypassing the stagnant zones formed on working surfaces of the gas distributing device (GDD). This leads to melting of material when using a high-temperature coolant. At that, in the heat-mass transfer is involved not the whole surface of granular material particles and therefore this leads to appearing of areas with an over moistened material.

To eliminate these phenomenons and to increase the efficiency of heat and mass transfer processes an intensive local injection of fluidizing agent into a bed of granular material is proposed.

Materials and methods

Experimental installation

Investigation of the hydrodynamic mode of fluidization were carried out using the experimental installation of granulator with the chamber sizes $A \times B \times H = 0.3 \times 0.11 \times 0.8$ m [13]. To create a jet-pulsing fluidization in an auto-oscillating mode, the chamber of

granulator in a bottom part is equipped with the gas distribution device (GDD) of a slit-type [2] 8 (Figure 1) and with the guiding insert at the top [2] 9 (Figure 1). The cross-section coefficient of GDD – $\varphi=4.9\%$, distance (step) between slits – $t=0.114$ m.

For video and photo analysis, the front wall of the chamber is transparent.

Materials

Granular polydisperse product obtained by dehydration of composite liquid systems that contain ammonium sulfate, sunflower ash and humic components was used as a granular material in the apparatus with a fluidized bed [2]. Equivalent diameter of particles was $D_e=3.97$ mm, density – $\rho_s=1450$ kg/m³. Mass of loaded in the apparatus granular material was $M_b=7.8$ kg, that determined the height of bed with porosity $\varepsilon_0=0.4$ – $H_0=0.32$ m and the nominal hydrostatic pressure $\Delta P_{nom.}=2780$ Pa, Injection height of a primary jet – $\Delta=40$ mm.

Measuring complex

Pressure drop in a fluidized bed was continuously measured by the computerized system with applying of MPXV7007DP – low pressure sensors with an accuracy of ± 0.1 Pa with frequency of 63 measurements per second (63 Hz) using computer and the Arduino Pro Mini controller. Scheme of devices and sensors placement is shown on Figure1.

Changes of a fluidized bed porosity in time was determined with the use of photo analysis with the step $\Delta\tau = 0.04$ s.

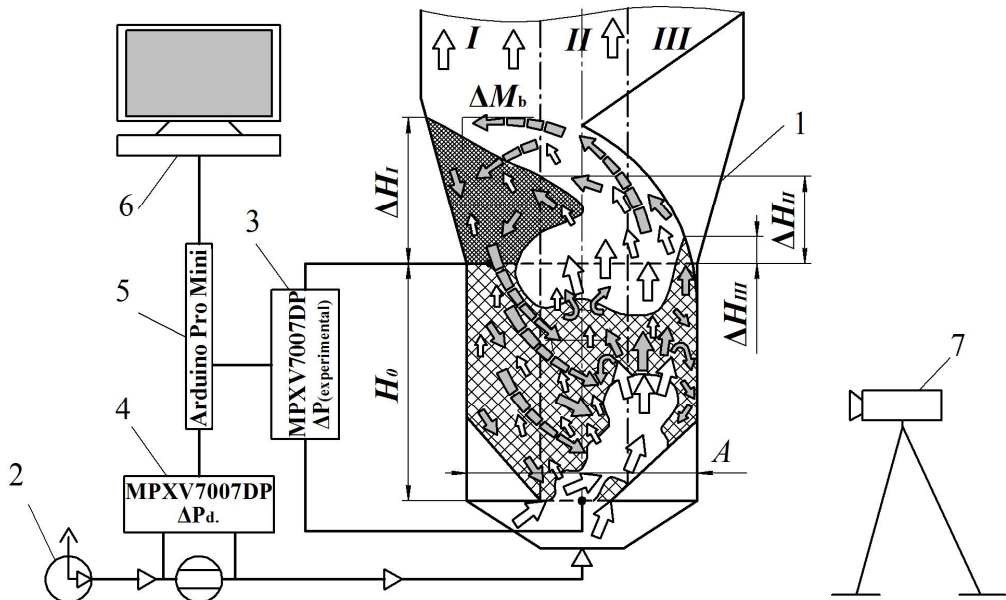


Figure 1. Scheme of computerized system for measuring the pressure drop in the experimental installation

1 – fluidized bed granulator; 2 – gas blower; 3, 4 – low pressure sensors; 5 – controller; 6 – computer; 7 – video camera.

Results and discussion

Physical modeling of the non-uniform jet-pulsating fluidization in an auto-oscillating mode

Essence of the method is that the granulator chamber with a given height bed H_0 is divided into three equal parts (Figure 2 a). At the conditional limit of the *II* and *III* zones, at an altitude Δ relative to the horizontal axis x in vertical direction through the slit of GDD is injected a gas carrier – m_1 . This leads to the formation of a vertical flat torch with a height y_f .

A secondary gas jet is injected through the GDD slit in a horizontal direction at a distance t from the first slit, that is equal to length of horizontal jet breakthrough (Figure 2 b). At that, mass flow from the second jet $m_2 > m_1$, (Figure 2 b).

As a result of combining of two gas mass flows from two jets, a gas bubble with cylindrical (barrel-similar) form with a horizontal axis of symmetry parallel to axis z begins to form on the top of primary vertical torch from the first jet y_f . Thus, as the inject velocity of a fluidizing agent to this zone significantly exceeds the gas filtration velocity in a fluidized bed of granular material, then size of the gas cylinder (bubble) begin to increase in diameter, and it's width is limited by width of the apparatus chamber – B (Figure 2).

The formed gas cylinder (bubble) tightly adjoins to the vertical walls along axis z and has a minimal clearance with the right vertical wall of the apparatus, (Figure 2 c).

That is, an elastic gas cavity forms in *II* and *III* zones and it begin to move the granular material in the frontal part of the gas bubble.

When the gas bubble reaches a critical size it begin to move with acceleration to the surface of the fluidized bed (Figure 2 d), and after exit causes the inertial ejection of the granular material into the over-bed space. The granular material that is ejected from the fluidized bed moves to zone *I* at the expense of contact with the special guiding device in the the apparatus. In this way the height of a fluidized bed increases (Figure 2). The movement of material from zones *II* and *III* occurs until the instant height of granular material in zone *III* will not be equal to $H_{\text{residual}} = y_f + \Delta$.

Then the whole inertially ejected material from a fluidized bed moves to the left part of the apparatus with width $A = A/3$ and causes the achievement of the maximum value of Δh_j (Figure 2 e). After this begins an intensive sliding down of material from the point j into zones *II* and *III* (Figure 2 e) until achievement of the initial equilibrium state (Figure 2 f). At the moment of an intensive movement of granular material the energy of gas jet is spending on slowing the velocity of particles movement that significantly intensifies the processes of mass transfer. Returning of granular material to the state of equilibrium (initial state) completes a cycle that is subsequently repeated and leads to the auto-oscillating mode of fluidization.

So, unlike the uniform fluidization, the energy supplied with a fluidizing agent is spent on the local injection of energy with the gas phase into a given zone of a fluidized bed, which leads to increasing of the potential energy of bed in 1.5–2 times, and dispersed system is deduced from the state of equilibrium.

Thus, applying of the jet-pulsating mode of fluidization allows to intensify renewing of the surface of phases contact and to increase coefficients of mass transfer between phases.

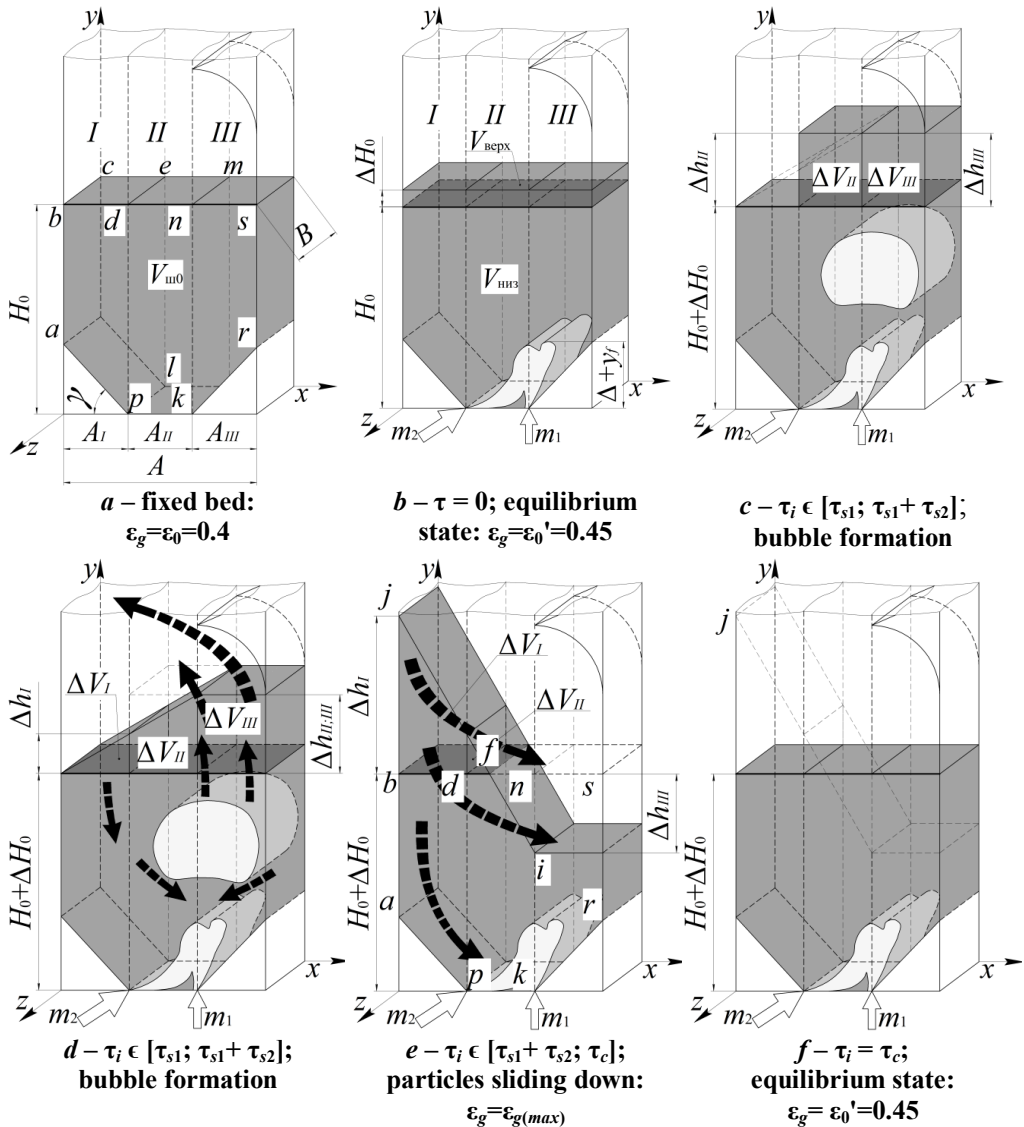


Figure 2. A gas and solid phases interaction model in a granulator chamber with a local injection of a fluidizing agent

According to the given physical model, one cycle consists of such stages:

1. Formation of a gas bubble with the partial expansion of bed in zones II and III – τ_{s1} ;
2. Moving of granular material from zones II and III up to the over-bed space (inertial ejection) and then – into zone I with the subsequent increase of the fluidized bed height in this zone – τ_{s2} ;
3. Moving of the granular material in the opposite direction (sliding down) from zone I to

zones *II* and *III*, returning the fluidized bed to the initial state (equilibrium state) – τ_{s3} . Then the total cycle time is:

$$\tau_c = \tau_{s1} + \tau_{s2} + \tau_{s3} \quad (1)$$

Justification of the mathematical model

It is quite obvious that the dependence of a fluidized bed height on porosity has a nonlinear character.

To describe this process is advisable to use the approach proposed in work [8].

$$\frac{d^2 H(\tau_i)}{d\tau_i^2} = \frac{\Delta P(\tau_i)}{\rho_m (1 - \varepsilon_{(average)}(\tau_i)) H(\tau_i)} - g \quad (2)$$

where $\Delta P(\tau_i)$ – current value of hydraulic resistance of granular material present in volume of initial bed (p. *j*) with height $H_0 + \Delta H_0$;

ΔH_0 – increase in height of a fluidized bed due to formation of gas torch (Figure 2 b).

Calculation of the total hydraulic resistance in fluidized bed was made out according to the equation with structure proposed by the author [14]:

$$\left(\frac{dP}{dy} \right)_{total} = \left(\frac{dP}{dy} \right)_{momentum} + \left(\frac{dP}{dy} \right)_{friction} + \left(\frac{dP}{dy} \right)_{hydrostatic} \quad (3)$$

or in an integral form:

$$\Delta P_{total}(\tau_i) = \Delta P_{momentum}(\tau_i) + \Delta P_{friction}(\tau_i) + \Delta P_{hydrostatic}(\tau_i) \quad (4)$$

To solve this equation it is necessary to determine experimentally the dynamics of change of a fluidized bed porosity values (average and in local zones).

According to the physical model porosity in zone *I* is constant and accepted as $\varepsilon_0=0.4$.

Moving of granular material comes from zones *II* and *III* and is associated with formation of gas bubble. Therefore, the equation for determining loss of pressure on displacement of mass from zones *II* and *III* is expressed by the values of porosity in these zones – $\varepsilon_{(II,III)}$:

$$\Delta P_{momentum}(\tau_i) = \frac{1}{2} \left[\rho_s \cdot \varepsilon_{s(II,III)}(\tau_i) \cdot w_s(\tau_i)^2 + \rho_g \cdot \varepsilon_{g(II,III)}(\tau_i) \cdot w_g(\tau_i)^2 \right] \quad (5)$$

where $\varepsilon_{s(II,III)}$, $\varepsilon_{g(II,III)}$ – porosity of solid and gas phases in *II* and *III* zones of the granulator chamber; w_s , w_g – instantaneous values of particle and gas velocities, m/s.

The instantaneous value of the relate gas velocity was determined from a known dependence [15] taking into account the porosity of a fluidized bed in zone *III* (ascending) of granulator chamber:

$$\operatorname{Re}(\tau_i) = \frac{\operatorname{Ar} \cdot \varepsilon_{g(III)}(\tau_i)^{4,75}}{18 \cdot 0,61 \sqrt{\operatorname{Ar} \cdot \varepsilon_{g(III)}(\tau_i)^{4,75}}} \quad (6)$$

$$w_g(\tau_i) = \frac{\operatorname{Re}(\tau_i) \cdot \nu}{d_e} \quad (7)$$

An average instantaneous velocity of solid particles in first two stages of the cycle, m/s:

$$w_s(\tau_i) = \frac{\Delta \varepsilon_{g(II;III)}}{\Delta \tau} = \frac{\varepsilon_{g(II;III)}(\tau_{i-t}) - \varepsilon_{g(II;III)}(\tau_i)}{\tau_i - \tau_{i-t}} \quad (8)$$

Calculation of the hydraulic resistance in a fluidized bed caused by overcoming the friction forces between solid particles and the friction due to motion of gas was carried out according to the proposed author [14, 16-22] by the expression:

$$\sum \Delta P_{friction}(\tau_i) = \Delta P_{gas\ friction}(\tau_i) + \Delta P_{solid\ friction}(\tau_i) \quad (9)$$

$$\Delta P_{gas\ friction}(\tau) = 2 \cdot f_g \cdot \varepsilon_{g(II;III)}(\tau_i) \cdot \rho_g \cdot w_g^2 \cdot H_0 \cdot \frac{1}{D_a} \quad (10)$$

$$\Delta P_{solid\ friction}(\tau) = 5,7 \cdot 10^{-2} \cdot \frac{1}{D_a} \cdot \varepsilon_{g(II;III)}(\tau_i) \cdot \rho_g \cdot w_{g(cr)} \cdot \theta \cdot H_0 \cdot \sqrt{g \cdot D_a} \quad (11)$$

$$\theta(\tau) = \frac{\varepsilon_{s(II;III)}(\tau) \cdot \rho_s \cdot w_s(\tau)}{\varepsilon_{g(II;III)}(\tau_i) \cdot \rho_g \cdot w_g(\tau)} \quad (12)$$

Hydraulic resistance of a fluidized bed was determined by the expression proposed by authors [14, 16–22]:

$$\Delta P_{hydrostatic}(\tau_i) = g \int_0^{H_i} (\rho_s \cdot \varepsilon_{s(average)}(\tau) + \rho_g \cdot \varepsilon_{g(average)}(\tau)) dz \quad (13)$$

where H_i – value of a fluidized bed height at a certain time τ_i , m.

Unlike to [14, 16-22], hydrostatic pressure is determined by taking into account the physical model:

$$\Delta P_{max} = \Delta P_{nom} + \Delta P_{bubble} = \rho_s \cdot (1 - \varepsilon_0') \cdot g \cdot (H_0 + \Delta H_0 + d_{bubble(max)}) \quad (14)$$

where ε_0' – porosity of a fluidized bed, taking into account formed and permanently existing gas torches; $d_{bubble(max)}$ – the maximum possible size of gas bubble at moment of breaking a bound from the gas torches.

In addition, the growth velocity of gas bubble is also determined taking into account the change in the porosity of a fluidized bed in II and III zones of the granulator chamber:

$$w_{bubble}(\tau_i) = \frac{\Delta \varepsilon_{g(II,III)}}{\Delta \tau} = \frac{\varepsilon_{g(II,III)}(\tau_{i-t}) - \varepsilon_{g(II,III)}(\tau_i)}{\tau_i - \tau_{i-t}} \quad (15)$$

Taking into account the model of displacement of mass of material from fixed volume of a fluidized bed ($A \times B \times H$), the amount of mass of granular material ejected beyond the boundary bed (with the starting height $H_0 + \Delta H_0$) is determined as:

$$\Delta M_{(max)} = \frac{(\Delta P_{max} - \Delta P_{nom}) \cdot F_a \cdot K_a}{g} \quad (16)$$

where K_a – coefficient that take into account the narrowing of the granulator chamber in zone of the fractional pressure (for the design of GDD $K_a=0,85$);

ΔP_{nom} – nominal value of the pressure difference of stationary bed, Pa:

$$\Delta P_{nom} = \rho_s \cdot (1 - \varepsilon_0) \cdot g \cdot H_0 \quad (17)$$

F_a – the cross-sectional area of the granulator chamber, with sizes $A \times B \times H_0$, m²:

$$F_a = A \cdot B \quad (18)$$

Then residual mass of a fluidized bed in apparatus is, kg:

$$M_{residual(min)} = M_0 - \Delta M_{ejected(max)} \quad (19)$$

or

$$M_{residual}(\tau_i) = M_0 - \Delta M(\tau_i) = V_{bed(0)} \cdot (1 - \varepsilon_{g(average)}(\tau)) \cdot \rho_s \quad (20)$$

Therefore, the current value of residual hydrostatic pressure is determined as, Pa:

$$\Delta P_{hydrostatic}(\tau_i) = \frac{M_{residual}(\tau_i) \cdot g}{F_a \cdot K_a} \quad (21)$$

Experimentally found that height of injection the vertical gas jet Δ in relation to the horizontal axis x is $\Delta=0.5y_f$.

To solve the equation (4) it was necessary to determine experimentally the dynamics of change in the average porosity of a fluidized bed $\varepsilon_{g(average)}=f(\tau)$ and in zones of the granulator chamber – $\varepsilon_{II}=f(\tau)$, $\varepsilon_{III}=f(\tau)$.

According to the physical model, in the first stage, when bubble is forming, the height of a fluidized bed is:

$$H_1 = H_0 + \frac{\Delta h_{II} + \Delta h_{III}}{2} \quad (22)$$

$$H_1 \cdot (1 - \varepsilon_{g(average)}(\tau_i)) = H_0 \cdot (1 - \varepsilon_0) \quad (23)$$

$$H_1 = \frac{H_0 \cdot (1 - \varepsilon_0)}{(1 - \varepsilon_{g(average)}(\tau_i))} \quad (24)$$

We accept that in zone *I* (the downstream) porosity of a fluidized bed is $\varepsilon_f = \text{const}$ and $\varepsilon_f = \varepsilon_0$.

Maximum values of porosity in zone *II* – $\varepsilon_{II} = 1,5\varepsilon_0$ and in zone *III* – $\varepsilon_{III} = 2\varepsilon_0$ and are calculated from the minimum residual height $H_{residual}$.

Residual height of a fluidized bed in zone *III* after reaching the maximum value of porosity of a bed in *III* zone is defined as, m:

$$H_{residual\ III} = \frac{H_0 \cdot (1 - \varepsilon_{g(III)max})}{(1 - \varepsilon_0)} \quad (25)$$

If the minimum permissible residual height of a fluidized bed in zone *III* is $H_{residual\ (III)} = \Delta + y_f$, then:

$$\varepsilon_{g(III)max} = 1 - \frac{(\Delta + y_f) \cdot (1 - \varepsilon_0)}{H_0} \quad (26)$$

For the case when $H_0 = 0.32$ m and $\Delta + y_f = 0.12$ m: $\varepsilon_{g(III)max} = 0.76$.

Assuming that the chamber of an apparatus is in form of parallelepiped, then the increase in height of a fluidized bed over the zone *I* can be written as follows:

$$\Delta h_I = \Delta h_{II} + \Delta h_{III} \quad (27)$$

That is, Δh_I is defined as the sum of decreases in the fluidized bed heights in zones *II* – Δh_{II} and *III* – Δh_{III} .

Values of these parameters are calculated by expressions:

$$\Delta h_{II} = \frac{H_0 \cdot (\varepsilon_{g(II)}(\tau_i) - \varepsilon_0)}{1 - \varepsilon_0} \quad (28) \quad \Delta h_{III} = \frac{H_0 \cdot (\varepsilon_{g(III)}(\tau_i) - \varepsilon_0)}{1 - \varepsilon_0} \quad (29)$$

Then, substituting (32) and (33) into equation (31), the increase in height in zone *I* acquires the following form, m:

$$\Delta h_I = \frac{H_0 \cdot (\varepsilon_{g(III)}(\tau_i) + \varepsilon_{g(II)}(\tau_i) - 2 \cdot \varepsilon_0)}{1 - \varepsilon_0} \quad (30)$$

Proposed to determine the sliding down velocity of a material using the Bernoulli law, m/s:

$$w_{sl.} = \sqrt{2 \cdot g \cdot H_{sl.}} \quad (31)$$

where $H_{sl.} = \Delta h_{I(max)}$ – the maximum excess of height (sliding down) of a fluidized bed increase over zone *I*, m.

Empirically determined that time of sliding down of a granular material $\tau_{sl.}$ is 1/4 from the total cycle time τ_c and is defined as, s:

$$\tau_{sl.} = \frac{\Delta h_{I(max)}}{w_{sl.}} \quad (32)$$

Experimental verification of simulating the non-uniform jet-pulsating fluidization in an auto-oscillating mode

For the steady hydrodynamic auto-oscillating mode of fluidization at the optimum value of the fluidization number – $K_w = 1.43$ the dynamics of change in porosity of a fluidized bed in zones by method of video fixation is determined. For this mode gas velocity in slits of GDD ($w_{slits}=27.33$ m/s) significantly exceeds the velocity of blowing out the particles with an equivalent diameter $D_e=3.97$ mm, $w_{slits}=3.5 \cdot w_{blow out}$, and the energy injected by gas coolant, W:

$$E_{kin.} = \frac{(m_1 + m_2) \cdot w_{slits}^2}{2} = 21.1$$

here m_1 ; m_2 – mass flow of gas coolant in slits of GDD ($m_1=0.04$ kg/s; $m_2=0.017$ kg/s).

As a result of an experimental study, the height of the gas torch is $y_f=0.08$ m and was obtained an experimental dependence for determination dynamics of change in porosity of a fluidized bed in a fixed volume of the apparatus chamber:

$$\varepsilon_g(\tau_i) = \varepsilon_{g(min)} + A + A \cdot \sin\left(\frac{2 \cdot \pi}{T} \cdot (\tau_i - \tau_c \cdot (n-1)) - K_{shift}\right) \quad (33)$$

where $\varepsilon_{g(min)}$ – minimum value of a fluidized bed porosity (at $\tau=0$), obtained experimentally ($\varepsilon_{g(average)(min)}=0.45$);

$A=(\varepsilon_{g(max)} - \varepsilon_{g(min)})/2$ – amplitude of oscillations;

$\varepsilon_{g(max)}$ – maximum value of a fluidized bed porosity (at $\tau=0.75 \cdot \tau_c$), obtained experimentally ($\varepsilon_{g(average)(max)}=0.63$);

T – period of oscillations, s: $T=1.5 \cdot \tau_c$ – for the first two stages of the cycle ($\tau_i=0 - 0.75 \cdot \tau_c$); $T=0.5 \cdot \tau_c$ – for the third stage of the cycle ($\tau_i=0.75 \cdot \tau_c - \tau_c$);

n – ordinal of an oscillation, unit;

$K_{shift}=5 \cdot \pi/10$ – magnitude of the phase shift of an oscillation.

Frequency of pulsations: $f=1/\tau_c=1/0.6=1.67$ Hz.

The obtained dependence with correlation coefficient $\sigma=0.989$ describes the experimental data.

Values of function $\varepsilon_{g(average)}=f(\tau)$ can be determined by the equation:

$$\varepsilon_{g(average)}(\tau_i) = \frac{\varepsilon_{g(I)}(\tau_i) \cdot V_I + \varepsilon_{g(II)} \cdot V_{II} + \varepsilon_{g(III)}(\tau_i) \cdot V_{III}}{V_I + V_{II} + V_{III}} \quad (34)$$

where $\varepsilon_{g(I)}$, $\varepsilon_{g(II)}$ and $\varepsilon_{g(III)}$ – values of porosity of a fluidized bed respectively to a current zone of granulator chamber (*I*, *II* and *III*), determined by experimental way;

V_I , V_{II} , V_{III} – volumes of zones respectively to a current zone (*I*, *II* and *III*) in a fixed volume of the apparatus.

Dynamics of change in porosity of a fluidized bed in a fixed volume of the apparatus chamber (average and in current zone (I, II and III) of chamber) obtained as a result of experimental study is shown on Figure 3.

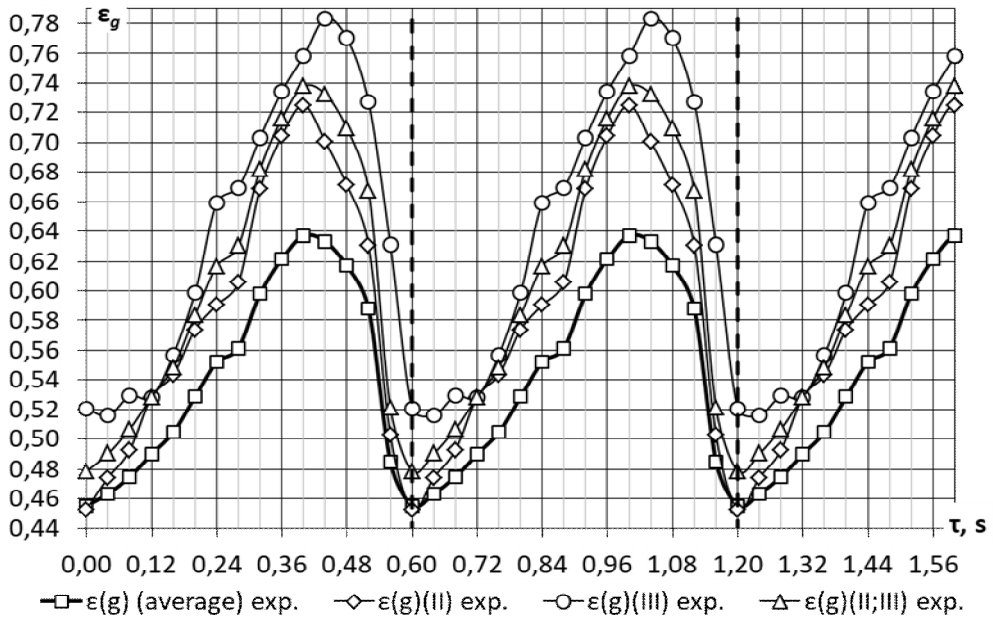


Figure 3. Dynamics of change in porosity of a fluidized bed obtained as a result of experimental study – $\varepsilon_g=f(\tau)$

As follows, velocity of change in porosity of a fluidized bed in a fixed volume of the bed is $d\varepsilon/d\tau=0.4$ for time $0 \leq \tau \leq 0.45$ s and $d\varepsilon/d\tau=0.9$ for time $0.45 \leq \tau \leq 0.6$ s, that is more than 2 times higher.

A similar character of change is for the dynamics of change in porosity of a fluidized bed in zone II and III, which differ from the average only by values of an extreme points. Accordingly, the minimum and maximum values of porosity in zone II – $\varepsilon_{g(II)(min)}=0.46$ and $\varepsilon_{g(II)(max)}=0.7$; in zone III – $\varepsilon_{g(III)(min)}=0.49$ and $\varepsilon_{g(III)(max)}=0.78$.

An average porosity of a fluidized bed in zone II and III:

$$\varepsilon_{g(II;III)}(\tau_i) = \frac{\varepsilon_{g(II)}(\tau_i) \cdot V_{II} + \varepsilon_{g(III)}(\tau_i) \cdot V_{III}}{V_{II} + V_{III}} \quad (35)$$

Dynamics of change in porosity of a fluidized bed (average and in zones II, III) obtained as a result of calculations, is shown on Figure 4.

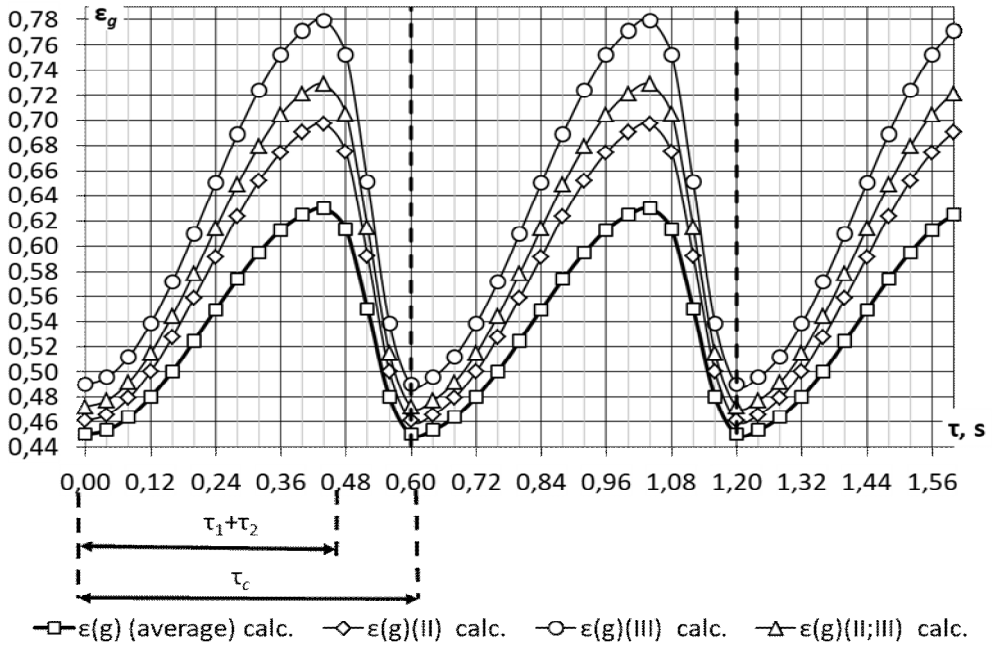


Figure 4. Dynamics of change in porosity of a fluidized bed obtained as a result of calculations – $\epsilon_g=f(\tau)$

Based on the obtained values of the average porosity of a fluidized bed by the equation (20), the dynamics of mass change of the granular material bed in a fixed volume of the granulator chamber is determined as the ratio of mass of transferred material to initial – $\Delta M_i/M_0$ (Figure 5).

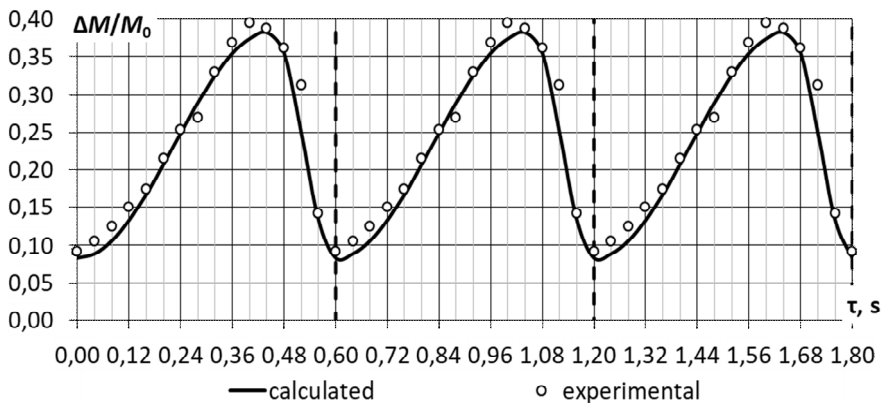


Figure 5. Dynamics of the change in mass of a bed in the over-bed space relative to the initial mass of bed – $\Delta M/M_0=f(\tau)$

Consequently, an application of the non-uniform jet-pulsating fluidization in an auto-oscillating mode with a frequency of 1.67 Hz allows ejecting into an outer-bed space up to 37% of the initial mass of bed, which in counteraction to a gas phase flow returns to the working volume of the granulator chamber. The estimated time of complete exchange of the surface in a fluidized bed is $3\tau_c=3\cdot0.6=1.8$ s, which is a very important factor in the intensive processes of dehydration and granulation.

Verification of the mathematical model was made in form of the dynamics of change in the hydraulic resistance of a fluidized bed (Figure 6), and shows that calculated dependence $\Delta P=f(\tau)$ by using the developed mathematical model with $\sigma=0.905$ describes the experimental data.

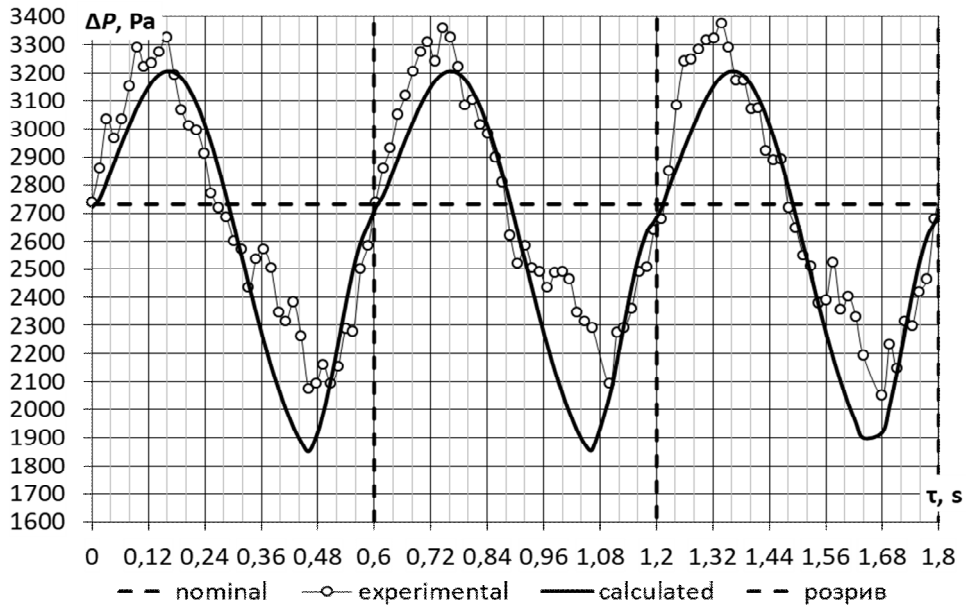


Figure 6. Dynamics of change in the hydraulic resistance of a fluidized bed – $\Delta P=f(\tau)$: $\sigma=0.912$

The injection of kinetic energy with the gas phase $E_{kin}=21.1$ W leads to an increase in the total hydraulic pressure of a fluidized bed by 18.5%. Taking into account the organization of motion of granular material in granulator chamber, this leads to an impulsive increase in the height of a fluidized bed (Figure 7) that is in accordance with increase of the potential energy of a fluidized bed and causes returning of the system into an equilibrium state. Estimated dependence $H_{bed}=f(\tau)$ by using the developed mathematical model with $\sigma=0.941$ describes the experimental data.

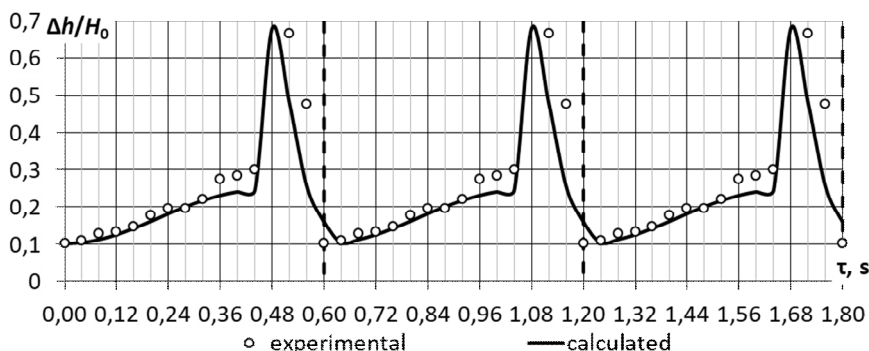


Figure 7. Dynamics of change in the height of a fluidized bed relative to the initial – $\Delta h/H_0=f(\tau)$: $\sigma=0.941$

Conclusions

The developed mathematical model of non-uniform jet-pulsating fluidization in an auto-oscillatory mode adequately describes a new way of interaction of gas and solid phases. All statements of the physical model of the process, in which the non-uniform disperse system turns into the auto-oscillatory mode, are experimentally tested and confirmed.

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Анотації

Харчові технології

Протеолітичні системи молочнокислих мікроорганізмів

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Вступ. Метою огляду є аналіз й узагальнення існуючої наукової інформації про особливості будови, умови утворення та властивості протеїназ і пептидаз молочнокислих мікроорганізмів, які широко використовуються при виробництві молочних продуктів.

Матеріали і методи. Досліджено протеоліз білків молока під дією молочнокислих мікроорганізмів. Проведено аналіз наукових статей, дисертації й монографії вчених даної галузі науки. Методологія дослідження ґрунтується на використанні методів аналізу, порівняння та узагальнення.

Результати і обговорення. Розщеплення білків і амінокислот ферментами молочнокислих і пропіоновокислих бактерій сприяє збагаченню молочних продуктів азотомісними та безазотними сполуками, у результаті чого продукт набуває необхідної консистенції, смаку й запаху. Окрім забезпечення органолептичних властивостей, у процесі протеолізу білків молока під час виробництва молочних продуктів відбувається також і утворення великої кількості пептидів з різними видами біологічної активності.

Протеолітична система молочнокислих бактерій складається з трьох складових: протеїназ, які забезпечують початкове розщеплення казеїну до пептидів з утворенням великої кількості олігопептидів; пептидаз, які розщеплюють пептиди до амінокислот; транспортної системи, яка забезпечує перенесення продуктів протеолізу через цитоплазматичну мембрану. Протеїнази функціонують поза клітинами мікроорганізмів, які їх продукують, а пептидази – в клітинах молочнокислих бактерій.

За специфічністю дії на фракції казеїнового комплексу молока протеїнази молочнокислих мікроорганізмів розділяють на 2 два типи – *PI* і *PIII*. Протеїнази *PI* здатні розщеплювати β -казеїни і не розщеплюють α_{S1} - і κ -казеїни, а протеїнази *PIII* гідролізують усі три фракції: α_S -, β - і κ -казеїни.

Серед великої кількості різних за специфічністю пептидаз молочнокислих бактерій не виявлено жодної з карбоксипептидазною активністю. До амінопептидаз, які виявлені у молочнокислих мікроорганізмів, відносять *PepN*, *PepC*, *PepA*. Крім амінопептидази, у молочнокислих бактерій виявлені дипептидази й трипептидази.

Висновки. Результати, висвітлені в огляді, рекомендовано використовувати під час підбору видового складу заквасок, а також застосовувати систематизовані характеристики протеїназ і пептидаз тих чи інших мікроорганізмів для забезпечення якісних органолептичних показників молочних продуктів та утворення біологічно активних пептидів.

Ключові слова: *протеоліз, протеїназа, пептидаза, молочнокислий, мікроорганізм.*

Вплив додавання лаврових ефірноолійних екстрактів на властивості салатних заправок

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Вступ. Метою дослідження була характеристика ефірних олійних екстрактів з лаврового листа (*Laurus nobilis* L.) і розробка сенсорних профілів салатних заправок із цими екстрактами.

Матеріали і методи. У дослідженнях був використаний лавровий лист (*Laurus nobilis* L.), що походить з Афонського півострова північної Греції, і відібраний в жовтні 2016 року. Салатні заправки, які належать до оліє-водяних емульсій, одержували додаванням екстрактів ефірних олій із сухого і вологого лаврового листа.

Результати і обговорення. У екстрактах було виявлено 46 компонентів, які представляють приблизно 97% від загального вмісту. Основними компонентами екстракту сухого листа є: 1,8-кінеол (43,65%), α -терпінілацетат (15,10%), карарен (8,48%), β -бісаболен (3,89%) та р-цимен (3,12%); у вологому листі екстракту – 1,8-кінеол (45,94%), α -терпінілацетат (15,89%), карарен (8,92%), β -бісаболен (5,09%), р-цимен (3,28%) і терпінен-4-ол (3.03%).

Обидва екстракти мають відмінність за вмістом ароматичних компонентів порівняно з тими, що отримувались з етанолом. Виявлено відмінності у складі ефірних олій, і це, можливо, було пов'язано з методом виробництва.

У екстракті, отриманому з сухого листа, переважають монотерпенові кисневмісні похідні (68,47%), секувітерпенові вуглеводні (13,65%), аліфатичні вуглеводні (7,90%), ароматичні сполуки (4,10%), монотерпенові вуглеводні (2,33%), тритерпен (1,43%), сесквітерпенові кисневмісні похідні (1,23%), дитерпен (0,52%) і аліфатичні кисневмісні похідні (0,37%). У екстракті, отриманому з вологого листа, переважають монотерпенові кисневмісні похідні (72,19%), півкватерпінглеводні (15,41%), ароматичні сполуки (4,32%), аліфатичні вуглеводні (3,64%), монотерпенові вуглеводні (2,45%), тритерпен (0,66%), сесквітерпенові кисневмісні похідні (0,70%), аліфатичні кисневмісні похідні (0,39%) і дитерпен (0,24%).

Заправки з екстрактом вологого листа мали найбільш інтенсивний запах лаврового листа. Те саме спостерігалось, коли цей зразок також сприймався з найбільш інтенсивним смаком лаврового листа. Кислотний та солоний смак оцінені однаково для всіх трьох зразків.

Екстракт олії, отриманий з вологого листа, був кращим. Між олійним екстрактом, отриманим із сухого листа, і контрольним зразком експерти не виявили переваги. Підвищена загальна оцінка була отримана для салатної заправки з олійним екстрактом, отриманим з вологого листа.

Висновок. Кращу оцінку здобув олійний екстракт, отриманий з вологого листа. Між олійним екстрактом, отриманим з сухого листа, і контрольним зразком відмінностей не виявлено. Підвищена загальна оцінка була отримана для салатної заправки з олійним екстрактом, отриманого з вологих листів.

Keywords: лавр, лист, екстракти, склад, композиція, салат, заправка.

Одержання активного вугілля із піролізованих деревних відходів (ПДВ) методом лужної активації КОН

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Вступ. Метою публікації є оцінка альтернативної відновлюваної сировини – технологічних відходів харчової промисловості (піролізованих деревних відходів (ПДВ) – як прекурсорів для виробництва поруватих вуглецевих матеріалів – потенційних сорбентів для використання при очищенні води у лікero-горілчаному виробництві.

Матеріали і методи. ПДВ м'ясопереробної промисловості як сировина для виробництва активного вугілля. Хімічна лужна активація ПДВ з використанням КОН. Метод адсорбції-десорбції азоту для визначення пористої структури при температурі 77 К; розподіл мезопор за розмірами і об'єм мезопор – метод *V_{JH}*; розподіл мікропор за розмірами – методом *QSDFT*; об'єм мікропор – метод Дубініна-Радушкевича; об'єм субнанопор – метод *QSDFT*.

Результати і обговорення. Мікропориста структура одержаного АВ має такі характеристики: діаметри пор знаходяться у діапазоні $D_{mi}=0,61-2,5$ нм, які найбільшим чином представлені порами з діаметром 0,61; 1,19; 1,54 нм; об'єм мікропор – $V_{mi}=0,11-0,30$ см³/г; площа поверхні пор – $S_{mi}=407-852$ м²/г; диференціальний об'єм пор $dV_{mi}/dD=(0,023-1,400) \cdot 10^{-2}$ см³/г; диференціальна площа пор $dS_{mi}/dD=(0,18-45,60)$ м²/г; частка мікропор у загальному об'ємі пор складає 70,31%. Домінуючий вклад мікропор у питому поверхню пор демонструє пропорційна залежність між об'ємом і площею поверхні пор, що також підтверджується лінійною залежністю між диференціальним об'ємом пор і диференціальною площею пор. У структурі мікропор були визначені найменші пори – субнанопори з $D \leq 1$ нм, розміри яких знаходяться у діапазоні $D_{1nm}=0,61-1,00$ нм; об'єм субнанопор $V_{1nm}=0,11-0,25$ см³/г; площа поверхні пор – $S_{1nm}=407-783$ м²/г; диференціальний об'єм пор $dV_{1nm}/dD=(11,3-140,0) \cdot 10^{-4}$ см³/г; диференціальна площа пор $dS_{1nm}/dD=(2,33-45,60)$ м²/г. Частка субнанопор в об'ємі мікропор складає 84,12%; частка субнанопор у загальному об'ємі пор складає 59,15%. Можна стверджувати, що лужна активація КОН призводить до переважного розвитку субнанопор у пористій структурі адсорбенту. Наведені дані свідчать, що запропонований спосіб дає змогу отримати АВ з високим коефіцієнтом виходу 70,4% і поровим простором $V_{\Sigma}=0,421$ см³/г, розвинутою питомою поверхнею $S_{BET}=777$ м²/г і пористістю.

Висновки. Вторинні «поновлювані» ресурси (ПДВ) дають змогу отримувати високопористі АВ із низькими енерговитратами, що робить можливим їх застосування у лікero-горілчаному виробництві.

Ключові слова: піроліз, дерево, відходи, лужна активація, активне вугілля, нанопора.

Харчова цінність десертів із додаванням ягідної сировини сімейства агрусових із Північного Причорномор'я

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Вступ. Моніторинг нової ягідної сировини на предмет збалансованості її хімічного складу, органолептичних, технологічних характеристик і можливості її використання у десертах. Розробка технології желе із йоштою.

Матеріали і методи. В дослідженнях були використані такі матеріали: ягоди сімейства агрусових, а саме: фейхоа, актинідія та йошта. Проводився аналіз джерел літературно-патентної інформації, які містять відомості про останні науково-технічні досягнення, пов'язані з використанням нової сировини і розробкою технологій страв. Структурну міцність желе визначали методом пенетрації.

Результати і обговорення. Показано, що в якості сировини для виробництва десертів з підвищеною харчовою цінністю доцільно використовувати нову ягідну сировину Чорноморського регіону, а саме: фейхоа, актинідію і йошту. Харчова цінність фейхоа, актинідії і йошти визначається вмістом в них широкого спектра біологічно активних речовин у доступній для організму людини формі. Так, вміст йоду в ягодах фейхоа становить 0,07–0,1 мг/100 г. Ягоди актинідії та йошти відрізняються високим вмістом вітаміну С – 400–800 мг/100 г і 450–600 мг/100 г, відповідно. Ці ягоди багаті вітамінами групи В, Р, Е і бета-каротином, органічними кислотами, мінеральними елементами, зокрема залізом і калієм, що дає змогу віднести їх до продуктів з високою харчовою цінністю. Завдяки високому вмісту пектину ягоди фейхоа, актинідії і йошти є перспективною сировиною для виготовлення структурованих десертів – желе, мусів і сорбетів.

Наведені результати дослідження технологічних показників желе з йошою. Показано, що при додаванні йошти в желе можливо повністю виключити з рецептури желатин без суттєвих змін структурно-механічних властивостей продукту. Так, значення показників щільності та граничної напруги зсуву зразків желе з додаванням 15% йошти до маси продукту становить – 1,27 кг/м³ та 5,53 кПа відповідно та відповідає вимогам. З наведеними даними щодо щільності та структурної міцності продукту корелюють результати досліджень тривалості застигання желе – із додаванням йошти час драглеутворення десерту суттєво скорочується, що є сприятливим фактором для виробництва.

Висновки. Використання нової ягідної сировини – фейхоа, актинідії і йошти є доцільним для розширення асортименту десертів із підвищеною харчовою цінністю.

Ключові слова: *фейхоа, актинідія, йошта, десерт, харчова цінність.*

Вплив генотипу і року врожайності на вміст каротиноїдів у шкірці болгарських культурних сортів помідорів

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Вступ. Проведено дослідження з метою визначення впливу генотипу і року врожайності на кількість відхідних шкірок від шести болгарських культурних сортів помідорів, і вмісту каротиноїдів у отриманих шкірках.

Матеріали і методи. Шість болгарських сортів помідорів вирощувалися у відкритих польових умовах у науково-дослідному інституті овочевих культур Мариця, Пловдив, Болгарія. Дослідження спільної дії досліджуваних факторів на кількість відходів, що утворюються в процесі очищення, проведено двофакторним дисперсійним аналізом. Вміст каротиноїдів у відходах визначено рідинною хроматографією.

Результати і обговорення. Встановлено, що генотип помідорів має суттєвий вплив на відсоток отриманих із них шкірок і на вміст каротиноїдів в них. Середня масова частка шкірки помідорів, що зібрані у 2013 році, коливалася від $2.45 \pm 0.13\%$ до $5.33 \pm 0.09\%$. Найбільша частка шкірок отримано з сортів “Каробета” і “Топаз”. Для сортів помідора, вирощених у врожаї 2014 року, середня частка отриманих шкірок змінювалася від $2.98 \pm 0.13\%$ до $3.50 \pm 0.25\%$, а найвища кількість шкірок отримувалося з сортів “Водолій Ф1” і “Каробета”. Отримані шкірки в основному містять лікопен, бета-каротин і лютеїн. У перший рік врожаю найвищий вміст лікопену (97.16 ± 0.81 мг/100г) і лютеїну (21.22 ± 0.10 мг/100г) знайдені в шкірці сорту помідорів “Стелла”, а сорт “Каробета” має високий вміст бета-каротину (108.48 ± 1.36 мг/100г), в той час як на другому році дослідження більшість лікопену (241.14 ± 1.24 мг/100 г) містилося в шкірках “Водолія Ф1”, а бета-каротину (293.36 ± 2.00 мг/100г) і лютеїну (13.58 ± 0.15 мг/100г) – в шкірках томату “Стелла”. Зі шкірки сортів помідорів “Стелла”, “Топаз”, “Водолій Ф1” і “Жаклін” отримали лікопен і бета-каротин, в той час як шкірки сортів “Меріголд” і “Каробета” були джерелом лише бета-каротину. Результати показали найбільший вплив генотипу помідорів на вміст лютеїну (69.43%), далі йдуть вміст бета-каротину (57.52%) і частка шкірок (46.55%). Встановлено, що умови навколишнього середовища сильно впливають на частку шкірок (41.66%) і вміст лікопену (38.73%), у той час їх вплив на вміст бета-каротину є нижчим (14.92%) і ще нижчим на вміст лютеїну (1.63%).

Висновки. Кількість лікопену у шкірках помідорів залежить від генотипу і врожаю, у той час як вміст бета-каротину і лютеїну залежить в основному від генотипу помідорів.

Ключові слова: *томат, шкірки, каротиноїди, генотип, рік, урожайність.*

Харчова цінність і споживчі властивості булочних виробів із фруктозою для діабетичного харчування

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Вступ. Харчова цінність і споживчі властивості є визначальними для оцінки якості виробів, привабливих для споживача. У пропонованій статті представлено дослідження цих характеристик у виробках діабетичного спрямування.

Матеріали і методи. Тісто готували безопарним способом за розробленими рецептурами. Характеристики визначали за органолептичними показниками методом експертної оцінки, структурно-механічні властивості м'якушки – на автоматизованому пенетрометрі, ступінь збереження свіжості – за показниками кришкуватості та вологоутримання, розподіл і форми зв'язку води – за допомогою диференційно-термічного аналізу на дериватографі, вміст ароматичних речовин – за кількістю бісульфітівв'язуючих сполук.

Результати і обговорення. Діабетичні хлібобулочні вироби, що виготовляються за поширеними рецептурами, мають невисоку харчову цінність і малий термін зберігання без втрати свіжості. Експертна оцінка розроблених нами діабетичних виробів «Булочний виріб 1» та «Булочний виріб 2», збагачених складовими казеїну, порошком топінамбуру, клітковини висівок гречки, цитратами кальцію, магнію, цинку та заліза підтвердила покращення органолептичних якостей виробів при внесенні цієї сировини. Визначенням деформації м'якушки та гідрофільних властивостей встановлено, що розроблені види виробів повільніше черствіють унаслідок підвищення водопоглинальної здатності. Це корелює з кращим збереженням ними зв'язаної вологи під час зберігання. Досліджувані вироби порівняно з контролем містять більше ароматичних сполук як у скоринці, так і в м'якушці. Розрахунок харчової цінності виробів показав значне підвищення вмісту поживних речовин у зразках з добавками.

Висновок. Розроблені вироби мають вищу харчову цінність і кращі характеристики якості, повільніше черствіють.

Ключові слова: хліб, фруктоза, харчування, свіжість, діабет, корисність.

Про- і антиоксидантна активність куркумінлідів з лецитином у соняшниковій олії

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Вступ. Куркумін, що є основним компонентом куркумінів у куркумі, привернув значну увагу завдяки широкому спектру біологічних і фармацевтичних заходів. Він чинить різні терапевтичні дії, такі як протизапальні, нематоцидні, антипаразитарні, спазмолітичні та антиканцерогенні. Крім того, це потужний поглинач реактивних видів кисню. Також спостерігається проокислювальний ефект куркуміна.

Матеріали і методи. Було проведено дослідження для оцінки активності куркумінів в сирій та очищеній соняшниковій олії, що містить синтетичний антиоксидант. Було підготовлено різні суміші олій. Оксидативну стабільність олійних сумішей перевіряли за температури 60 °C протягом 30 днів з регулярним інтервалом 5 днів відповідно до офіційних методів AOCS за пероксидним значенням, величиною р-анізидину і загальним окисленням.

Результати і обговорення. Тенденція виникнення куркуміна з тавтомерією кетенолу визначає його фізико-хімічні та антиоксидантні властивості. Було відзначено, що куркумініди демонструють помітну різну поведінку в обох оліях. Подання атома водню у випадку куркуміна відбувається з активної метиленової групи, яка існує лише в кето-формі. Форма кето переважає в нейтральних і кислих розчинах, тоді як форма енолу переважає в лужному розчині. У лужному середовищі куркумін зазнає деградації. Ця теорія також застосовується до інших двох куркумінів, наприклад, деметоксикуркуміну та бісдеметоксикуркуміну. Отже, стає вирішальною підтримування куркумінів в кето-формі, які будуть використовуватися як антиоксиданти.

У сирій соняшниковій олії, через наявність вільних жирних кислот, куркумініди не зазнали деградації, що приносить маргінальну антиоксидантну активність.

Лецитин хелатує іони металів, присутні у олії, що сприяє її окисленню, тим самим гальмуючи її окислення. Проте синергетична активність куркуміноїдів і лецитину виявила надзвичайну антиоксидантну активність.

У соняшниковій олії, що містить третичний бутилгідрокінон (ТВНҚ), куркумініди показали активність прооксидантів через відсутність кислого середовища. Лецитин демонструє синергічну активність з ТВНҚ в рафінованій соняшниковій олії. Тим не менше, прооксидантний ефект куркумінідів не спостерігається в присутності лецитину і ТВНҚ. Таким чином, лецитин і ТВНҚ стабілізують рафіновану соняшникову олію за наявності куркумінідів.

Висновок. Структурно-активні відносини відіграють важливу роль у визначенні активності (антиоксидант або проокислювач) конкретної сполуки. Складова повинна існувати у відповідній структурній формі для її використання як антиоксиданта.

Ключові слова: куркумініди, синергізм, таутомерія, структурна активність, соняшник, олія.

Інгібування мікробіологічних процесів при екстрагуванні сахарози

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Вступ. Унаслідок інтенсивного розвитку мікробіологічних процесів у дифузійній установці виникають додаткові втрати сахарози через розкладання, а також погіршуються якісні показники дифузійного соку, що негативно впливає на всі подальші стадії виробництва цукру.

Матеріали і методи. Об'єктами досліджень були: дифузійний сік; чисті культури бактерій *Leuconostoc mesenteroides*, *Bacillus subtilis*, *Pseudomonas spp.*, *Escherichia coli*, які спричиняють значні втрати цукрози у виробництві цукру з цукрових буряків; дезінфікуючі засоби нового покоління.

Результати і обговорення. Найбільші втрати сахарози в дифузійному соку спричинені бактеріями роду *Pseudomonas spp.*, оскільки після 24 год термостатування проб дифузійного соку вміст сахарози в них зменшився в 2 рази. У пробах соку з *B. subtilis* і *E. coli* спостерігався значний приріст нітритів протягом усього терміну термостатування. Так, кінцевий вміст нітритів у пробах через 24 год термостатування збільшився в 10–15 разів. У пробі соку з *L. mesenteroides* відбувалось значне підвищення рівня молочної кислоти порівняно з початковим значенням. Після термостатування протягом 2 год при 37 °С вміст молочної кислоти становив 10,63 мг/100 см³ порівняно з початковим вмістом молочної кислоти – 3,07 мг/100 см³. У разі розвитку слизоутворювальних бактерій у дифузійному соку спостерігається інтенсивне накопичення декстрану, що корелює зі збільшенням кількості клітин тест-культури *L. mesenteroides*.

Засоби на основі полігексаметиленбігуанідин гідрохлориду, четвертинних сполук амонію, натрієвої солі дихлоризоціанурової кислоти, надощтової кислоти та перекису водню мають високу ефективність стосовно більшості мікроорганізмів, які спричиняють втрати сахарози в процесі її екстрагування з бурякової стружки та призводять до погіршення технологічної якості напівпродуктів бурякоцукрового виробництва. Крім того, зазначені засоби є також ефективними щодо слизоутворювальних бактерій.

Висновки. Досліджувані засоби характеризуються високою бактерицидною дією щодо мікроорганізмів, наявних у дифузійному соку. Дані засоби також ефективні для пригнічення розвитку слизоутворювальних бактерій.

Ключові слова: *сахароза, екстрагування, дезінфікація, слизоутворення, бактерія.*

Порівняльні дослідження якості судешу із чхани на основі коров'ячого молока з додаванням соєво-молочної чхани*

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Вступ. Судеш – популярний десерт Бангладешу, виготовлений із чхани. Дане дослідження було проведено з метою порівняння якості судешу із чхани на основі коров'ячого молока та з додавання різної кількості соєвомолочної чхани.

Матеріали та методи. Чотири різних виду судешу, а саме S1 (із 100%-го чхани із коров'ячого молока), S2 (75%-ва чхана із коров'ячого молока + 25% соєвомолочна чхана), S3 (25%-ва чхана із коров'ячого молока + 75% соєвомолочна чхана) і S4 (100%-ва молочносоєва чхана) обробляли в лабораторії відділу харчової промисловості та інженерії, Університеті ветеринарії та тваринництва Читтагонг. Підготовлені зразки судешу були проаналізовані на вологість, білок, жир, золу, вміст вуглеводів, кислотність та сенсорні властивості. Прийнятність зразків судешу вивчалася експертною комісією, що складалася із 15 учасників.

Результати і обговорення. Результати показали, що вологість зразків становила 22,53±0,12, 22,95±0,20, 23,54±0,22 та 25,44±0,17% відповідно; вміст білка 21,87±0,32, 23,02±0,17, 25,92±0,42 і 29,62±0,23%; вміст жиру 20,44±0,05, 19,02±0,03, 17,00±0,05 і 16,42±0,10%; вміст золи 0,88±0,04, 1,39±0,03, 1,53±0,04 і 1,95±0,02%; кислотність 0,05, 0,033, 0,023 і 0,22%, вміст вуглеводів – 34,28±0,22, 33,62±0,16, 32,01±0,59 і 27,15±0,31% відповідно. На основі сенсорної оцінки кольору, смаку, текстури та загальної прийнятності судеш, виготовлений зі свіжої чхани на основі коров'ячого молока забезпечує найвищу прийнятність і був оцінений дуже високо. Судеш, виготовлений на 75% із чхани із коров'ячого молока і 25% соєвомолочної чхани (S2) був оцінений задовільно, а інші види (S3 і S4) не були прийнятними.

Висновки. Соєвомолочна чхана може використовуватися як замітник чхани із коров'ячого молока для виготовлення судешу.

Ключові слова: *молоко, судеш, чхана, соя, якість.*

* Примітка редакції. Судеш – це популярний південноазіатський десерт на основі кисломолочного сиру. Чхана – сирний продукт, у який замість сичугу додаються харчові кислоти; зазвичай використовується у південній Азії як сировина для виробництва солодошів.

Математичне моделювання стабілізації емульсій Пікерінга твердими наночастинками

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Вступ. Мета дослідження полягає у передбаченні й вивченні умов для стабілізації харчових і косметичних емульсій ефектом Пікерінга, що забезпечує можливість математичного моделювання умов для найефективнішої стабілізації емульсій.

Матеріали і методи. Вивчені модельні емульсії з введеними твердими наночастинками на основі води і тригліцеридів карбонових кислот, таких як трибутират (C4), трикаприлат (C6) і триолеат гліцерину, льняної олії (суміш тригліцеридів кислот: 9–11% пальмітинової і стеаринової, 13–29% олеїнової, 15–30% лінолевої, 44–61% ліноленової кислот) та їх етилові естери з подібним складом, а також парфумерна олія. Обчислення поверхневого натягу і стабільності для модельних харчових і косметичних емульсій виконані за допомогою програмного забезпечення MathCAD-2000 за методом Бінкса.

Результати і обговорення. Розраховані значення вільної енергії сферичної наночастинки (в одиницях $k_B T$, $T = 298$ K) на поверхні поділу фаз вода/олія (трибутирин, трикапроїн, триолеїн, льняна олія та їх етилові естери, парфумерна олія). Стабільність частинки характеризується енергетичним бар'єром з боку однієї з рідин. У зв'язку з тим, що енергетичні профілі є параболою, отримана інформація про величину бар'єрів і положення мінімуму, коли частинка переміщується від мінімуму з координатою z_m у воду ($z = -1$) і в олію ($z = 1$). Найкращі значення цієї енергії для твердого емульгатора складають приблизно 2830 (у льняній олії та в їх естерах), 4010 (парфумерна олія), 400 (триолеїн) і 150 $k_B T$ (трибутирин). Визначено, що наночастинка кремнезему, яка має 50% гідрофільної поверхні, має кращі властивості стабілізації.

Висновки. Доведено можливість теоретичного передбачення умов для стабілізації харчових і косметичних емульсій ефектом Пікерінга. Оптимальний вибір матеріалу наночастинки для стабілізації відповідає кремнезему з 50-відсотковою гідрофільністю поверхні.

Ключеві слова: пікерінг, наночастинки, кремнезем, вуглець, моделювання.

Визначення форм зв'язку вологи білково-трав'яних згустків

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Вступ. Інтерес викликає дослідження форм зв'язків вологи в модифікованих молочно-білкових концентратах, а саме в білково-трав'яних згустках, які отримують термокислотним осадженням білків молока.

Матеріали і методи. Досліджувався білково-трав'яний згусток (контроль) та білково-зернова суміш на його основі з екстудатом рису. Визначення вмісту вологи проводили термогравіметричним методом. Дослідження кількості вологи різної форми зв'язку здійснювали методом диференціально-термічного аналізу на в діапазоні температур 20–250 °C за швидкості нагрівання зразків масою 1000 мг – 2,5 °C за хвилину.

Результати і обговорення. Вилучення основної частини вологи (вільної) із білково-трав'яних згустків (БТЗ) без екструдату рису відбувається швидше – за 6,0–6,5 хв, а з додаванням екструдату рису – повільніше і цей показник знаходиться в межах 7,5–8,0 хв. Гідрофільні речовини екструдату взаємодіють з вологою БТЗ за рахунок утворення Н-зв'язаних поліасоціатів із участю молекул води та Н-зв'язаних функціональних груп гідрофільних речовин. Молекули гідрофобних груп стають більш упорядковані, про що свідчить зменшення ентропії. За рахунок дисперсійних сил гідрофобні групи агрегуються. Взаємодія екструдату рису з білками молока після коагуляції призводить до утворення конгломератів, що не відрізняються міцністю зв'язків, але цілком достатні для зв'язування вільної вологи, яка міститься у БТЗ у вигляді сироватки. Для зразків білково-трав'яних згустків і білково-зернових сумішей на їх основі з екструдатом рису характерним є наявність чотирьох критичних температур (T_I 49–58 °С, T_{II} 91–98 °С, T_{III} 131 °С, T_{IV} 179–186 °С), за яких видаляється волога різних типів, що розрізняється міцністю зв'язку. Додавання екструдату рису до БТЗ дозволяє підвищити кількість зв'язаної вологи на 36,07% порівняно з контролем.

Висновок. Додавання екструдату рису до білково-трав'яних згустків для зв'язування вільної вологи є доцільним. Це забезпечує сталі показники якості білково-трав'яних згустків під час зберігання.

Ключові слова: *молоко, щавель, коагуляція, білок, екструдат, зв'язок вологи.*

Процеси і обладнання харчових виробництв

Вплив тиску і температури на коефіцієнт тертя гранульованих полімерів по металевій поверхні

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Вступ. Проведені дослідження з метою визначення коефіцієнтів тертя полімерних гранульованих матеріалів по металевій поверхні, зокрема для опису законів їх руху у зоні живлення черв'ячного екструдера.

Матеріали і методи. Для досліджень руху полімерних гранул у каналі екструдера використано чотири типи гранул: поліетилен високої густини (ПВГ), співполімер етилену з вінілацетатом (севілен), полістирол (ПС) та полівінілхлорид (ПВХ). Коефіцієнти тертя визначено з використанням плоскопаралельної моделі процесу екструзії.

Результати і обговорення. Аналіз результатів показав загальне зменшення залежності коефіцієнта тертя (КТ) при збільшенні тиску, однак при досягненні максимальних значень майже на всіх кривих відбувався перехід через мінімум, після якого значення КТ починали зростати.

Для ПВГ КТ зменшується від 0,35 до 0,26 при навантаженні 200 Па та від 0,23 до 0,17 при 2000–2200 Па, зі збільшенням глибини каналу від 7 до 23 мм. Для севілену КТ збільшується від 0,15 до 0,44 при 200 Па та від 0,15 до 0,17 при 1900–2100 Па. Для ПС КТ змінюється від 0,6 при 200 Па до 0,3 при 2100 Па і не залежить від

збільшення глибини каналу. Для ПВХ КТ збільшується від 0,3 до 0,7 при 200 Па та від 0,22 до 0,43 при 1900–2100 Па.

При нагріванні робочої поверхні до температури 90 °С КТ для ПВХ перестав залежати від глибини каналу і набуває середніх значень – 0,3 при 200 Па та 0,2 при 2100 Па. Для севілену при 80 °С КТ зростає для кожної глибини і досягає значень від 0,25 до 0,4 при 200 Па та від 0,19 до 0,23 при 1600–1700 Па. Для ПС при 100 °С КТ зменшується до 0,5 при 200 Па та 0,2 при 2100 Па. Для ПВХ КТ не залежить від нагрівання робочої поверхні.

Відмінності в отриманих залежностях можна пояснити різними механічними властивостями досліджуваних полімерів, зокрема значеннями міцності, коефіцієнта тертя, деформованості за різних температур.

Висновки. Отримані результати дають змогу удосконалити процес екструзії, збільшити продуктивність і знизити енергоємність за рахунок підвищення точності розрахунків.

Ключові слова: полімер, гранула, екструдер, тертя.

Термодинамічний аналіз систем анаеробного бродіння

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Костянтин Васильківський, Олег Степанець

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Вступ. У статті досліджено можливість використання особливостей процесів мікробіологічних і термодинамічних трансформацій у зброджуваних середовищах, які поєднуються принципами мінімізації енергетичних потенціалів і спрямування до найбільш імовірних станів.

Матеріали і методи. Методи досліджень базуються на теоретичних пошуках, вивченні особливостей матеріальних і енергетичних трансформацій у бродильних циклах у зв'язку з ентропійними перетвореннями у біологічних системах.

Результати і обговорення. Перебіг технологій анаеробного і аеробного бродіння є локальною складовою загального колообігу вуглецю, в якому спостерігаються ентропійні перетворення і втрати у формі теплової енергії. Самоплинність і незворотність процесів підготовки цукровмісних середовищ і самого процесу бродіння є відображенням законів термодинаміки, на основі аналізу яких запропоновано систему утилізації теплоти бродіння.

Технології анаеробного й аеробного бродіння мають потенціал нетрадиційних енергетичних джерел, використання яких можливе на основі теоретичної бази теплових насосів. За Р. Клаузіусом, перебіг природних процесів є самоплинним і це стосується хімічних і біохімічних реакцій. Це положення можна застосувати і до технічних систем, що доповнюють природні самоплинні явища і процеси, в яких, у тому числі, реалізуються природні властивості дріжджів-цукроміцетів. Наведена термодинамічна оцінка біологічних систем у формі характеристик швидкостей зміни ентропії та енергетичних трансформацій живильних компонентів за участю АТФ і АДФ та вільної енергії Гіббса. Показано, що насичення культурального середовища діоксидом вуглецю створює перепони на шляху ендогенних процесів синтезу етилового спирту й діоксиду вуглецю. Запропоновано схему утилізації вторинних енергетичних ресурсів процесів бродіння з урахуванням того, що потенціал теплоти бродіння майже вдвічі перевищує теплоту перегонки.

Висновки. Кількість теплоти бродіння достатня для процесу перегонки при паралельному поєднанні цих процесів, а величина і швидкість генерування вільної енергії Гіббса в культуральних середовищах пов'язана з динамікою зростання його ентропії.

Ключові слова: масообмін, енергообмін, мікроорганізм, анаеробне бродіння, ентропія, термодинаміка.

Неоднорідне псевдозрідження в автоколивальному режимі

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Вступ. Метою статті є математичне моделювання гідродинаміки неоднорідного псевдозрідження в автоколивальному режимі, який забезпечить суттєве підвищення ефективності тепло- і масообмінних процесів шляхом створення інтенсивного направленного перемішування зернистого матеріалу при проведенні процесів зневоднення та грануляції.

Матеріали і методи. Гранульований матеріал, що знаходиться в камері гранулятора, спорядженій спеціальним газорозподільним пристроєм у нижній частині та направляючою вставкою у верхній. Визначення порозності та перепаду тиску в шарі, а також відеофіксація процесу здійснювалися за допомогою спеціалізованого обладнання.

Результати і обговорення. Реалізовано неоднорідне псевдозрідження у автоколивальному режимі при застосуванні оригінального газорозподільного пристрою з коефіцієнтом живого перерізу $\phi=4,9\%$ та удосконаленої камери гранулятора. Забезпечено інтенсивне макроперемішування зернистого матеріалу з еквівалентним діаметром $D_e=3,97$ мм і густиною $\rho_r=1450$ кг/м³ при відношенні номінального перепаду тиску до висоти шару $\Delta P_{ш}/H_0 \geq 8500$ Па/м із частотою пульсацій $f=1,67$ Гц. Неоднорідне псевдозрідження в автоколивальному режимі забезпечує коефіцієнт гранулоутворення $\psi \geq 90\%$, та питоме навантаження поверхні шару за вологою $a_f=0,8-0,9$ кг_{вол.}/(м²·год). Обрано та на основі експериментальних досліджень модифіковано математичну модель, яка з урахуванням неоднорідності дає змогу визначити умови проведення процесу, при якому до 25% маси шару перебуває в активній фазі поза межами шару з частотою $f=1,67$ Гц. Математична модель з точністю 94,1% підтверджує результати дослідження.

Висновки. Реалізована гідродинаміка в камері гранулятора без утворення застійних зон. Модифікована математична модель дала змогу визначити інтенсивність активного пульсаційного об'ємного циркуляційного перемішування, що суттєво підвищить стійкість кінетики гранулоутворення при зневодненні композитних рідких систем.

Ключові слова: гідродинаміка, пульсація, псевдозрідження, добриво, зола.

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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).

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Структура статті:

1. УДК.
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3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озеряно).
4. *Установа, в якій виконана робота.*
5. Анотація. **Обов'язкова** структура анотації:
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Пункти 2–6 виконати англійською і українською мовами.

7. Основний текст статті. Має включати такі обов'язкові розділи:
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За необхідності можна додавати інші розділи та розбивати їх на підрозділи.

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Рисунки виконуються якісно. Скановані рисунки не приймаються. Розмір тексту на рисунках повинен бути **співрозмірним (!)** тексту статті. **Фотографії можна використовувати лише за їх значної наукової цінності.**

Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

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Скорочені назви фізичних величин в тексті та на графіках позначаються латинськими літерами відповідно до системи СІ.

В списку літератури повинні переважати статті та монографії іноземних авторів, які опубліковані після 2000 року.

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В Ukrainian Food Journal взято 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.

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1. Приклад:

Popovici C., Gitin L., Alexe P. (2013), Characterization of walnut (*Juglans regia* L.) green husk extract obtained by supercritical carbon dioxide fluid extraction, *Journal of Food and Packaging Science, Technique and Technologies*, 2(2), pp. 104–108.

2. Посилання на книгу:

Автори (рік), Назва книги (курсивом), Видавництво, Місто.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

Приклад:

2. Wen-Ching Yang (2003), *Handbook of fluidization and fluid-particle systems*, Marcel Dekker, New York.

Посилання на електронний ресурс:

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Приклади:

1. (2013), *Svitovi naukovometrychni bazy*, available at:
http://www1.nas.gov.ua/publications/q_a/Pages/scopus.aspx
2. Cheung T. (2011), *World's 50 most delicious drinks [Text]*, Available at:
<http://travel.cnn.com/explorations/drink/worlds-50-most-delicious-drinks-883542>

Список літератури оформлюється лише латиницею. Елементи списку українською та російською мовою потрібно транслітерувати. Для транслітерації з українською 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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