

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

Ukrainian Food Journal

Volume 5, Issue 4
2016

Київ

2016

Київ

Ukrainian Food Journal is an international scientific journal that publishes innovative papers of expert in the fields of food science, engineering and technology, chemistry, economics and management.

The advantage of research results publication available to students, graduate students, young scientists.

Ukrainian Food Journal is abstracted and indexed by scientometric databases:

Ukrainian Food Journal – міжнародне наукове періодичне видання для публікації результатів досліджень фахівців у галузі харчової науки, техніки та технології, хімії, економіки і управління.

Перевага в публікації результатів досліджень надається студентам, аспірантам та молодим вченим.

Ukrainian Food Journal індексується наукометричними базами:

Index Copernicus (2012)
EBSCO (2013)
Google Scholar (2013)
UlrichsWeb (2013)
Global Impact Factor (2014)
CABI full text (2014)
Online Library of University of Southern Denmark (2014)
Directory of Research Journals Indexing (DRJI) (2014)
Universal Impact Factor (2014)
Directory of Open Access scholarly Resources (ROAD) (2014)
European Reference Index for the Humanities and the Social Sciences (ERIH PLUS) (2014)
Directory of Open Access Journals (DOAJ) (2015)
InfoBase Index (2015)
Chemical Abstracts Service Source Index (CASSI) (2016)

Ukrainian Food Journal включено у перелік наукових фахових видань України з технічних наук, в якому можуть публікуватися результати дисертаційних робіт на здобуття наукових ступенів доктора і кандидата наук (Наказ Міністерства освіти і науки України № 1609 від 21.11.2013)

Editorial office address:

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

Адреса редакції:

Національний університет
харчових технологій
вул. Володимирська, 68
Київ 01601

e-mail: ufj_nuft@meta.ua

Scientific Council of the National
University of Food Technologies
recommends the journal for printing.
Minutes № 7, 27.12.2016

Рекомендовано вченою радою
Національного університету
харчових технологій.
Протокол № 7 від 27.12.2016 р.

© NUFT, 2016

© НУХТ, 2016

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

Topic covered by the journal include:

Food engineering	Food nanotechnologies
Food chemistry	Food processes
Food microbiology	Economics and management
Physical property of food	Automation of food processes
Food quality and safety	Food packaging
Health	

Periodicity of the journal – 4 issues per year.

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

Ukrainian Food Journal is abstracted and indexed by scientometric databases:

Index Copernicus (2012)

EBSCO (2013)

Google Scholar (2013)

UlrichsWeb (2013)

Global Impact Factor (2014)

Online Library of University of Southern Denmark (2014)

CABI full text (2014)

Directory of Research Journals Indexing (DRJI) (2014)

Universal Impact Factor (2014)

Directory of Open Access scholarly Resources (ROAD) (2014)

European Reference Index for the Humanities and the Social Sciences (ERIH PLUS) (2014)

Directory of Open Access Journals (DOAJ) (2015)

InfoBase Index (2015)

Chemical Abstracts Service Source Index (CASSI) (2016)

Reviewing a Manuscript for Publication. All scientific articles submitted for publication in “Ukrainian Food Journal” are double-blind reviewed by at least two academics appointed by the Editors' Board: one from the Editorial Board and one independent scientist.

Copyright. Authors submitting articles for publication warrant that the work is not an infringement of any existing copyright and will indemnify the publisher against any breach of such warranty. For ease of dissemination and to ensure proper policing of use papers and contributions become the legal copyright of the publisher unless otherwise agreed.

Academic ethics policy. The Editorial Board of "Ukrainian Food Journal" follows the rules on academic writing and academic ethics, according to the work by Miguel Roig (2003, 2006) "Avoiding plagiarism, self-plagiarism, and other questionable writing practices. A guide to ethical writing". The Editorial Board suggests to potential contributors of the journal, reviewers and readers to dully follow this guidance in order to avoid misconceptions in academic writing.

For a **full guide for Autor** please visit website at

<http://ufj.ho.ua>

Editorial board

Editor-in-Chief:

Valerii Mank, Ph. D. Hab., Prof., *National University of Food Technologies, Ukraine*

Members of Editorial board:

Aleksandr Mamtsev, Ph. D. Hab., Prof., *Branch of Moscow State University of Technologies and Management, Meleuz, Bashkortostan, Russia.*

Anatolii Saiganov, Ph. D. Hab., Prof., *Institute of System Research in Agroindustrial Complex of NAS of Belarus*

Galyna Simakhina, Ph. D. Hab., Prof., *National University of Food Technologies, Ukraine*

Cristina Popovici, Ph.D., As. Prof., *Technical University of Moldova*

Mark Shamtsian, PhD, As. Prof, *St. Petersburg State Technological Institute, Russia*

Mykola Sychevskiy, Ph. D. Hab., Prof., *Institute of Food Resources of National Academy of Sciences of Ukraine*

Olga Rybak, Ph.D., As. Prof., *Ternopil National Technical University "Ivan Puliui", Ukraine*

Pascal Dupeux, Ph.D., *University Claude Bernard Lion 1, France*

Stefan Stefanov, Ph.D., Prof., *University of Food Technologies, Bulgaria*

Tetiana Mostenska, Ph. D. Hab., Prof., *National University of Food Technologies, Ukraine*

Tetiana Pyrog, Ph. D. Hab., Prof., *National University of Food Technologies, Ukraine*

Tomasz Bernat, Ph. D. Hab., Prof., *Szczecin University, Poland*

Valerii Myronchuk, Ph. D. Hab., Prof., *National University for Food Technologies, Ukraine*

Viktor Stabnikov, Ph.D., As. Prof., *National University for Food Technologies, Ukraine*

Virginija Jureniene, Ph. D., Prof., *Vilnius University, Lithuania*

Vladimir Grudanov, Ph. D. Hab., Prof., *Belarusian State Agrarian Technical University*

Volodymyr Ivanov, Ph. D. Hab., Prof., *Iowa State University, USA*

Yuliia Dziazhko, Ph. D. Hab., Prof., *Institute of general and inorganic chemistry «Vernadskii» of National Academy of Sciences of Ukraine*

Yordanka Stefanova, Ph.D, *University of Plovdiv "Paisii Hilendarski", Bulgaria*

Yurii Bilan, Ph.D., As. Prof., *Szczecin University, Poland*

Oleksii Gubenia (*accountable secretary*), Ph.D., As. Prof., *National University of Food Technologies, Ukraine*

Contents

Food technologies	629
<i>Valerii Sukmanov, Andrii Marynin, Halyna Dubova, Anatoliy Bezusov, Valentina Voskoboinik</i> Study of aroma formation from lipids of the fruit raw material.....	629
<i>Eugenia Boaghi</i> Impact of treatment with oxidative bleaching agents on walnut (<i>Juglans Regia L.</i>) shell chromatic parameters	644
<i>Galina Selyutina, Oksana Gapontseva</i> Component composition of radish root essential oil.....	653
<i>Habibeh Azizi, Vahid Hakimzadeh, Hossein Alizadeh Golestani</i> Purification of Raw Sugar Beet Juice by Electrocoagulation.....	667
<i>Viktoria Ostapenko</i> Analysis on application of different grape varieties in the production of icewine. A review.....	678
<i>Stanka Damyanova, Silvia Mollova, Albena Stoyanova, Oleksii Gubenia</i> Chemical composition of <i>Salvia officinalis</i> L. essential oil from Bulgaria...	695
<i>Tijani Akeem Olumide, Bakare Henry Adegoke, Oke Emmanuel Kehinde, Oyedeji Ajibola Bamikole</i> Effect of processing parameters on the proximate composition and sensory characteristics of breadfruit “Elubo”	701
<i>Andgela Dyakonova, Victoria Stepanova</i> Usage of the nut raw materials and chia seeds to improve fatty acid composition of the smoothies.....	713
<i>Anatolii Ukrainets, Vasyl Pasichniy, Maksym Polumbryk, Maniefa Polumbryk</i> Effect of collagen based protein isolate «Belkozine» on biological value of boiled sausages.....	724

<i>Valerii Mank, Oksana Tochkova, Oksana Melnyk, Oleksandr Bessarab</i>	
Relaxation behavior of aqueous dispersion polysaccharides.....	732
Processes and equipment of food productions.....	739
<i>Yurii Zmieviskii, Yuliia Dziazko, Valerii Myronchuk, Ludmyla Rozhdestvenska, Alexander Vilenskii, Ludmyla Kornienko</i>	
Fouling of polymer and organic-inorganic membranes during filtration of corn distillery.....	739
<i>Nataliia Dunaievskia, Mykola Chernyavskiy, Taras Shchudlo</i>	
Co-combustion of solid biomass in pulverized anthracite-coal firing boilers	748
<i>Pavlo Zasiadko, Mykola Priadko</i>	
Thermocouple errors in temperature measurements and validation of CFX and FLUENT models of natural gas combustion.....	765
<i>Yaroslav Korniyenko, Serhii Haidai, Andrii Liubek, Serhii Turko, Oleksandr Martynyuk</i>	
Modelling of pulsating mode of fluidization when obtaining organic- mineral fertilizers.....	781
Abstracts.....	795
Instructions for authors.....	819
Content of Volume 5 (Year 2016).....	825

Study of aroma formation from lipids of the fruit raw material

Valerii Sukmanov¹, Andrii Marynin², Halyna Dubova¹,
Anatoliy Bezusov³, Valentina Voskoboynik¹

1 – Poltava University of Economics and Trade, Poltava, Ukraine

2 – National University of Food Technologies, Kyiv, Ukraine

3 – Odesa National Academy of Food Technologies, Odesa, Ukraine

Abstract

Keywords:

Aroma
Homogenate
Precursor
Enzyme
Substrate

Article history:

Received 22.09.2016

Received in revised
form 23.11.2016

Accepted 27.12.2016

Corresponding author:

Valerii Sukmanov

E-mail:

Sukmanov53@mail.ru

DOI: 10.24263/2304-
974X-2016-5-4-3

Introduction. It was studied the formation of fruit flavor involving precursors and enzymes. It has a certain advantage over other methods.

Materials and methods. Lipid emulsions fruits (cucumber, squash, watermelon) were prepared in the Soxhlet apparatus according to the classical procedure using chloroform-ethanol solvent. The intensity of oxidative processes was evaluated using the developed technique based on the reactions of carbonyl compounds (CC) in the vapor phase with 2,4-dinitrophenylhydrazine. The particle size distribution (PSD), ζ -potential of the colloidal fraction was made on the analyser Malvern Zetasizer Nano ZS with a detection angle 173 °C. Recovery of fresh taste and aroma lost during thermal treatment was calculated by using organoleptic methods.

Results and discussions. The molecules of a precursor-compound can withstand the processing modes, while enzymes and aromatic compounds break down frequently. Most of the aromatic components are reaction intermediates formed between the substrate (lipid hydroperoxide derivatives, HPO) and the corresponding enzymes (hydroperoxide lyase HPL). The fruit and vegetable pretreatment conditions and subsequent environment in which enzymatic reactions take place can be considered as potential factors in the formation of fresh flavors.

The changes of the plant aromatic components during heat or combined processing are associated with transformations of lipid components. The availability of these components for enzymatic reactions depends on the distribution of lipid particles according to their size and potential mobility. Pre-treatment of samples positively influences binding energy in the complex of enzyme-substrate. The change of iodine number in treated homogenates, as compared to fresh ones, shows isomerization of flavor precursors. The minimal quantity of homogenates introduced (up to 20 g) and the duration of aroma-restoring reaction (from 5 to 7 minutes) were defined.

During heating in vacuum (with underpressure 6 ± 1 kPa, at temperature 32 ± 2 °C) of the suspended plant homogenates, substrate-enzyme interactions are the most intensive because of the conditions of interphase activation when the hydrophobic interaction, covalent links, and Van der-Vaalsovyh forces change. These effects ensure multimolecular adsorption and biosynthesis of green leaf volatiles (GLVs) in the fruits after heat treatment.

Introduction

The studies in the field of aroma formation mechanisms have showed that fragrances are formed from precursors and enzymes. Amino acids, carbohydrates, and lipids can be flavor precursors of the plant raw material under different conditions (DeMan John M., 1999; Guentert M.,2007). It has been found that thioglycosides, conjugate S-cysteine in grapes, and alliin in garlic can be precursors of fresh fruits of cabbage family (Ho Ch.-T at el,1990; Yu T.H. at el,1994; Tominaga T. at el,1998). As a result of reactions between the precursors of lipid nature, polyunsaturated fatty acids (PUFAs) and enzymes, the "green flavor" of crushed leaves (GLVs - Green Leaf Volatiles) occurs (Kalbrener J. E, 1974; Yang, X. et al, 2011; Gigot C., et al., 2010). The formation of fruit flavor involving precursors and enzymes is important and has a certain advantage over other methods. This advantage ensures fast formation of food flavor shortly before a meal or in the mouth. The conditions of flavor formation by virtue of precursors of lipid nature and enzymes have been sufficiently studied at different pH, temperature, presence of specific isoforms of enzymes, localization in the cell of fresh fruits (Luning P. A., 1995; R. Davidovich-Rikanati, 2008; Song J., 2010). The possibility of formation of really different volatile components has been shown on the test solutions of PUFAs extracted from the plant raw material (Kalbrener, J. E, 1974).

Mechanical grinding is sufficient for carrying out enzymatic reactions involving lipids cells in fresh fruits (cucumber, tomato, banana, etc.). Changes in lipid structures after heat, physical or combined processing of fruits have been considerably investigated only from point of view of peroxide processes (Jiménez-Monreal, A. M., 2009). The study of aroma formation from lipids *in vitro* is connected with large methodological difficulties; so lipid transformation processes due to thermal, physical or combined effects on the plant raw material are not much discussed in scientific publications. According to the theory of flavor restoration by G.Reed, with the availability of precursors, flavor can be restored in the fruit raw material after heat treatment when interaction conditions are created (Reed G.,1966). The preconditions for the repetitive flavor formation from precursors in fruits after heat treatment have been previously investigated (Dateo G. P. at el., 1957; Hasselstrom T., 1962; Schwimmer S.,1963), but the participation of lipid substrates in these processes is not still clarified (Gargouri M., 2008;Oey I.,2010).

Since lipid precursors are of hydrophobic nature and enzymes are of hydrophilic one, enzymatic reactions under *in vitro* conditions occur at very low speed. Surface active agents (surfactants) are used in aquatic lipid systems to increase the contact surface area in lipid-substrate reactions and to decrease water shell thickness. Similar effects can result from the physical effect and lead to the recovery of the lost flavor. In this study, enzyme catalysis is studied to a greater extent from physical perspective, since enzymes alter energy levels of the system intermediates using nonvalent interactions.

The theory of enzyme kinetics considers enzymatic reactions to be multistage ones accompanied by the formation of temporary intermediates. Most of the aromatic components are reaction intermediates formed between the substrate (lipid hydroperoxide derivatives, HPO) and the corresponding enzymes (hydroperoxide lyase HPL) (Damodaran S., Parkin K. L., 2008; Hui Y. H., 2010). Therefore, changes of aroma components can fairly quickly reflect the results of enzymatic hydrolysis *in vitro*. The study of structural changes in flavor lipid precursors will enable to determine the optimum conditions of physical effects on the enzyme-substrate system.

Materials and methods

Materials. Cucumbers, pumpkins, watermelons, and basil leaves were purchased from Poltava farmers during mass harvesting in summer.

Fruit heat processing: hydrothermal processing such as convective processing (fruits were immersed in boiling water, kept for 20 minutes and cooled) and combined processing including vacuum one with microwave heating (in the vacuum plant for steam distillation combined with a Selekt microwave oven with capacity of 0.6 kW, frequency of 2450 Hz, vacuum depth of 6 ± 1 kPa, the material temperature of 32 ± 2 °C), freezing (at temperature of -18 °C) in a freezer, and defrosting in a microwave unit).

Aqueous suspensions of fruits were prepared from fresh or heat treated fruits by mixing them with water at room temperature in the ratio 1:1 followed by homogenization.

Lipid emulsions were prepared in the Soxhlet apparatus according to the classical procedure using chloroform-ethanol solvent.

Centrifugation of the lipid fraction was carried out on the laboratory centrifuge MPW-223e with the drum rotation speed of 300–4000 r/min.

Method for determination of hydroperoxides and diene conjugates is based on measuring the light absorption by diene hydroperoxides at 234 nm on the spectrophotometer SF-42 at room temperature, with a molar extinction coefficient $2,5 \cdot 10^4$ $M^{-1}cm^{-1}$.

Determination of aldehydes. The intensity of oxidative processes was evaluated using the developed technique based on the reactions of carbonyl compounds (CC) in the vapor phase with 2,4-dinitrophenylhydrazine. The plant raw material weighing 100 gr was transferred to a 500 ml volumetric flask. A special container of 5 cm^3 was filled with 1% alcoholic solution of 2,4 - dinitrophenylhydrazine and hung inside the flask.

The flask was sealed with a ground-in stopper and put in the thermo cabinet for 5 hours at 60 °C. The flask was cooled for 50 minutes on the glazed tile, the 1% alcoholic solution of 2,4-dinitrophenylhydrazine was transferred from the special container to a standard glass cuvette of 24 mm wide and 5 mm thick. The absorption spectra of light waves at 490 nm in photocolimeter were determined. The concentration of C_6 – C_9 carbonyl compounds in pairs of the plant product was defined with the help of the pre-constructed calibration line.

Analysis of volatile components was carried out on the chromatography-mass spectrometry system Agilent 6890N/5973 inert (Agilent Technologies, the USA). The capillary column: HP-5ms 30m \times 0,25mm \times 0,25mkm (Agilent technologies, the USA). Temperature mode: 50 °C (5 min.), the temperature gradient: 5 °C/min to 220 °C (5 min.), the second gradient: 5 °C/min to 300 °C (10 min.), carrier gas: helium, flow velocity through the column: 1.0 ml/min. The evaporator temperature is 250 °C, interface temperature is 280 °C, the sample was introduced in the mode of 1:25 flow separation. Registration of ions was performed in SCAN mode in the range of 30–420 m/z. The mixture components were identified using a mass spectra library NIST02.

The distribution of size, particle size distribution (PSD), ζ -potential of the colloidal fraction was made on the analyser Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., UK) with a detection angle 173 °C. All measurements were performed in a temperature-controlled cell by 25 °C using ditch/cuvette DTS0012. At least five replicate measurements were made to control results repeatability on each sample. Size distribution in terms of intensity was obtained from the analysis of the correlation functions using an algorithm of General-purpose software analyser Zetasizer Software 7.11.

The descriptive sensory analysis of flavor in aqueous suspensions was made by the session of qualified judges of 12 women of different age groups who had the experience in the field of sensory evaluation. The evaluated attributes (aroma identity, other flavors, correspondence to the fresh raw material, shades) were grouped into conventional categories by the distribution method. The team members practiced assessment of defining attributes and their intensity during training on the basis of the differential threshold such as the minimum perceptible presence or change of flavor shades. Every descriptive attribute was verbally described; the patterns of fruit sample flavors were submitted to judges at the time of preparation; identification of descriptors served as a guidemark during testing.

Results and discussions

In spite of the diversity of the plant volatile components, most of them belong to three main groups: terpenes, phenylpropanoids/benzenoids and PUFA derivatives. By the accumulation point, volatile components are divided into those concentrated in: protoplasm or cell sap, idioblasts, and in special structures such as receptacles of essential oils. Isolation and extraction of the plant aromatic complex depends on the mode and intensity of the heat effect on aroma-containing structures of the raw material. The brief exposure at high temperature (80 °C) is the most commonly used in industry when there is an intense flavor separation from one or more accumulation points, depending on their sensitivity to temperature. The method of heat treatment at low temperature (32±5 °C) and the prolonged exposure was developed in order to increase the concentration of aromatic components by activating the specific enzymatic complex of the raw material (Mactavish H. S., 1998). The mechanism of enzymatic processes is specific and has many particular features; so with this method, flavor of the final product will be different at various heat input methods (volumetric and surface) to the product. For example, various heat treatment of basil leaves contributes in each case to occurrence of special components of aroma. Both identical components (eucalyptol, heptan-2-one, eugenol, phenol, 1,6-octadien-3-ol, mono (2-ethylhexyl) ester, 1,2-benzenedicarboxylic acid), and specific ones appropriate to this type of pretreatment were identified in the samples with preliminary freezing (№1), convective processing (№2) and combined processing (№3) (Table 1).

Table 1
Aromatic components and characteristics of basil flavor

№	Distinctive aroma components	Flavor characteristics
1	1,3,6-octatriene, 1-Hepten-6-one, 7-Octen-2-ol, 2-methyl-6-methylene, acetic acid, hexyl ester, limonene, (E)-2-butenylcyclopropane, 1,3,6,10-Dodecatetraene, 1,4-methanophthalazine, 1-Cyclopentene, 6,6-dimethylcycloocta-2,4-dienone	Basil, ethereal, spicy
2	2-aminobenzoate, 3-cyclohexene-1-methanol, 4-trimethyl-, (S)-p-menth-1-en-8-ol, octahydro-7-methyl-3-methylene-4-(1-methylethyl), 2-methylenecyclopropyl	Grassy, hay, of specific bitterness
3	1,5-heptadiene, 1,3,6-heptatriene, trans-isobornyl acetate, 1-naphthalenol	Saturated basil, fresh, clove

The identified aromatic components of basil leaves differ from the well-known ones due to the heat treatment temperature range and heating method. In the sample with leaves pre-frozen and then defrosted in the microwave field, the presence of ether shades is explained by specific enzymatic processes during and after thawing (Damodaran S., Parkin K. L., 2008). In the sample with convective and microwave processing, the sequence of thermal effects on various enzyme-containing structures is different. The shade of fresh hay prevails with convective processing, and a pleasant clove shade dominates with microwave processing. Thus, the way of heat input and the method of heat treatment at low impact temperatures on the raw material influence the product overall aroma profile.

Aromatic components of melons (cucumber, pumpkin and watermelon) are characterized by distinct sensibility to the thermal effect; they contain similar key and shade C₆-C₉ aldehydes, their alcohol derivatives (Bezysov A., 2015). Only trace amounts of aromatic components which are not recorded on aromograms were identified by smell in the samples of these fruits after freezing and hydrothermal treatment, as their concentration was below the detection threshold of chromatographs. Our earlier studies of the fruit lipids demonstrated that the fruit content was not changed after cooking but the accumulation of hydroperoxide derivatives of PUFA occurs. Also, as a result of heat processing, the accumulation of hydroperoxides (HPO) occurs after heat treatment in artichoke, asparagus, green beans, pepper, spinach, carrots and others (Jiménez-Monreal, A. M., 2009).

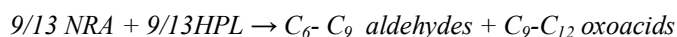
Hydroperoxides (HPO) of fatty acids are split by the enzyme of hydroperoxide lyase (HPL) (Feussner and Wasternack, 2002; Noordermeer et al., 2001). Depending on the characteristics of the carrying base, HPL_S can be classified into three groups (Matsui K. et al., 2001; Mita et al., 2005):

– 13-HPL which specifically splits fatty acids 13-HPO to form C₆-aldehydes (polyhexenal (1) or (Z) -3-hexenal (2)) and 12-oxo- (Z) -9-dodecenoic acid;

– 9/13 HPL which can split both 13 and 9-HPO-HPO with virtually the same efficiency;

– 9-HPL which specifically splits 9-HPO to C₉-aldehydes ((Z) -3-nonanal (3) or (Z, Z) -3,6- nonadienal (4)) and 9-oxo-nonanoic acid.

Hydroperoxide lyase HPL belongs to membrane bound enzymes. Without exception, all cellular membranes are thin lipoprotein films consisting of a double layer of lipid molecules that includes protein molecules. When freezing, heating, or undergoing microwave exposure, protein components of the raw material are coagulated. The main factors determining the behavior of particles in the coagulated structure are as follows: size of particles, the hydrophilic-hydrophobic balance of the particle surface, overall and electrokinetic potential of the surface. The activity of HPL using insoluble substrates such as hydroperoxides essentially depends on the dynamic properties of the general lipid phase of membranes. Most hydroperoxides in thermally processed fruits are formed from linoleic and linolenic acid. The hydroperoxide catalysis can be represented schematically as follows:



The reactions of hydroperoxide lyase in fresh fruits are sufficiently studied (Klee, H. J., 2010; Lanciotti R. et al, 2004), and their participation in the thermally processed raw material causes aroma-forming reactions. To identify and understand the conditions of catalysis with the participation of hydroperoxide lyase, the comparative analysis of physical and chemical parameters of the lipid system of fresh and thermally processed samples of the cucumber extract was made (Table 2).

Table 2

Physical and chemical characteristics of lipids in the cucumber extract

Index name	Fresh	Frozen	Hydrothermal processing
ζ -potencial, mV	-2,87±0,15	-4,11± 0, 30	- 5,50±0,22
Size, nm	10000...5000	5000...1000	1000...500
Total content of hydroperoxide compounds	8	12	18
Characteristics of aroma of aqueous suspension	Intense cucumber	Weak vegetable, mushroom shade	Grassy, soup
Total aldehydes, mg/g	0,079	0,055	0,043

According to the traditional view, the greater the absolute value of ζ is, the greater the electrostatic repulsion between droplets is, and hence the more sustainable the system stability is (Nakauma et al., 2008). Experimental measurements of ζ -potential indicate steric repulsion of particles in the hydrocolloid system and characterize stabilizing properties of the emulsifier represented by phospholipids in cell walls (Ferezou, J., & Bach, A. C., 1999). The samples ζ -potential ranges from -2,5 to -5,5 mV. As a comparison, ζ -potential range of industrial flavorings after enzymatic processes ranges from -22 to -25 mV. According to these data, we can characterize the stability of the studied emulsion of triglycerides; ζ -potential in the fruit raw material may indicate the system instability and the behavior of reactions involving enzymes. For the test samples, ζ -potential is distributed in the following order: fresh raw material < frozen raw material < hydrothermal processing. Dimensions of triglycerides extracted from cucumber are distributed in reverse sequence relative to ζ -potential. Thus, with the increase of the particle size their mobility rises. A similar pattern was described for liposomes (Tsukagoshi K., 1996; Radko S., 2000). The samples of pumpkin and watermelon after heat treatment showed identical distribution patterns of ζ -potential and the particle hydrodynamic diameter.

Dynamic properties of the membrane lipid matrix provide conformational flexibility of enzymes. The properties of the lipid matrix are associated with structural rearrangement in biological membranes. For example, water crystallization in frozen fruits induces activation of membrane-bound lipolytic enzymes and, subsequently, results in significant changes in structure, physical and chemical characteristics of fatty acids of membrane lipids. Thermal processing of membrane lipids affects physical properties of lipids and the oxidation process by endogenous enzymes. Thermal effects, freezing, electrical breakdown, and osmotic pressure are factors determining structural adjustments and the activity of endogenous enzymes (Gonzalez, M. E. et al, 2010). Maximum number of hydroperoxides in the extracts of fruit lipids after hydrothermal processing and the minimum amount of aldehydes (Table 2) are the conditions for maximum effect of HPL. The expected result of this action is the reduced amount of hydroperoxides and increased concentration of C₆-C₉ aldehydes.

The data on nanodimensional areas are a powerful approach to the study of the dynamics of biomolecules. The size of single molecules of the plant lipids is about 5–200 nm. According to some studies, single lipids don't exist in cell membranes but lipid nanodomains do (Eggeling C. et al., 2009), with average size of 710 nm. It is shown that the size of more than 700 nm testifies about the presence of cluster proteins, the hydration shell, and hydrophobic hydration which hinder detection of lipids through electron microscopy and their subsequent diffusion. To isolate lipid domains from extracts and analyze their hydrodynamic diameter, the samples were examined before and after centrifugation at different frequency and amount of time of the emulsion separation (Figures 1–4).

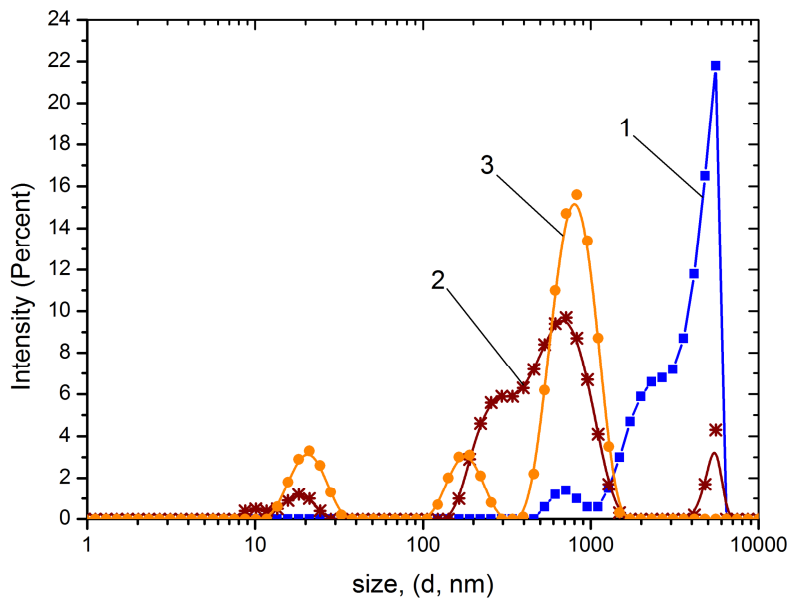


Figure 1. PSD of lipids from the fruits after hydrothermal processing:
1 – without separation, 2 – separation for 10 minutes at frequency of 1500 rev/min,
3 – separation for 10 min at frequency 4000 rev/min)

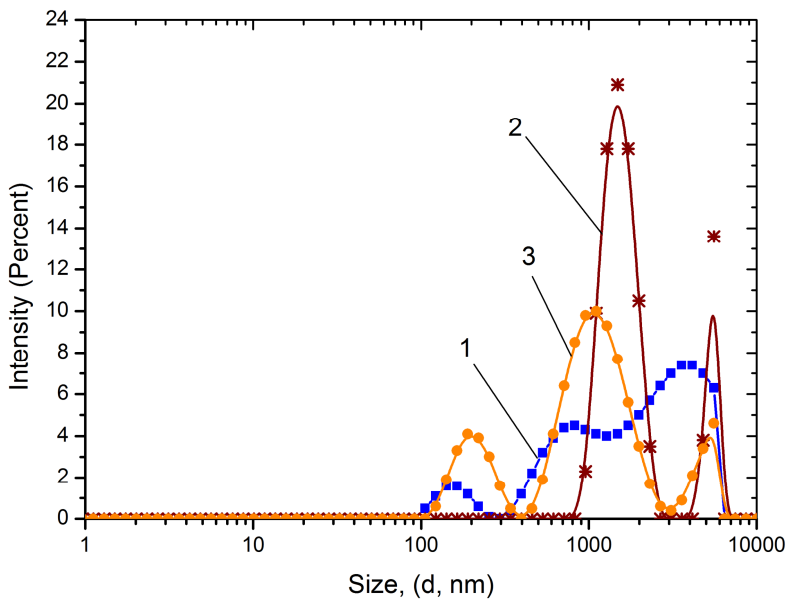


Figure 2. PSD of lipids from the fruits after hydrothermal processing:
1 – without separation, 2 – separation for 20 minutes at frequency of 1500 rev/min,
3 – separation for 20 minutes at frequency of 4000 rev/min

Lipid domains in the extract that was not separated in the centrifugal field are mainly composed of particles with a hydrodynamic diameter of 5000 nm. Separation in the centrifugal field for 10 minutes at frequency of 1500 rev/min decreases a hydrodynamic diameter of lipid domains to 2000 nm and separation at frequency of 4000 rev/min reduces it to 1000 and 300 nm. In order to understand the impact of the physical effect of the centrifugal field on protein-lipid associates, the separation time in the centrifugal field was increased to 20 minutes (Figure 2).

Lipid extracts that were not separated in the centrifugal field are mainly composed of particles with a hydrodynamic diameter of 6000 nm. Separation in the centrifugal field for 20 minutes at frequency of 1500 rev/min decreases a hydrodynamic diameter of lipid domains to 800 nm and 25 nm and separation at frequency of 4000 rev/min reduces it to 900, 250 nm and 25 nm. The increase of separation time in the centrifugal field to 20 minutes results in the decrease of a hydrodynamic diameter of lipid domains.

The impact on the cell lipid structures to enhance or diminish the hydrophobic interactions, covalent links, and Van der Waals forces is made using chemical, enzymatic or physical methods. The combination of the physical impact and enzymatic processes leads to the preservation of natural flavor that was shown in plants with high hydrostatic pressure and low temperature (Van Buggenhout S., 2006). Intermolecular forces are components of disjoining pressure which depends on the thickness of the lipid film, temperature, the composition and properties of the interacting phases (bodies). The study of disjoining pressure forms the basis of the theory of stability of hydrophobic colloids – DLVO theory; it explains many surface phenomena.

Overcoming positive disjoining pressure preventing thinning of the film under the influence of external forces leads to adhesion or fusion of contacting bodies. It means coalescence or coagulation of the particles of the dispersed phase in the context of colloidal systems; in this study it denotes the enzyme-substrate interaction. The combined processing of fruits in vacuum with depth of 6 ± 1 kPa is accompanied by the optimal temperature mode for activation of fruit enzymes (32 ± 2 °C).

Changes in properties of lipid structures of plant cells and membrane-bound enzymes in vacuum comply with DLVO theory (Gennis R. B., 2013; de Jesus, S. S., & Filho, R. M., 2011). This theory considers the combined effect of several components of surface energy. According to this theory, colloidal protein-lipid particles can loosely approach each other until they come in contact with their watery diffuse shells or layers. In these conditions, there are no interaction forces between them. For the reaction approximation of particles of enzymes and lipids, it is necessary to achieve deformation of diffuse shells to reach their mutual overlapping (or penetration into each other). While the thickness of the liquid layer or film is greater than the total thickness of boundary layers with special structure, the influence of these layers is manifested only through the relevant changes in electrostatic and molecular components of disjoining pressure.

The implementation of these processes causes some change of the PSD profile described above. Hydrodynamic diameters of lipids in the extract are distributed more evenly due to the combined processing (Figures 3–4).

The comparison of the results of the samples after hydrothermal and combined processing testifies about the system greater permanence and stability, which is expressed in the adjustment of a hydrodynamic diameter to the range of 1000 nm and 100 nm.

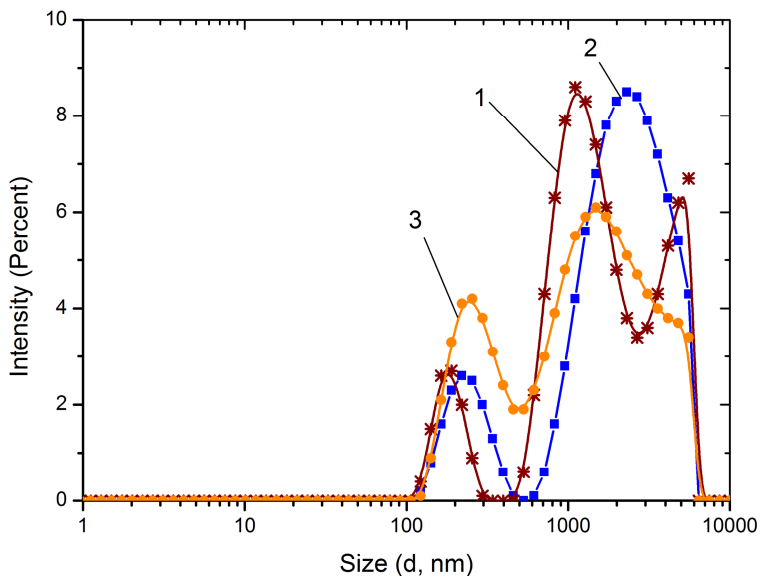


Figure 3. PSD of lipids from the fruits after vacuum treatment:
1 – without separation, 2 – separation for 10 minutes at frequency of 1500 rev/min,
3 – separation for 10 minutes at frequency of 4000 rev/min

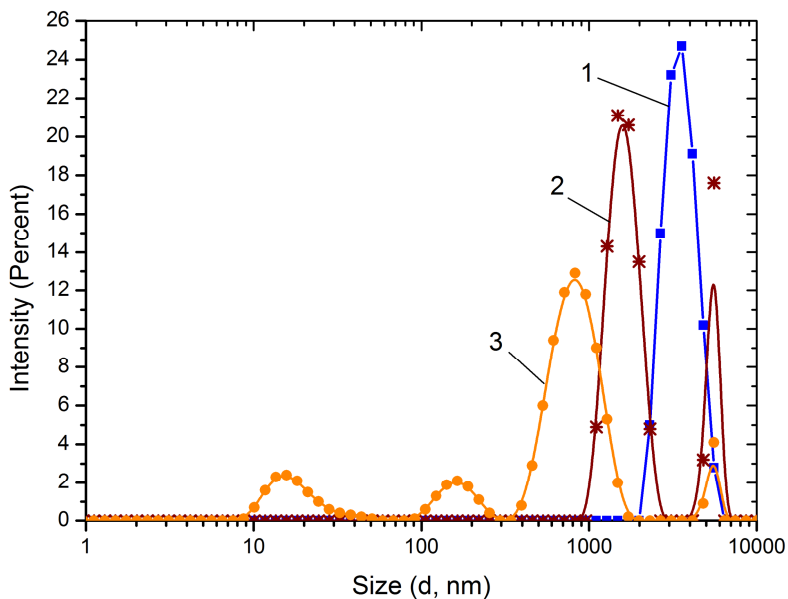


Figure 4. PSD of lipids from the fruits after vacuum treatment:
1 – without separation, 2 – separation for 20 minutes at frequency of 1500 rev/min,
3 – separation for 20 minutes at frequency of 4000 rev/min

The analysis of the PSD profile of the samples after hydrothermal and vacuum processing with separation for 20 minutes shows approximate results and the similar stability after the impact of the centrifugal field. Thus, the increase of the physical impact on lipid nanodomains is efficient under certain conditions. The expansion of the local zone of the lipid layer surface leading to adjustment of a hydrodynamic diameter (Figure 3) and favorable conditions of enzymatic hydrolysis is observed in vacuum. Strengthening of the further physical impact on this system changes the conditions of disjoining pressure; so the particles demonstrate repulsion resulting in the decreased hydrodynamic diameter and different PSD profile.

In the case of peripheral proteins (membrane bound enzymes of HPL), the described bilayer modifications lead to their activation. For example, when Ca^{2+} ions or products of lipid peroxidation are added to membrane fractions, the activation of mitochondrial phospholipases is observed (Halliwell B., & Chirico S., 1993; Adibhatla R. M., & Hatcher J. F., 2008). After combined processing, due to changes in the activity of hydroperoxide lyase HPL, alterations in the fruit flavor occurring during the accumulation of C_6 - C_9 aldehydes were registered (Figures 5,6).

The intensity and peak area of aromatic components indicate the formation of C_6 - C_9 aldehydes of the GLVs profile from lipid hydroperoxide compounds. The effectiveness of combined processing of fruits in the context of reactions implies activation of hydroperoxide lyase and reactions between hydrophilic enzymes and hydrophobic precursors. Under disjoining pressure in vacuum, the sheet of water in the interphase interlayer of the lipid bilayer, hydration shells around polar portions of lipids and membrane proteins is sufficiently reduced to make these reactions possible.

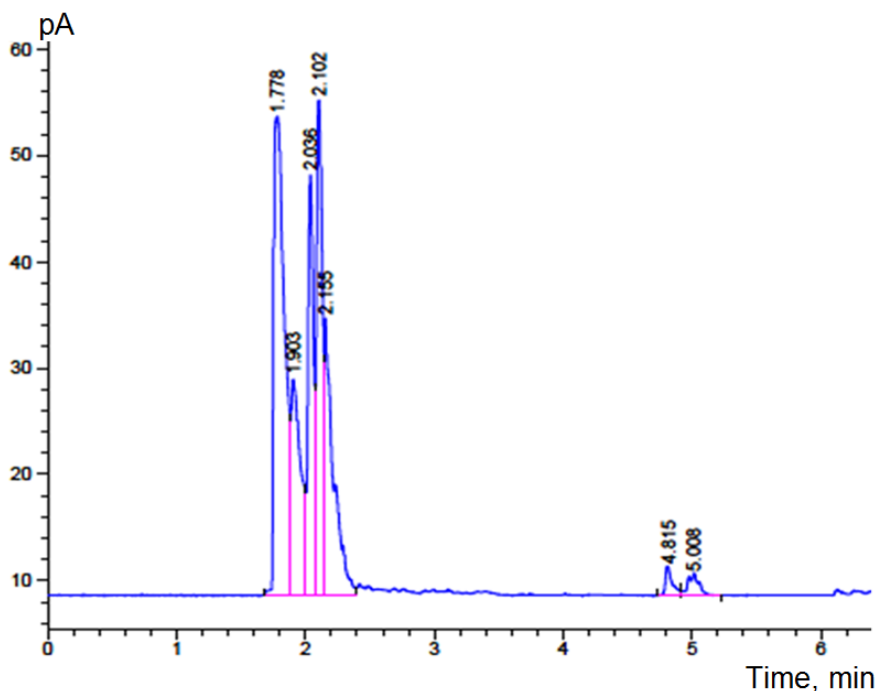


Figure 5. Aromatogram of the lipid extract after combined processing of fruits with active HPL

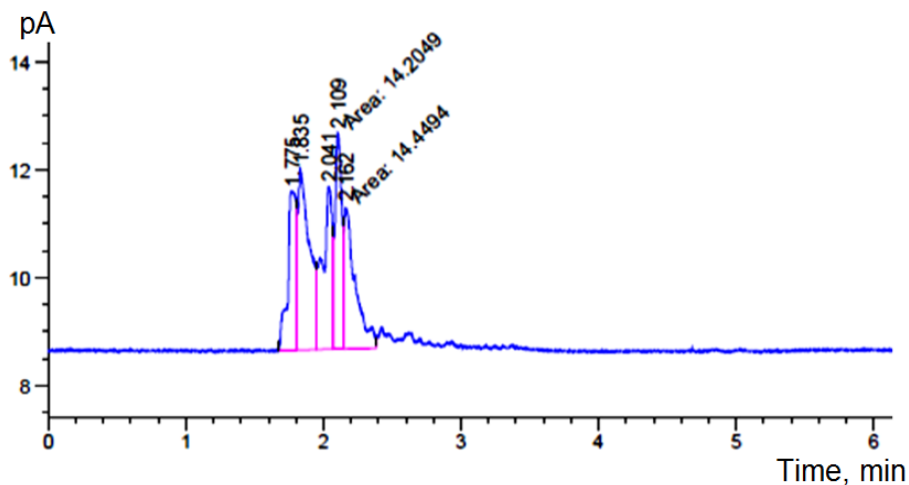


Figure 6. Aromatogram of the fruit lipid extract with inactive HPL

The physical effect of vacuum on the colloidal solution causing changes in the size of the diffuse layers and the value of ζ -potential depends on the method of heat input. In the discussed combined plant, microwave heating in a range of 32 ± 2 °C was used, which was replaced by convective heating in subsequent experiments. The purpose for replacing the heat input method to convection is the focused study of conditions for interaction between lipids and their oxidation products and enzymes in the fruit system. The statistical analysis of experimental data on the effect of vacuum depth and processing temperature mode fruit pulp is represented as the following relationship:

$$Y = 2,94 - 0,0125 \cdot X_1 - 20,73/X_2$$

where X_1 – pressure, kPa. Upper level is 91,3 kPa, lower level is 1.3 kPa, variation interval is 10 kPa.

X_2 – temperature, °C. Upper level is 46°C, lower level is 20 °C, variation interval is 3 °C

Y – number of flavor, relative units

The received data are valid according to the value of the Student's coefficient for the mathematical model.

Thus, regardless of the method of heat input, the functional activity of membrane proteins and dynamic properties of the membrane lipid matrix contributing to conformational flexibility of enzymes were shown. Therefore, vacuum processing of watermelon flesh which lost its flavor results in aroma recovery due to the repeated enzyme-substrate interactions down to measurable concentration which can be recorded on a chromatograph (Figure 7). The peaks responsible for fresh flavors of Nonadienal, 3-hexenal, 3-nonenal, 12-oxo- (Z) -9-dodecenoic acid, 5-Nonanol corresponding to enzymatic

hydrolysis of peroxide compounds of fatty acids were identified among the compounds (2-Propenoic acid, 2-hydroxyethyl ester, Propane, 2- (ethenyloxy) - 2-Propanamine, Adenosine, 4'-de (hydroxymethyl) -4' - [N-ethylaminoformyl], 2-Furanmethanol, Propanoic acid, 2-oxo-, methyl ester, Ethyl 3-hydroxy-3-methylbutanoate, dl-Glyceraldehyde dimer, S-Ethyl ethanethioate, 2-Butanone, Cyclohexanone, 2,4-Dihydroxy-2,5-dimethyl-3 (2H) - furan-3-one, Propane, Cyclopropanecarboxamide, ethyl ester, Furyl hydroxymethyl ketone, Propanal, 4-Mercaptophenol, 1,2,3-Propanetriol, 1-acetate).

It is known that the protein molecule may be fixed in the bilayer using various types of interactions including electrostatic ones (at the level of polar heads of lipids) and hydrophobic ones (in the bilayer thickness). During heating fruits or aqueous suspensions in vacuum (underpressure is 6 ± 1 kPa, temperature is 32 ± 2 °C), substrate-enzyme interactions are the most intensive because of the conditions of interphase activation, when there is a change in mobility, structure and spatial position of lipid domains. These effects ensure multimolecular adsorption and biosynthesis of GLVs in the fruits that lost their flavor after thermal processing.

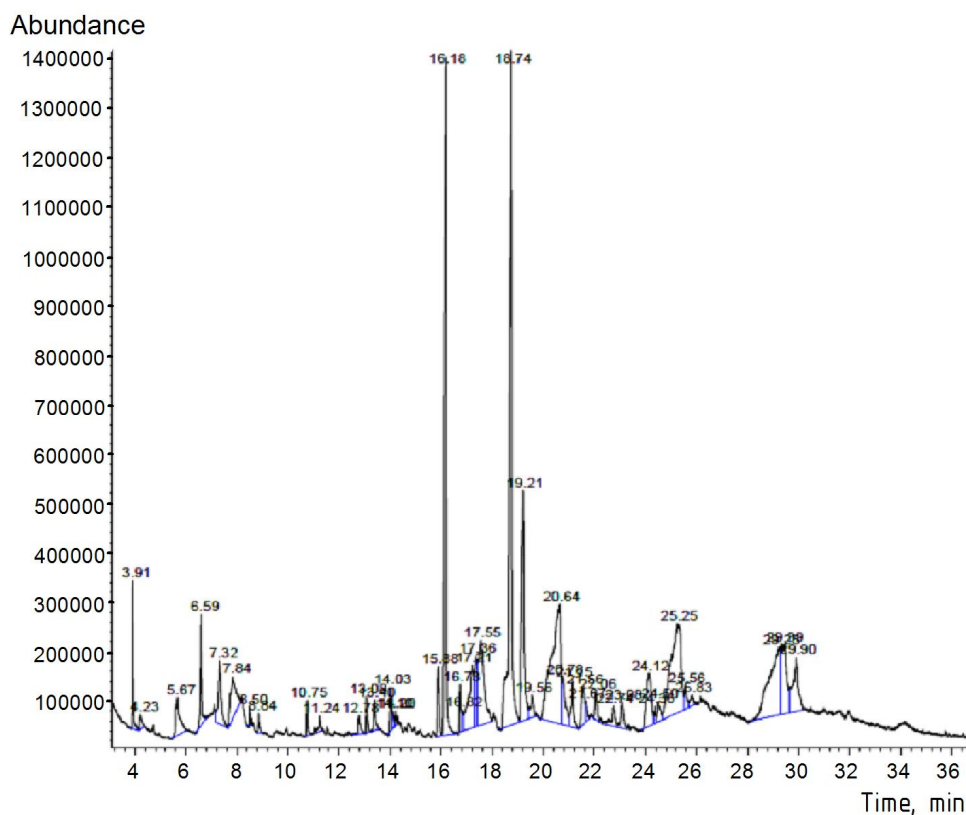


Figure 7. Aromatogram of the restored flavor of watermelon samples

Conclusions

Heat processing (convection and microwave) of the raw material in vacuum allows purposefully affect the aromatization enzymatic process. The availability of flavor precursors of lipid nature for enzymatic reactions can be assessed by the distribution of their hydrodynamic diameter and ζ -potential mobility. Changes in these parameters of the plant lipid components during processing affect the concentration of aromatic components.

The influence of triglyceride dimensional characteristics on the possibility of aroma-forming reactions involves the change in the conditions of the contact interaction of hydrophilic-hydrophobic colloidal systems. It has been established that during vacuum heating (underpressure is 6 ± 1 kPa, temperature is 32 ± 2 °C) of the suspended plant homogenates, substrate-enzyme interactions are the most intensive because of the conditions of interphase activation when the hydrophobic interaction, covalent links, and Van der -Vaalsovyh forces are weaken. These effects ensure the multimolecular adsorption and biosynthesis of GLVs in the fruits after thermal processing.

Many structurally simple aroma-forming substances found in certain foods affect the completeness of sensation and perception of the product as being delicious, fresh and fragrant. Their presence or absence can be regulated by introducing small quantities of fresh homogenized material. Aroma recovery is the enzymatic process which depends on availability of enzymes and flavor precursors in foods. In order to improve enzyme activity, the material may not necessarily be fresh, but also frozen or stored at low temperatures, and processed in the microwave field. More experiments are needed on recovery of fresh flavor by using enzymes from plant materials, especially in creation of flavored food glazes and foam. Reinforcement of the flavor profile will be reflected in reducing the amount of salt or sugar used in preparation of products and in manufacturing fat-free products. The increased demand for organic foods and flavors should support the interest in this area of research.

References

1. deMan J. M. (1999), *Principles of food chemistry*. 3rd ed., Aspen Publishers, Gaithersburg, Maryland.
2. Guentert M. (2007), The flavour and fragrance industry – past, present, and future. In *Berger, R. G. (Ed.), Flavours and fragrances: chemistry, bioprocessing and sustainability*, Springer.
3. Ho Ch.T., Sheen L.Y., Wu P., Kuo M.-Ch., Hartman T.G., Rosen R.T. (1990), *Glycosidically bound aroma compounds in pineapple and peach*. *Science and Technology*, John Wiley & Sons, New York, pp. 77–80.
4. Yu T.H., Lin L.Y., Ho C.T. (1994), Volatile compounds of blanched, fried blanched, and baked blanched garlic slices, *Journal of agricultural and food chemistry*, 42(6), pp. 1342–1347.
5. Tominaga T., Peyrot des Gachons C., & Dubourdieu D. (1998), A New Type of Flavor Precursors in *Vitis v inifera* L. cv. Sauvignon Blanc: S-Cysteine Conjugates, *Journal of Agricultural and Food Chemistry*, 46(12), pp. 5215–5219.
6. Kalbrener, J. E., Warner, K., & Eldridge, A. C. (1974), Flavors derived from linoleic and linolenic acid hydroperoxides. *Cereal Chem*, pp. 51(406).
7. Yang X., Song J., Fillmore S., Pang X., Zhang Z. (2011), Effect of high temperature on color, chlorophyll fluorescence and volatile biosynthesis in green-ripe banana fruit. *Postharvest biology and technology*, 62(3), pp. 246–257.

8. Gigot C., Ongena M., Fauconnier M. L., Wathelet J. P., Du Jardin P., Thonart P. (2010), The lipoxygenase metabolic pathway in plants: potential for industrial production of natural green leaf volatiles, *Biotechnologie, Agronomie, Société et Environnement*, 14(3), pp. 451.
9. Luning P.A., Carey A.T., Roozen J.P., Withers H.J. (1995), Characterization and Occurrence of Lipoxygenase in Bell Peppers at Different Ripening Stages in Relation to the Formation of Volatile Flavor Compounds, *J. Agric. Food Chem*, 43, pp. 1493–1500.
10. Davidovich-Rikanati R., Yaniv Azulay, Yaron Sitrit, Yaakov Tadmor, Efraim Lewinsohn (2009), Tomato aroma: Biochemistry and biotechnology, In: Havkin-Frenkel D., Belanger F.C. (Ed.), *Biotechnology in Flavor Production*, Blackwell Publishing, pp.118–130.
11. Song J. (2010), Major enzymes of flavor volatiles production and regulation in fresh fruits and vegetables, In A. Bayindirli (Ed.), *Enzymes in Fruit and Vegetable Processing Chemistry and Engineering Applications*, Taylor & Francis Group, pp. 45–63.
12. Jiménez-Monreal A.M., García-Diz L., Martínez - Tomé M., Mariscal M., Murcia, M.A. (2009), Influence of cooking methods on antioxidant activity of vegetables, *Journal of Food Science*, 74(3), pp. H97–H103.
13. Reed G. (1966), *Enzymes in Food Processing*, Access Online via Elsevier.
14. Dateo G.P., Clapp R.C., Mackay D.A. M., Hewitt E.J., Hasselstrom T. (1957), Identification of the volatile sulfur components of cooked cabbage and the nature of the precursors in the fresh vegetable, *Journal of Food Science*, 22(5), pp. 440–447.
15. Hasselstrom T., Bailey S., Reese E.T. (1962), *Regeneration of Food Flavors through Enzymatic Action*, Army Research Office Washington DC.
16. Schwimmer S. (1963), Alteration of the flavor of processed vegetables by enzyme preparations, *Journal of Food Science*, 28(4), pp. 460–466.
17. Gargouri M., Akacha N. B., Kotti F., Rejeb I. B. (2008), Voie de la lipoxygénase: valorisation d'huiles végétales et biosynthèse de saveurs, *Biotechnologie, Agronomie, Société et Environnement*, 12(2), pp. 185–202.
18. Oey I. (2010), Effect of novel food processing on fruit and vegetable enzymes, In: A. Bayindirli (Ed.), *Enzymes in Fruit and Vegetable Processing Chemistry and Engineering Applications*, Taylor & Francis Group, pp. 245–312.
19. Damodaran S., Parkin K. L. (2008), *Fennema's food chemistry*, 4, Boca Raton, FL, CRC press.
20. Hui Y.H., Chen F., Nollet L.M. (2010), *Handbook of fruit and vegetable flavors*, John Wiley and Sons.
21. Mactavish H.S., Menary R.C. (1998), Biosynthesis of volatiles in brown boronia flowers after harvest: effect of harvest time and incubation conditions, *Annals of Botany*, 81(1), pp. 83–89.
22. Bezysov A., Dubova H., Rogova N. (2015), New Methods Of Plant Selection For Food Aroma Recovery Aided By Oxidation Processes, *Acta Universitatis Cibiniensis, Series E: Food Technology*, 19(2), pp. 15–26.
23. Feussner I., Wasternack C. (2002), The lipoxygenase pathway, *Annual review of plant biology*, 53(1), pp. 275–297.
24. Noordermeer M.A., Veldink G.A., Vliegthart J.F. (2001), Spectroscopic studies on the active site of hydroperoxide lyase; the influence of detergents on its conformation. *FEBS letters*, 489(2), pp. 229–232.

25. Matsui K., Fukutomi S., Wilkinson J., Hiatt B., Knauf V., Kajwara T. (2001), Effect of overexpression of fatty acid 9-hydroperoxide lyase in tomatoes (*Lycopersicon esculentum* Mill.), *Journal of agricultural and food chemistry*, 49(11), pp. 5418–5424.
26. Mita G., Quarta A., Fasano P., De Paolis A., Di Sansebastiano G. P., Perrotta C., Casey R. (2005), Molecular cloning and characterization of an almond 9-hydroperoxide lyase, a new CYP74 targeted to lipid bodies, *Journal of experimental botany*, 56(419), pp. 2321–2333.
27. Klee H.J. (2010), Improving the flavor of fresh fruits: genomics, biochemistry, and biotechnology, *New Phytologist*, 187(1), pp. 44–56.
28. Lanciotti R., Gianotti A., Patrignani F., Belletti N., Guerzoni M. E., Gardini F. (2004), Use of natural aroma compounds to improve shelf-life and safety of minimally processed fruits, *Trends in food science & technology*, 15(3), pp. 201–208.
29. Nakauma M., Funami T., Noda S., Ishihara S., Al-Assaf S., Nishinari K., Phillips G. O. (2008), Comparison of sugar beet pectin, soybean soluble polysaccharide, and gum arabic as food emulsifiers. 1. Effect of concentration, pH, and salts on the emulsifying properties. *Food Hydrocolloids*, 22(7), pp. 1254–1267.
30. Ferezou J., Bach A. C. (1999), Structure and metabolic fate of triacylglycerol-and phospholipid-rich particles of commercial parenteral fat emulsions, *Nutrition*, 15(1), pp. 44–50.
31. Tsukagoshi K., Tanaka A., Nakajima R., Hara T. (1996), Notes On-Line Capillary Zone Electrophoretic Separation-Chemiluminescence Detection of Protein Labeled with Fluorescamine, *Analytical sciences*, 12(3), pp. 525–528.
32. Radko S.P., Stastna M., Chrambach A. (2000), Size-dependent electrophoretic migration and separation of liposomes by capillary zone electrophoresis in electrolyte solutions of various ionic strengths. *Analytical chemistry*, 72(24), pp. 5955–5960.
33. Gonzalez M.E., Anthon G.E., Barrett D.M. (2010), Onion cells after high pressure and thermal processing: comparison of membrane integrity changes using different analytical methods and impact on tissue texture, *Journal of food science*, 75(7), pp. 426–432.
34. Eggeling C., Ringemann C., Medda R., Schwarzmann G., Sandhoff K., Polyakova S., Hell S.W. (2009), Direct observation of the nanoscale dynamics of membrane lipids in a living cell, *Nature*, 457(7233), pp. 1159–1162.
35. Van Buggenhout S., Messagie I., Van der Plancken I., Hendrickx M. (2006), Influence of high-pressure–low-temperature treatments on fruit and vegetable quality related enzymes, *European Food Research and Technology*, 223, pp. 475–485.
36. Gennis R. B. (2013), *Biomembranes: molecular structure and function*, Springer Science & Business Media.
37. de Jesus S.S., Filho R.M. (2011), Optimizing drying conditions for the microwave vacuum drying of enzymes, *Drying Technology*, 29(15), pp. 1828–1835.
38. Halliwell B., Chirico S. (1993), Lipid peroxidation: its mechanism, measurement, and significance, *The American journal of clinical nutrition*, 57(5), pp. 715–724.
39. Adibhatla R. M., Hatcher J. F. (2008), Phospholipase A2, reactive oxygen species, and lipid peroxidation in CNS pathologies, *BMB reports*, 41(8), pp. 560.

Impact of treatment with oxidative bleaching agents on walnut (*Juglans Regia L.*) shell chromatic parameters

Eugenia Boaghi

Technical University of Moldova, Chisinau, Republic of Moldova

Abstract

Keywords:

Walnut
Color
Bleaching
Okoron 12
Hydrogen peroxide
Sodium perborate
Calcium hypochlorite

Article history:

Received 26.09.2016
Received in revised form
12.12.2016
Accepted 27.12.2016

Corresponding author:

Eugenia Boaghi
E-mail:
eugenia.boaghi@
toap.utm.md

DOI: 10.24263/2304-
974X-2016-5-4-4

Introduction. Walnuts were formerly marketed in an unbleached condition, but the demand of the trade has led to the general practice of bleaching. Some walnuts are still sold in an unbleached condition, but most of those destined for out-of-state markets must be bleached. The objectives of this study are to present the effect of different bleaching agents on walnuts (*Juglans Regia L.*) shell.

Materials and methods. For color quantifying it was used the most popular color space system for measuring color of agricultural products – the Commission International de l'Éclairage (CIE) color system which uses the L^* , a^* , and b^* indices. Also, the total color difference (E), a single value which takes into account the differences between the L^* , a^* , and b^* of the sample and standard was calculated.

Results and discussion. Analyzing the obtained values for chromatic parameters for each of used bleaching agents it was established that those vary depending on the bleaching agent, concentration, pH of the medium, temperature and retention time of walnuts in bleach. The concentration has a major significance, with its growth reduces the time required to achieve an expected result. The pH of the medium plays an important role in the catalytic oxidation. Speed of walnut shell bleaching and brightness (L) increase with increasing pH from 3 to 10. The studied agents form the following series of bleaching activity: $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4 > \text{Okoron 12} > \text{H}_2\text{O}_2 > \text{Ca}(\text{ClO})_2$. It has been established that the optimal conditions for bleaching with $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4$ are: $C = 5\%$, $\text{pH} = 10$; $t = 60^\circ\text{C}$.

Conclusions. All bleaching agents proved to be suitable to lighten the walnut shell. In comparison with the widely used H_2O_2 the ageing process developed simultaneously, but there were differences in the total lightness change, the Sodium perborate treated samples stayed lighter.

Introduction

The walnut tree (*Juglans regia* L.) is cultivated commercially throughout southern Europe, northern Africa, Eastern Asia, the USA and western South America [1].

Walnut cultivars differ in the ability to produce light-coloured kernels under different climatic conditions. Important quality factors of walnuts are the size, colour, level of internal damage caused by insects, and level of external damage, such as adhering hull tissue and broken shells [2].

In Moldova, the walnut sector has seen rapid growth, from a very low base, in recent years, founded on three factors: the comparative advantage in production, the presence of a low cost labour force which is able to extract manually for the confectionary market with a much higher extraction rate of unbroken kernels than mechanised methods, and preferential access to the EU market with no tariff duties. The result has been a proliferation of marketing and processing operators. In recent years the walnut production has grown from 22 700 in 2012 to 31 000 metric tons, in shell basis in 2016 [3].

Color of the food is the first parameter of quality evaluated by consumers. What is important is the acceptance of the product even before being consumed.

Food colour is governed by the chemical, biochemical, microbial and physical changes which occur during growth, maturation, postharvest handling and processing.

Most walnuts of good commercial quality have shells of a brownish straw color and in some instances the shells will be of a light straw color which is more favored in the trade. Walnuts were formerly marketed in an unbleached condition, but the demand of the trade has led to the general practice of bleaching. Some walnuts are still sold in an unbleached condition, but most of those destined for out-of-state markets must be bleached. In general, the quality of the walnut kernel is not indicated by the color of the shell, but it is the general practice in the nut-packing industries to bleach the shells in order to produce a more attractive appearance^c in view of the preference which buyers exhibit for light-colored nuts. Walnut shell is composed of constituents responsible for its skeleton: cellulose, hemicellulose, lignin and chemical compounds responsible for color: phenols, quinones, coumarins, tannins and flavonoids, studies and research have shown, however, that lignin is involved in the color changing.

About 25.16% cellulose, 21.32% hemicelluloses, and 53.52% lignin were reported in the Walnut shell [4].

Bleaching is the treatment of cellulose with chemical solutions in order to lighten the color or discoloration. Brightness can be carried out by solubilization and removal of lignin, a macromolecular aromatic compound that confers rigidity, cloaks to water and a high resistance to decomposition, at the same time has an influence on walnut shell color changing.

Besides removing lignin, bleaching serves to disinfect the walnuts from mold spores that can result from processes of mesocarp traces decay. Besides lignin, extractive substances also have an influence on the phenomenon of color change or fading.

Both oxidizing and reductive agents are used for bleaching cellulosic products. In reactions caused by the treating agents the number of covalent bonds in cellulose, hemicellulose and lignin is reduced. With the decreasing number of covalent bonds the color of the wood appears lighter.

Nowadays, the bleaching agents are based primarily on hydrogen peroxide (HP). The bleaching agents provide whitening of cellulosic products through decomposition of peroxides into unstable free radicals. These radicals further breakdown into large pigmented molecules either through an oxidation or a reduction reaction, that leads to the change of the chemical structure of product interacting organic substances, which results in color change [5, 6].

Materials and methods

Materials

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

Sample preparation

The walnut samples were cleaned to remove trash and damaged, sunburned, and broken walnuts.

Bleaching

For walnut bleaching were selected oxidising agents: H_2O_2 , Okoron12, $Na_2B_2O_4(OH)_4$ and $Ca(ClO)_2$ (concentrations in the neighborhood of 1-10% being found satisfactory). The process was performed in the temperature range -20-60 °C and at the pH range 3 to 10 (pH adjusted with HCl or NaOH to the desired value).

Prepared walnut samples were immersed in the solution of bleaching agent being agitated to insure complete contact, the time of retention varied from 10 to 120 min, being considered as a sufficient period to secure thorough impregnation of the shells, after which the walnuts were withdrawn from the solution and allowed to dry.

Quantification of Colour

CIELAB analysis are used in many different experiments in organic chemistry [7], anorganic chemistry [8], and in food chemistry as well.

All color data were expressed by L^* , a^* , b^* , where L^* corresponds to lightness; a^* corresponds to the transition from green (- a^*) to red (+ a^*); and b^* corresponds to the transition from blue (- b^*) to yellow (+ b^*). The international standards and the nomenclature for the measurement of color used by the food industry were defined by the Commission Internationale de l'éclairage (CIE) in 1931. In the present study, the CIELAB system (L^* , a^* , b^*) was used.

Colour change was calculated acc. to the following formula [PN-ISO 105- B02:2006]:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

where: ΔE – colour difference, L – colour achromatic coordinate (lightness); $L = 100$ indicates approximation of a given colour to white, and $L = 0$ to black, a , b – colour chromatic coordinates; (+ a) indicates red colour, (- a) indicates green colour, (+ b) indicates yellow colour, (- b) indicates blue colour. The measurement of colour coordinates L^* , a^* , b^* of walnuts before and after bleaching was done in the same, accurately marked places.

Hue angle (h^*) and chroma (C^*) are two effective parameters for describing visual color appearance [9-11]. The h^* and C^* values were calculated using the following Eqs. [12]:

$$h = \tan^{-1} \frac{b}{a}$$

$$c = \sqrt{(a^2 + b^2)}$$

Results and discussion

There were no literary data available on the mechanism of bleaching with some agents, thus the first question was whether are they effective or not for bleaching walnuts and in how much time a 1 to 10% concentration will manifest its effect.

The results of walnuts bleaching with all used bleaching agents according their concentration are presented in Tables 1–4.

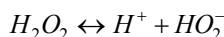
Table 1

The effect of hydrogen peroxide concentration on chromatic parameters of walnuts shell

C, %	t, min	a	b	L	ΔE	h	C
3	10	2.8	28.23	42.94	11.46	1.47	28.37
	30	2.38	30.52	46.96	15.29	1.49	30.61
	60	2.3	32.27	51.09	18.46	1.50	32.35
	90	2.01	33.2	58.48	22.98	1.51	33.26
	120	1.89	33.9	60.59	23.81	1.52	33.95
6	10	2.34	30.24	45.42	12.93	1.49	30.33
	30	2.06	31.68	54.96	17.42	1.51	31.75
	60	1.8	32.96	58.11	21.17	1.52	33.01
	90	1.6	34.2	62.35	23.25	1.52	34.24
	120	1.55	34.61	63.43	24.96	1.53	34.64
8	10	1.68	31.1	54.76	15.56	1.52	31.15
	30	1.2	34.65	59.81	20.66	1.54	34.67
	60	0.9	35.11	62.53	22.57	1.55	35.12
	90	0.5	36.23	63.48	24.10	1.56	36.23
	120	0.1	36.65	65.7	25.09	1.57	36.65
10	10	1.2	31.45	58.44	16.21	1.53	31.47
	30	0.8	34.78	64.78	22.02	1.55	34.79
	60	0.5	35.82	65.23	23.31	1.56	35.82
	90	0.3	37.64	65.96	24.10	1.56	37.64
	120	0.2	38.17	66.5	25.75	1.57	38.17

The results show that an important role in walnut bleaching with hydrogen peroxide plays the agent concentration. The higher the concentration is (8–10%), the more it increases the concentration in solution, which results in decreasing the time necessary to achieve the necessary bleaching level.

The oxidation reaction is directed to the chromophore groups of lignin, destruction of which leads to the high degree of cellulose bleaching. Hydrogen peroxide bleaching occurs due to peroxide ion HO_2^- originated as a result of hydrolytic cleavage of peroxide:



It is believed that non etherified phenolic units of lignin are initially processed in alkaline environment in ortho and para-benzoquinones that are then subjected to oxidation to produce acid fragments. In these conditions the etherified phenolic units are stable [13].

This leads to a substantial increase in the number of carboxyl groups of the lignin (Figure 1).

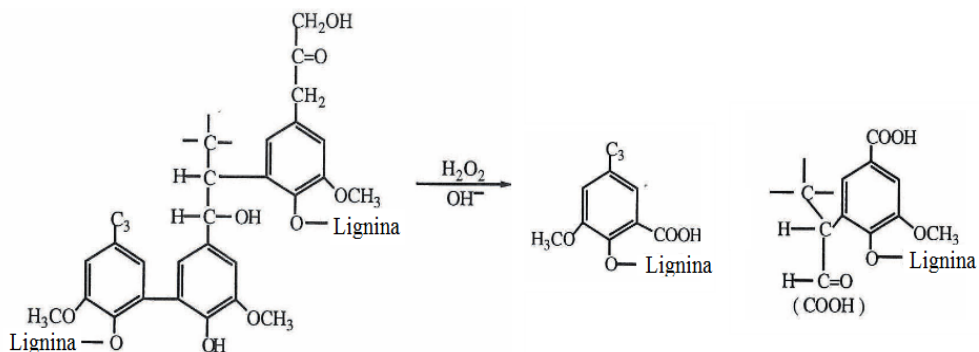


Figure 1. The reaction of the interaction of lignin with hydrogen peroxide in the bleaching

The effect of hydrogen peroxide concentration on the bleaching process was studied at four concentrations of hydrogen peroxide: 3, 6, 8 and 10%. The results show that increasing the concentration of hydrogen peroxide increases the brightness of the product. The initial Luminosity values of samples was 35.37 to 48.77, and bleached samples were from 42.94 to 66.5. Analyzing the presented values (Table 1) it can be noted that there is a tendency to increase the brightness parameter.

Hypochlorite aqueous solution that is commonly used in bleaching, contains molecular chlorine, hypochlorous acid and hypochlorite ions. The molecular chlorine predominates at low pH, at a pH of 4–6 basically only the hypochlorous acid is present, and at a pH above 9.5 the only form of active chlorine present in the solution is the hypochlorite ion.

Hypochlorite reaction with lignin stems initially quite fast and slower towards the end. In result of the reaction occurs oxidative degradation of lignin and chlorination and demethylation reactions are practically missing [14].

Analyzing the results blanching nuts with calcium hypochlorite (Table 2) was found that calcium hypochlorite bleaching which is less efficient, increasing temperature and an alkaline pH increases the brightness of shells and accelerates destruction of lignin and bleaching respectively. The optimum temperature is considered to be 40–45 °C and optimal pH value is about 10.0 during 1.5–2.0 hours.

Okoron 12 it is a stabilized composition, which contains peracetic acid CH_3CO_3H (15%), hydrogen peroxide and organic acids, produced by FINK TEC GmbH (Germany) and widely used as a disinfectant.

Table 2
The effect of calcium hypochlorite (Ca(OCl)₂) concentration on chromatic parameters of walnuts shell

C, %	t, min	a	b	L	ΔE	h	C
3	10	7.66	25.65	40.10	2.34	1.28	26.77
	30	6.68	27.60	41.11	3.04	1.33	28.40
	60	4.39	27.90	42.57	2.40	1.41	28.24
	90	3.96	28.11	44.79	3.75	1.43	28.39
	120	1.84	28.30	45.39	5.55	1.51	28.36
6	10	7.18	28.31	40.76	3.83	1.32	29.21
	30	6.20	29.10	43.74	5.61	1.36	29.75
	60	3.90	29.60	45.77	7.99	1.44	29.86
	90	2.79	30.10	45.78	8.29	1.48	30.23
	120	1.29	30.20	46.37	8.76	1.53	30.23
8	10	6.11	29.81	41.32	7.16	1.37	30.43
	30	4.98	31.20	44.17	9.51	1.41	31.59
	60	3.87	31.90	47.13	11.80	1.45	32.13
	90	2.50	32.10	52.30	16.13	1.49	32.20
	120	1.10	32.23	54.10	18.01	1.54	32.25
10	10	3.08	32.00	46.03	17.25	1.47	32.15
	30	2.5	33.90	49.12	19.26	1.50	33.99
	60	2	34.80	54.78	21.54	1.51	34.86
	90	0.89	35.20	55.57	22.38	1.55	35.21
	120	0.11	35.63	56.79	23.08	1.57	35.63

Table 3
The effect of Okoron 12 concentration on chromatic parameters of walnuts shell

C, %	t, min	a	b	L	ΔE	h	C
1	10	4.92	29.67	40.19	5.64	1.40	29.27
	30	4.21	30.16	43.35	6.32	1.43	30.16
	60	3.56	31.1	44.81	11.81	1.46	31.10
	90	3.02	33.60	45.19	5.99	1.48	33.60
	120	2.80	35.16	45.52	12.85	1.49	35.16
5	10	4.03	29.88	42.09	3.76	1.44	30.88
	30	3.40	30.25	46.13	11.47	1.46	31.95
	60	2.56	32.89	49.09	12.79	1.50	33.89
	90	1.89	35.49	50.32	15.40	1.52	35.49
	120	1.60	36.13	52.09	24.31	1.53	36.13

Whitening effect of Okoron 12 is due to its active component peracetic acid. The main reaction of peracetic acid with phenol and ether phenols are shown in Figure 2 being typical for the hydroxylation of aromatic rings and their oxidation in ortho- and para-quinones. The oxidised ring is fragmented in muconic acid and ester structures [15].

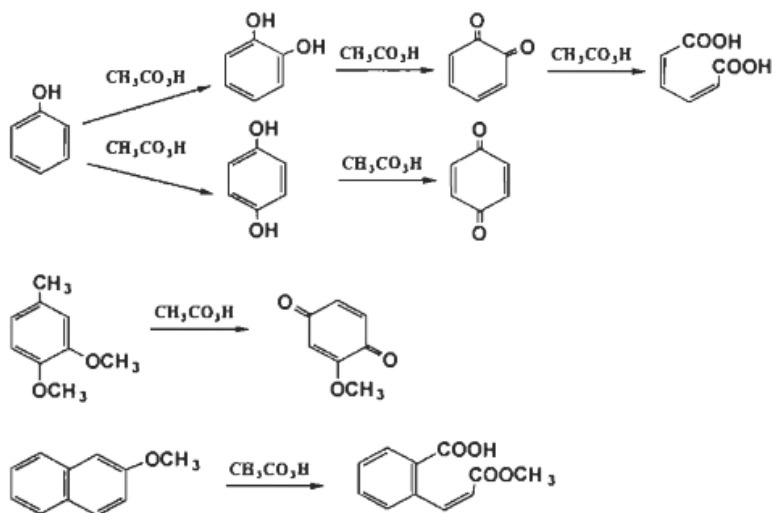
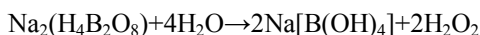


Figure 2. Oxidation of lignin compounds by peracetic acid

Table 4
The effect of Sodium perborate $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4$ concentration on chromatic parameters of walnuts shell

C, %	t, min	a	b	L	ΔE	H	C
1	10	4.6	29.8	57.56	21.26	1.42	30.15
	30	3.9	30.6	60.04	21.96	1.44	30.85
	60	2.89	31.12	63.59	22.62	1.48	31.25
	90	2.52	31.4	66.51	23.44	1.49	31.50
	120	1.98	31.9	70.64	25.15	1.51	31.96
5	10	2.63	30.2	65.48	22.49	1.48	30.31
	30	2.1	31.5	61.41	23.19	1.50	31.57
	60	1.84	32.2	71.26	28.78	1.51	32.25
	90	1.4	33.08	73.34	29.22	1.53	33.11
	120	1.2	33.2	73.56	31.10	1.53	33.22

Analyzing the presented data Sodium perborate dimierized $[\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4]$ was found to be the most effective bleaching agent. Its bleaching action is due to its property to decompose rapidly in aqueous solution generating hydrogen peroxide according to the reaction:



The advantage of using sodium perborate is that it is not necessary to add sodium hydroxide, for alkalization of the environment because the sodium borate from the

reaction has an alkaline reaction with a pH value of about 10.5. In addition, at high temperatures sodium perborate is more active than hydrogen peroxide. These two features make the perborate to be considered a reliable and effective whitening agent [16]. Sodium perborate releases oxygen rapidly at temperatures over 60 °C. To make it active at lower temperatures (40–60°C), it has to be mixed with a suitable activator, typically tetraacetythylenediamine (TAED) [17].

The obtained results show that the walnuts shell brightness (*L*) increases with increasing perborate concentration, yellow hue decreases (increases the value of component *b*). The maximum value of brightness is reached after 60–80 minutes of immersing in bleaching agent. The results have shown that bleaching speed increases significantly with increasing ambient temperature from 20 to 60 °C.

The mechanism of bleaching with sodium perborate is similar to the mechanism of bleaching with hydrogen peroxide. As it was mentioned hydroperoxide anion (HOO^\ominus) attacks practically all organic structures, including those that contain hydroxyl and etheral bonds [18]. Similar reactions occur and treated with sodium perborate, but its alkalinity is higher than that of hydrogen peroxide; in this respect, sodium perborate has the most significant effect on the process of delignification at the same concentration of active oxygen [19].

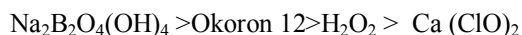
Total color difference E. The total color difference (*E*) values at different concentration of bleaching agents are shown in tables 1-4. It is clear that *E* values were affected by the concentration for all tested agents. For all bleaching agents, *E* increased with the increased concentration. For example, when using H_2O_2 , the *E* increased from 23,81 to 25.75 when the *C* (%) increased from 3 to 10%. A similar trend was also observed for the rest of used agents. The results indicate that the walnuts shell tends to get lighter as the concentration increased due to increased amount of active components.

Conclusion

Colour is one of the most important quality attributes influencing consumer food choices, perceptions and purchase behaviour. Colour measurement and analysis is therefore important in postharvest handling and biopro-cessing to optimize the quality and value of food. There were quantified chromatic characteristics of walnuts in shells by CIELAB system and conducted experimental studies on their bleaching with oxidizing agents (hydrogen peroxide, Okoron 12 calcium hypochlorite and sodium perborate).

By analyzing the color parameters values *L*, *a* and *b* there have been studied the effects of independent parameters of bleaching and their interactive effects on the color profile and on walnut shell bleaching process.

It has been found that oxidative bleaching agents are more effective, and that whitening depends on the concentration of agents, the temperature and pH of the medium and walnuts lasting retention in bleaching environment. After blanching nuts shell, bleaching agents studied form the following series:



Considering the activity of bleaching agents and their toxic emissions, walnuts can be bleached with $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4$ (concentration 5%, pH-10, temperature – 60 °C, retention time – 40–50 min).

References

1. Labuckas D.O., Maestri D.M., Perello M., Martinez M.L., Lamarque A.L., (2008), Phenolics from walnut (*Juglans regia* L.) kernels: antioxidant activity and interactions with proteins, *Food Chemistry*, 107, pp. 607–612.
2. Ramos D.E. (1998), *Walnut Production Manual*, University of California, Division of Agriculture and Natural Resources, Oakland, California, Publication 3373.
3. Foreign Agricultural Service (2017), *Tree Nuts: World Markets and Trade*.
4. Wei Q., Ma X.H., Zhao Z., Zhang S.S., Liu S.C. (2010b), Antioxidant activities and chemical profiles of pyrolygneous acids from walnut shell, *J. Anal. Appl. Pyrol.*, 88(2), pp. 149–154, DOI:10.1016/j.jaap.2010.03.008
5. Yarborough D.K., (1991), The safety and efficacy of tooth bleaching: a review of the literature 1988–1990, *Compendium of Continuing Education in Dentistry*, 12(3), pp. 191–196.
6. Dahl J.E., Pallesen U. (2003), Tooth bleaching—a critical review of the biological aspects, *Critical Reviews in Oral Biology and Medicine*, 14(4), pp. 292–304.
7. Robert I., Lazau R. (2014), *Dyes and pigments*, 105, p. 152.
8. Pop M., Lupea A.X., Popa S., Gruescu C., (2010), *Int. J. of Food Prop.*, 13(4), p. 771.
9. Driscoll R.H., Madamba, P.S. (1994), Modeling the browning kinetics of garlic, *Food Australia*, 46, pp. 66–71.
10. Moss J.R., Otten L. (1989), A relationship between color development and moisture content during roasting of peanut, *Canadian Institute of Food Science and Technology Journal*, 22, pp. 34–39.
11. Salvador A., Sanz T., Fiszman S.M., (2007), Changes in color and texture and their relationship with eating quality during storage of two different dessert bananas, *Postharvest Biology and Technology*, 43, pp. 319–325.
12. Bernalte M.J., Sabio E., Hernandez M.T., Gervasini C. (2003), Influence of storage delay on quality of “Van” sweet cherry, *Postharvest Biology and Technology*, 28, pp. 303–312.
13. Suess H.U. (2010), *Pulp Bleaching Today*, Walter de Gruyter, Berlin.
14. Milovidova L.A., Komarova G.V., Koroleva T.A., (2005), *Otbelka tselliulozy*, AGTU, Arkhangelsk.
15. Proulx Lyne (1998), *Effet de l'acide peracétique sur la pâte thermomécanique*, Mémoire, Trois-Rivières, Université du Québec à Trois-Rivières, p. 109.
16. Lopez F., Diaz M.J., Eugenio M.E., Ariza J., Jimenez L. (2002), Hydrogen peroxide and sodium perborate bleaching of pulp from olive tree residues, *Eng. Life. Sci.*, Wiley-Vch, Weinheim, pp. 201–208.
17. Bayça S.U., Köseoğlu K., Batar T. (2004), Mineral and compound of Boron essential use in industrial area, *J. Vocational School and Technical Science of Soma*, 2, pp. 1–21.
18. Onur Tolga Okan, İlhan Deniz, İbrahim Yildirim (2013), Bleaching of Bamboo Kraft-AQ Pulp with Sodium Perborate Tetrahydrate (SPBTH) after Oxygen Delignification, *Bio Resources*, 8(1), pp. 1332–1344.
19. Pesman E., Kalyoncu E.E., Kirci H. (2010), Sodium perborate usage instead of hydrogen peroxide for the reinforcement of oxygen delignification, *Fib. and Tex. in Eastern Europe*, 18, 6(83), pp. 106–109.

Component composition of radish root essential oil

Galina Selyutina, Oksana Gapontseva

Kharkiv State University of Food Technology and Trade, Kharkiv, Ukraine

Abstract

Keywords:

Radish
Essential oils
Volatile substances
Odour

Article history:

Received 09.10.2016
Received in revised form
11.10.2016
Accepted 27.12.2016

Corresponding author:

Galina Selyutina
E-mail:
sinps@meta.ua

Introduction. Radish roots contain in their composition essential oils, which are in the form of glucosides and cause its specific odor and taste. The content of volatile substances is an important indicator for determining of root consumer characteristics.

Materials and methods. Radish roots of varieties Black radish, White radish, Marushka, Lebidka, Troyandova, Sertse drakona, Margelan radish and daikon were investigated. The identification and quantitative composition of the radish essential oils were determined by chromatography-mass spectrometry method.

Results and discussion. Complex volatile compositions isolated from radish roots of various economic and botanical varieties are, mainly, represented by the following compounds: hydrocarbons, sulfur-containing substances, organic acids, aldehydes, esters, ketones, terpenes, alcohols and arenas, total mass fraction of which is in the range of 23,69 mg/kg (Lebidka) to 1605,94 mg/kg (White radish). From 26 to 40 chemicals compounds are found, most of which are specific to each analyzing variety, but 14 substances are common to all the varieties of radish: nonanal, pentadecanal, dioktylfталат, dyizobutyлталат squalene, linoleic acid, linolenic acid, oleic acid, stearic acid, trycosane, tetracosane, pentacosane, hexacosane and heptacosane.

Diverse component composition of radish volatile substances determines specificity and intensity of its flavor, has a significant impact on taste properties and makes antibacterial activity against gram-positive and gram-negative microorganisms.

Conclusions. The complex research of qualitative and quantitative composition of radish root volatile substances in varietal perspective was conducted for the first time.

DOI: 10.24263/2304-974X-2016-5-4-5

Introduction

Radish (*Raphanus*) belongs to the family cruciferous (cabbage) of one- or two-year plants, this family has from 6 to 8 species and has geographical varieties, which are European (radish) is grown in many countries of the Northern Hemisphere and Asian (Chinese – lobo, Japanese – daikon) is distributed mainly in Asia.

It is known from the literature [1, 2] that the radish contains a number of essential oils, which are in the form of glucosides and determine its specific smell and taste. Their content in different varieties ranges from 8,4 to 50 mg per 100 g of raw material, black radish contains them from 8,4 to 21,4 mg per 100 g. So, F.V. Tserevytnov's researchers show that the essential oil of radish (sulforafen) consists of liquid and crystalline parts. The crystalline part contains lactone rafanolid ($C_{29}H_{55}O_4$) with melting temperature of 62 °C. In addition, the volatile oils of the radish contain allyl mustard oil, methylmercaptan (which causes smell), glycoside synalbin [3]. The crystalline part consists mainly of lactoneurafapolid which precipitates in the form of crystals.

The radish is used as a remedy that increases the formation and secretion of bile from the gallbladder to the intestine due to the content in its roots of rafanous and sulfurous oils, and it is extremely important in the treatment of cholecystitis and for cholelithiasis prevention [4].

The substance trans-4-methylthio-3-butenyl-isothiocyanate causes spicy taste and has antimicrobial activity against a number of fungi and bacteria in the range of 50 to 400 mg/ml, while the yeast is more resistant and is not affected by this substance. Sis-isomeryd in ratio of Trans-cis 4 : 1 is also contained [5].

The content of essential oils defines the consumable characteristics of vegetable raw material as they participate in the formation of flavor, thereby provide consumers with an idea about food quality and whet appetite.

It should be noted that the complex studies of component and quantitative compositions of volatile substances in terms of varietal perspective were not conducted. These studies are of great practical importance, since volatile components are widely used in medicine as antiseptic preparations and remedies for aromatherapy, aromatic substances are used in food, perfume, cosmetics production.

With taking into account the specific organoleptic properties of radish, the aim of our study is research the complex of different varieties of radish volatiles, it allows providing comprehensive description of the root, which later will become the basis for the distribution of varieties according to tendencies of use (for industrial processing or for health care purposes).

Materials and methods

Study of quantitative and qualitative composition of volatile fraction of radish root is carried out with use Agilent Technologies 6890 chromatograph with mass spectrometric detector is 5973, column is capillary DB-5 with length of 30 meters and inner diameter of 0.25 mm, according to the method of L.B. Chernohorod and B.A. Vynohradova. [6,7] The sample (5 g of radish root) is put in vial of 20 ml and internal standard is added. Tridecane is used as internal standard, at 50 mg per sample, with following calculation of the resulting concentration of internal standard, which is then used for calculation of the substance

amount. 10 ml of distilled water is added to the sample and volatiles of the sample are distilled off with steam for 2 hours with use of the air-cooled inverse refrigerator. During the distillation volatiles are adsorbed on the inner surface of inverse refrigerator. Adsorbed substances after cooling of the system are washed off with slow addition of 3 ml of pure pentane in dry vial of 10 ml. Washout is concentrated by blowing (100 ml/min) of pure nitrogen to extract residual volume of 10 ml, which is fully selected by chromatographic syringe. Further concentration of the sample is carried in the syringe to the volume of 2 ml.

Putting the sample in chromatographic column is carried out in splitless mode (without flow division) that allows putting the sample without losing for division and significantly (in 10–20 times) increasing sensitivity of the chromatography method. The speed of the sample putting is 1,2 ml/min during 0,2 minutes. The speed of gas carrier (helium) is 1,2 ml/min. The temperature of the sample putting heater is 250 °C. Thermostat temperature is programmed from 50 to 320 degrees at speed of 4 °/min.

The library of mass spectra NIST05 and WILEY 2007 with total number of spectra more than 470000, combined with programs for identifying AMDIS and NIST is used for identifying the components.

The method of internal standard is used for quantitative calculations. Calculation of components content (mg/kg) is carried out by the formula:

$$C=K_1 \cdot K_2 \quad (1)$$

where: $K_1 = P_1/P_2$ (P_1 – peak area of the analyzing substance, P_2 – standard peak area); $K_2 = 50/M$ (50 – weight of internal standard (mg) which is added to the sample, M – mass of the sample (g) [8].

Results and discussion

The identification of compounds was carried out by comparing the mass spectra of the chromatographic peak with the mass spectra of reference compounds; with high probability they were identified by the identified program on the array of spectra database (Figures 1 – 8).

Comparison component composition of volatile substances of different varieties of radish showed (Table 1) that their composition in the sample Black radish were represented with 35 components (2 of them were not identified), White radish – 31 (1 was not identified), Marushka – 27, Lebidka – 38 (2 were not identified), Troyandova – 40 (1 was not identified), Sertse drakona – 36 (1 was not identified), Margelan radish – 26 (1 was not identified), daikon – 39 (2 were not identified). Complex volatile compositions isolated from radish are represented with chemical compounds of such groups: carbonyl (aldehydes, ketones), alcohols, organic acids, esters, terpenes, hydrocarbons, sulfur and aromatic compounds.

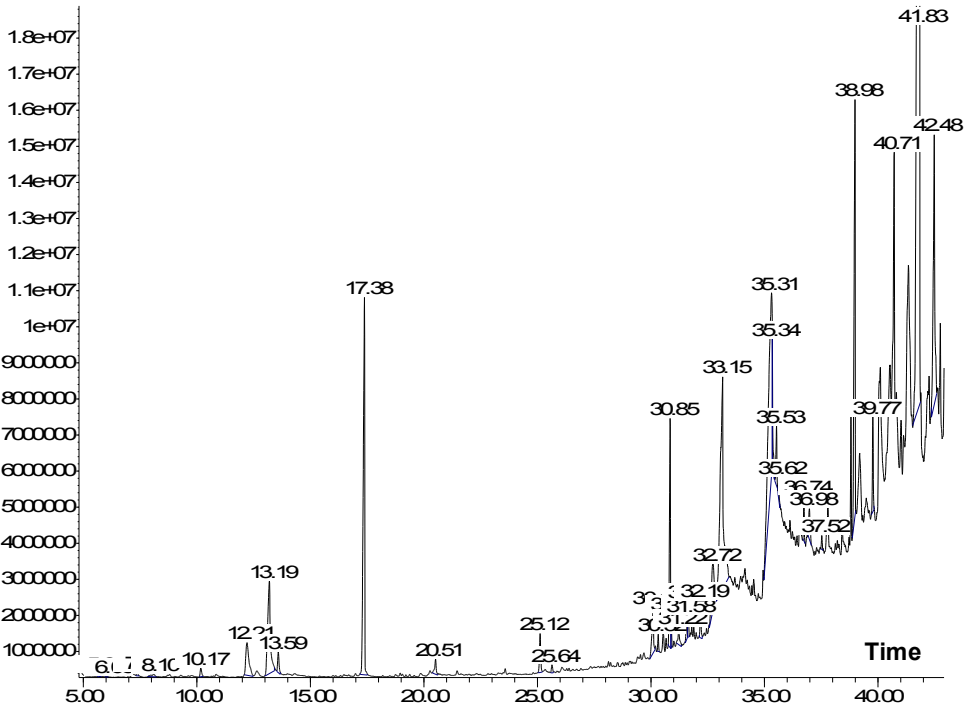


Figure 1. The composition of volatile components of radish Black

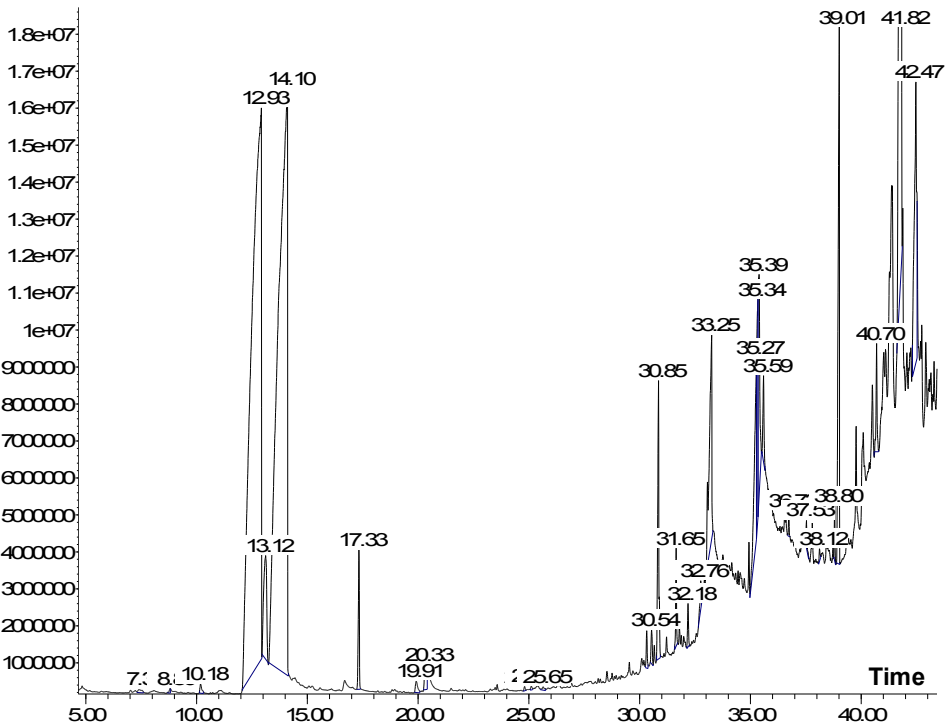


Figure 2. The composition of volatile components of radish

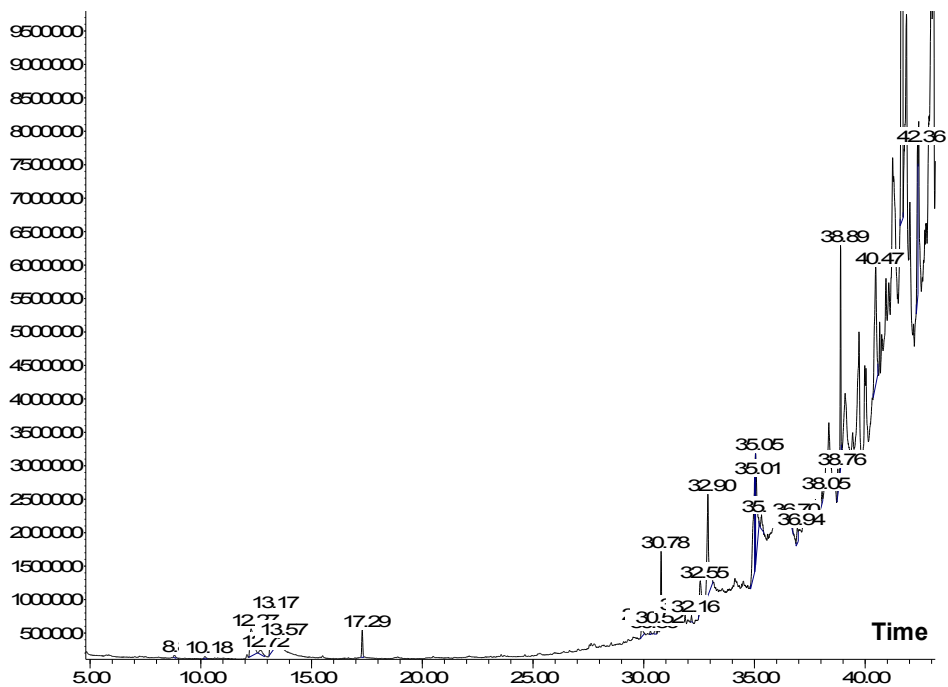


Figure 3. The composition of volatile components of radish Marushka

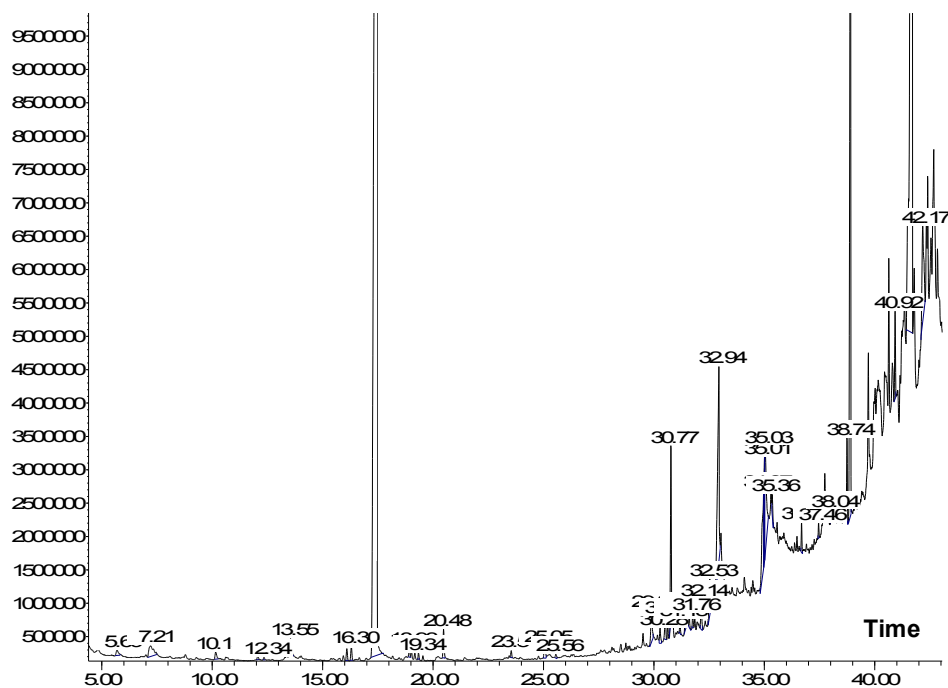
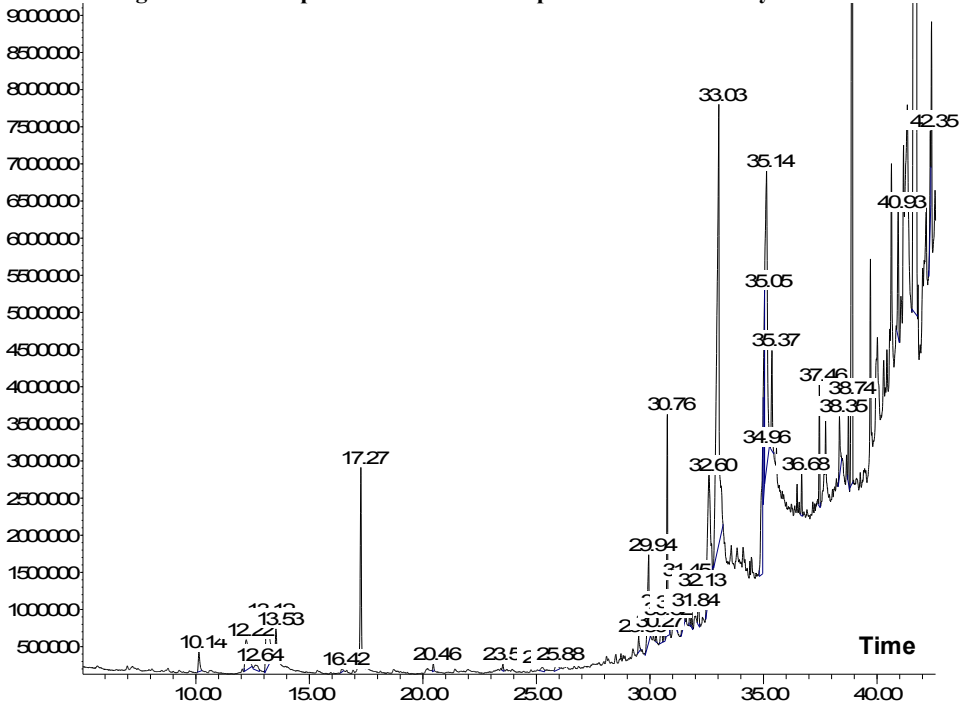
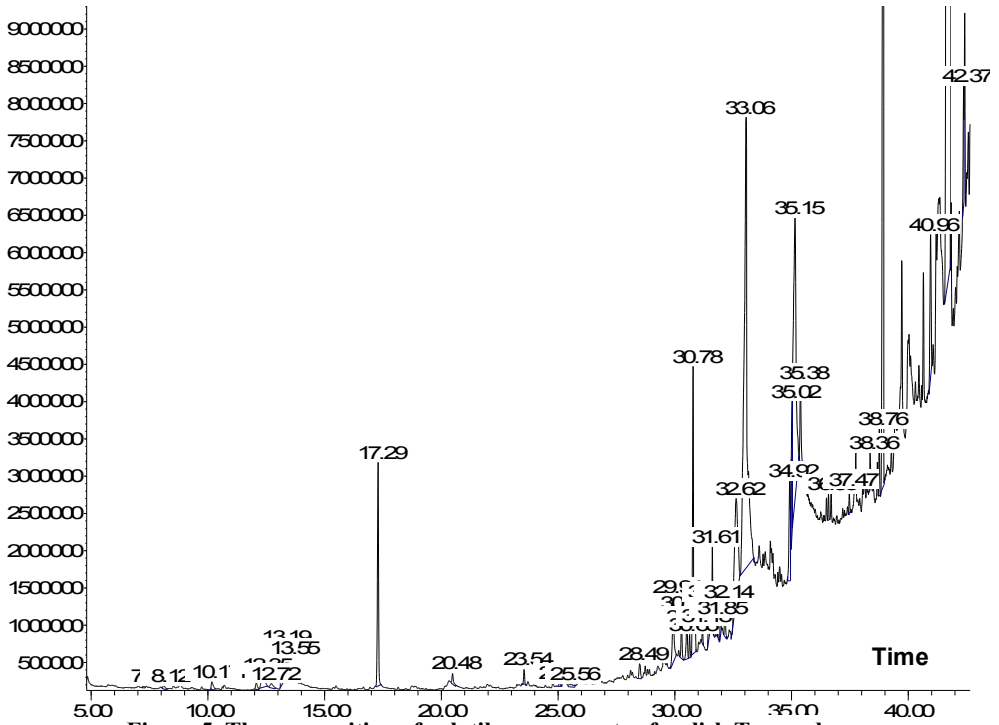


Figure 4. The composition of volatile components of radish Lebidka



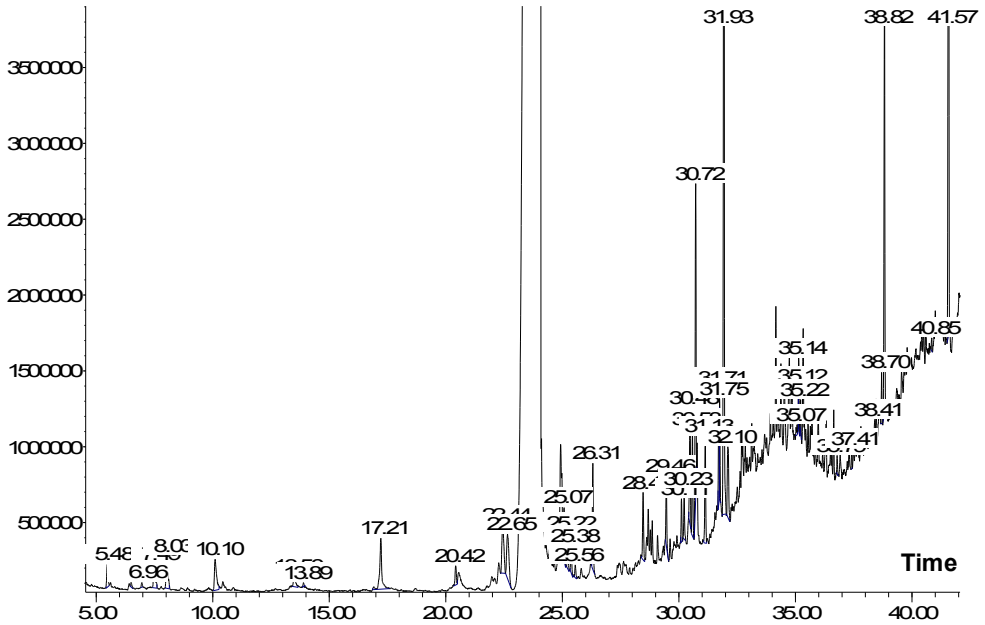


Figure 7. The composition of volatile components of radish Margelan

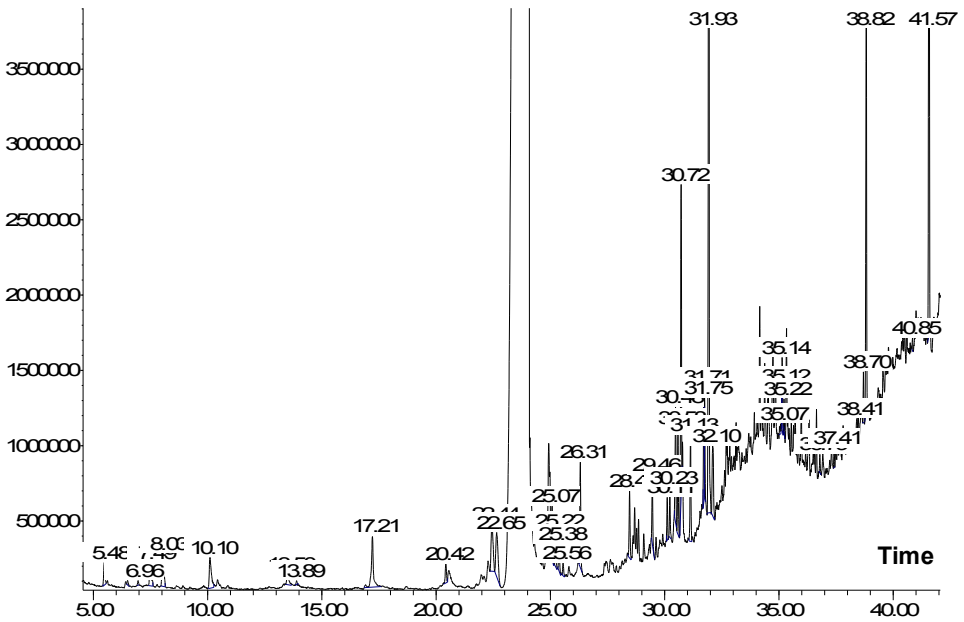


Figure 8. The composition of volatile components of radish Daikon

Table 1

Comparison component composition of volatile fraction of various varieties radish roots

Component	Number of economically botanical varieties mg / kg							
	Black radish	White radish	Marushka	Lebidka	Troyandova	Sertse drakona	Margelan radish	Daikon
1	2	3	4	5	6	7	8	9
Aldehydes								
Dekanal	0,95		4,20	0,11	1,56	2,66	1,16	0,41
Nonanal	0,42	1,61	2,27	0,05	0,86	1,89	0,74	7,26
Pentadekanal	0,46	3,44	1,91	0,07	2,44	0,56	1,19	4,22
Dodekanal	-	-	-	0,06	-	-	-	-
Tetradekanal	-	-	-	-	1,24	-	-	7,18
Hexadec-7,11-dienal	-	-	-	-	-	0,88	0,81	-
Ethers								
Diisobutylphthalate (3)	7,75	31,35	32,50	0,61	16,99	13,77	22,54	30,45
Dibutylphthalate (3)	-	3,97	2,49	0,14	-	2,38	0,83	10,61
Diethylphthalate (3)	15,45	64,97	43,20	3,46	66,91	74,72	34,97	38,08
Methylpalmitate	-	-	-	-	-	-	-	90,74
Methylmyristate	-	-	-	-	-	-	-	-
Sulfur-containing compounds								
1-Cyano-4, epityopentan	3,33	519,82	53,41	0,02	2,29	7,44	-	2,54
1- Cyano -4,5- epityopentan (isomer)	8,25	508,19	84,15	0,01	8,16	11,99	-	-
5-(methylthyo) Pentanenitrile	-	29,90	8,10	-	0,78	1,30	-	-
4- Methylthyo-3- butenylisothiocyanate	-	2,51	-	-	-	-	-	-

Table 1 (Continuation)

Component	Number of economically botanical varieties mg / kg							
	Black radish	White radish	Marushka	Lebidka	Troyandova	Sertse drakona	Margelan radish	Daikon
1	2	3	4	5	6	7	8	9
Alcohols aliphatic								
Docosanol	-	-	-	0,03	0,81	0,48	-	-
Alcohols cyclic								
Ledol	0,32	0,76		0,02	0,70	1,19	-	-
Terpenes and their derivatives								
α -Pinene	0,17	-	-	0,49	-	-	-	4,02
Limonene	0,32	0,57	2,38	-	0,51	-	-	5,71
Nerolidol	1,60	0,48	-	0,07	0,34	0,73	-	3,11
β -Myrcen	0,05	-	-	-	-	-	-	0,60
δ -Karen	0,17	1,15	-	0,20	0,18	-	-	4,31
Squalene	80,75	182,53	409,90	13,04	328,21	332,84	381,19	70,11
Organic acids								
Myristic	2,36	-	11,04	0,19	5,83	8,91	8,53	7,36
Pentadecanoic	-	-	-	0,09	2,31	4,29	-	-
Lauric	-	-	-	0,02	-	-	-	-
Palmitoleic	4,12	5,44	27,28	0,29	19,23	22,89	8,39	-
Palmitic	22,19	50,01	104,59	1,35	78,11	69,28	36,39	-
Linoleic	22,76	36,45	86,91	0,55	7,39	11,36	3,71	1,04
Linolenic	1,86	26,85	43,89	0,28	4,65	13,14	1,06	0,83
Oleic	1,83	34,79	76,23	0,71	45,50	44,89	9,81	4,86
Stearin	0,54	8,88	10,76	0,07	4,90	6,88	1,19	1,82
11-Cyclopentylundecanoic	0,89	-	-	-	-	-	-	-

Table 1 (Continuation)

Component	Number of economically botanical varieties mg / kg							
	Black radish	White radish	Marushka	Lebidka	Troyandova	Sertse drakona	Margelan radish	Daikon
1	2	3	4	5	6	7	8	9
Hydrocarbons (saturated and unsaturated)								
Tricosane	1,09	1,62	4,52	0,09	1,01	1,95	1,16	1,31
Tetracosane	0,39	2,70	5,47	0,04	0,95	5,80	2,85	1,52
Pentacosane	1,45	1,08	3,66	0,03	1,90	4,27	0,87	0,84
Hexacosane	2,55	3,64	4,78	0,24	2,58	3,65	4,46	3,66
Heptadecane	-	-	-	-	-	-	-	3,75
Heptacosane	9,47	10,36	62,90	0,29	9,35	8,36	5,56	0,93
Nonacosane	13,62	60,65	36,03	0,73	5,58	4,33	8,00	
Tetradecane	0,77			0,13	0,89	0,52	-	2,79
3-Methylpentadecane	-	-	-	-	-	-	-	10,46
2,6-Dimethylpentadecane	-	-	-	-	-	-	-	11,08
4-Methyl-hexadecane	-	-	-	-	-	-	-	5,38
6-Methyloctadecane	-	0,50	-	-	-	-	-	-
Nonadeca-1,4,6,9-tetraen	-	3,87	5,69	0,11	2,57	2,82	-	-
Ketones								
Hexadecane -2-oh	0,94	7,85	2,76	0,05	3,72	-	-	9,51
Aromatic compounds								
1-(Propilnonyl) Benzol	-	-	-	-	-	-	-	3,60
1-(Methyl-dodecyl) Benzol	1,19	-	-	0,05	0,74	0,91	0,70	6,49
1-(Butyl-nonyl) Benzol	-	-	-	-	1,08	1,27	0,59	9,30
Amylbenzol	-	-	-	-	0,69	-	2,84	
1-(Hexylheptyl) Benzol	-	-	-	-	-	-	-	11,82
Mass fraction of volatile components, mg/kg	208,01	1605,94	1131,00	23,69	630,96	668,87	539,54	389,17

It is reasonable to consider in detail the classes of chemical compounds which are identified in various varieties of radish for understanding the impact of each substance on the formation of biological value and taste, aromatic properties.

Radish aroma forming components include aldehydes [9]: dekanal has strong aldehyde smell and during the dilution its smell has citrus, floral notes (all experimental varieties of radish contain dekanal, except variety White radish); nonal has strong, fatty, muscat smell (all varieties of radish); pentadekanal has strong aldehyde smell (all varieties of radish); dodekanal has strong smell with floral and grass notes (only variety Lebidka); tetradekanal has soft, fatty smell with notes of toffee (varieties Troyandova and daikon); hexadek-7,11-dienal has soft, floral-aldehyde smell with grass notes (varieties Sertse drakona and Margelan radish).

Ethers of complex aromatic acids in the investigated samples of radish are presented by the following substances: diisobutylphthalate in an amount of 0,61 (Lebidka) to 31,35 mg/kg (White radish) and dioctylphthalate from 3,46 (Lebidka) to 74,72 mg/kg (Sertse drakona); the concentration of dibutylphthalate is from 0,14 mg/kg (Lebidka) to 10,61 (daikon), varieties Black radish and Troyandova don't contain this component. In addition the variety of radish Sertse drakona contains ether methylmyristate in amount of 0,5 mg/kg, daikon contains methylpalmitate (90,74 mg/kg). Identified ethers are characterized by relatively pleasant expressionless fruity smell, it to a certain extent promotes the balancing of radish flavor [10].

Volatile fractions of radish in the composition have large numbers of sulfur-containing compounds, namely, 1-cyano-4,5-epitiopentan, 1-cyano-4,5-epityopentan (isomer), 5-(methylthio) pentanenitrile, 4-methylthio-3-butenylisothiocyanate, which have strong, unpleasant smell. It is known that essential oils with sulfur should be used with great caution and under strong dilution. However, the concentration of these substances in roots is non-toxic. The radish of variety White radish has the highest total number of sulfur-containing compounds – 1060,42 mg/kg, and the radish of variety Lebidka has the smallest number of sulfur-containing compounds – 0,03 mg/kg, the radish of variety Margelan radish hasn't sulfur-containing compounds in its composition.

Aliphatic and cyclic alcohols are present in radish roots in the small amount but they have high antiviral and antimicrobial properties [11]. Docosanol is identified in varieties Lebidka, Troyandova, Sertse drakona and ledol is identified in varieties Black radish, White radish, Lebidka, Troyandova and Sertse drakona.

Terpenes are the main components of radish essential oils; they provide spicy taste and specific flavor. In addition, the presence of terpenes allows naturally without the use of chemicals to keep pests from radish. The composition of radish varieties Black radish and daikon includes all identified terpenes (α -pinene, limonene, nerolidol, β -Myrcen, δ -Karen, squalene), the total mass of them is 83,06 and 87,86 mg/kg respectively. The varieties of radish White radish and Troyandova contain four representatives of the class of terpenes (limonene, nerolidol, δ -Karen and squalene), and the sample of variety Lebidka contains α -pinene, nerolidol, δ -Karen, squalene. Limonene and squalene are contained in the radish of variety Marushka and the radish of variety Sertse drakona contains nerolidol and squalene. The radish of variety Margelan radish only contains squalene.

Radish terpenes have substantial differences in chemical properties. So, α -pinene is bicyclic terpene, which is a colorless, volatile liquid with characteristic «pine» smell; limonene is monocyclic terpene, has citrus flavour; nerolidol is colorless oily liquid with faint floral flavour; β -Myrcen is oily liquid with pleasant spicy flavor; δ -Karen is colorless liquid with pleasant sweet smell

The presence in radish roots of squalene (acyclic polyunsaturated liquid hydrocarbon, colorless and odorless, soluble in many organic solvents) is extremely interesting, because it is believed that the main its source is the only shark liver (35%) and olive and rice oils (to 0,8%) [12].

It is ascertained that the concentration of squalene in different varieties of radish has significant divergence from 13,04 mg/kg (Lebidka) to 409,9 mg/kg (Marushka). Its chemical formula is quite unstable because of the lack of hydrogen, which is filled with reaction with water, during this reaction the oxygen releases and this terpene saturates body tissues, and it helps to eliminate free radicals. It provides squalene with certain antioxidant properties. In addition, it is an intermediate substance in the biological synthesis of steroids, including cholesterol (by the use of lanosterol), and it is involved in metabolism [13].

Fatty acids, including essential – linoleic and linolenic were found during the study volatile components of radish also were found. All varieties contain in their composition linoleic acid (0,55...86,91 mg/kg), linolenic acid (0,28...43,89 mg/kg), oleic acid (0,71...76,23 mg/kg), stearic acid (0,54...10,76 mg/kg). Myristic fatty acids are contained in the range of 0,19...11,04 mg/kg in all samples of radish except White radish. Palmitic and palmitoleic acids are contained in all varieties of radish (1,35...104,59 mg/kg and 0,29...27,28 mg/kg, respectively), but daikon doesn't contain these acids. It should be noted that the presence of palmitoleic acid, which has high antimicrobial action, in vegetable products with low fat content is rarity, because basically its sources are the fat of marine animals (15...20%), chicken egg yolk (5%) macadamia oils (6...12%), avocados (5...10%), olive oil (9%) [14].

Varieties of radish Lebidka, Troyandova and Sertse drakona also contain such organic acid as pentadecanoic acid in an amount of 0,09...4,29 mg/kg. In addition, the variety of radish Black radish contains 11-cyclopentylundecanoic acid (0,89 mg/kg) and lauric acid is contained in radish Lebidka (0,02 mg/kg). Notably, that radish Marushka has record high concentrations of organic acids, while variety of radish Lebidka is characterized by low content of these substances.

Saturated hydrocarbons (tricosane, tetracosane, pentacosane, hexacosane, heptadecane, nonadecane, heptacosane nonacosane, tetradecane) and unsaturated hydrocarbons (3-methylpentadecane, 2,6-dimethylpentadecane, 4-methyl-hexadecane, 6-methyloctadecane, nonadeca-1,4,6,9-tetraen) are identified in radish roots, they are characterized by more or less intense smell of petrochemical products. Tricosane in amount of 0,09...1,95 mg/kg, tetracosane – 0,04...5,8 mg/kg, pentacosane – 0,03...4,27 mg/kg, hexacosane – 0,93...62,80 mg/kg are common for all varieties of radish. 3-methylpentadecane, 2,6-dimethylpentadecane, 4-methyl-hexadecane, heptadecane, nonadecane are specific and identified only in daikon, mass fraction of this substances is dominated in daikon. Unsaturated hydrocarbon 6-methyloctadecane is identified only in the sample of radish Marushka (0,5 mg/kg). It should be noted that this variety contains the largest amount of hydrocarbons (123,05 mg/kg) and the sample Lebidka contains the smallest amount of hydrocarbons (1,66mh / kg).

The representative of the ketones class – hexadecane -2-oh also is identified, the mass fraction of which is from 0,05 mg/kg (Lebidka) to 9,51 mg/kg (daikon). In addition, arenas (aromatic compounds) are similar in chemical structure to the hydrocarbons are identified as the study result; they have sweet smell and are not inclined to joining or oxidation reactions that leads to disruption of aromaticity [303]. So, samples of Black radish and Marushka contain only one representative of this group of chemicals – 1-(methyl-dodecyl) benzol; sample of Sertse drakona contains two arenas (1-(methyl-dodecyl) benzol and 1-(butyl-nonyl) benzol), varieties Lebidka and Margelan radish contain amylbenzol, 1-

(methyldecyl) benzol and 1-(butylonyl) benzol; daikon contain the largest amount of arenas (31,21 mg/kg): 1-(propilonyl) benzol, 1-(butylonyl) benzol, 1-(Hexylheptyl) Benzol and 1-(methyldecyl) benzol.

Conclusions

Thus, complex volatile composition are isolated from various economic and botanical varieties of radish roots are presented by such chemicals as hydrocarbons, sulfur-containing substances, organic acids, aldehydes, ethers, ketones, terpenes, alcohols and arenas, total mass fraction of which is in the range of 23,69 mg/kg (Lebidka) to 1605,94 mg/kg (White radish). From 26 to 40 compounds are identified, most of which are specific for each sample of variety, but 14 compounds are common to all varieties of radish. They are nonanal, pentadecanal, dioctylphthalate, diisobutylphthalate, squalene, linoleic acid, linolenic acid, oleic acid, stearic acid, tricosane, tetracosane, pentacosane, hexacosane and heptacosane. It is established that the various component composition of radish volatile substances determines specificity and intensity of flavor, has significant impact on taste properties and makes antibacterial activity against gram-positive and gram-negative microorganisms. The results are major quality criteria for the distribution of varieties of radish according to tendencies of use. Varieties of roots White radish and Marushka have high total content of volatiles that causes intense specific smell, spicy taste and strong bactericidal effect, and varieties (Lebidka, Black radish, daikon, Margelan radish, Troyandova, Sertse drakona) with minimum and average number of essential oils have less intensity smell and are suitable for industrial processing.

References

1. Gilani A.H., Ghayur M.N. (2004), Pharmacological basis for the gut stimulatory activity of *Raphanus sativus* leaves, *J. Ethnopharmacol*, 95, pp. 169–172.
2. Terras F.R., Schoofs H.M., DeBolle M.F., Van Leuven F., Rees S.B., Vanderleyden J., Cammue B.P., Broekaert W.F. (1992), Analysis of two novel classes of plant antifungal proteins from Radish (*Raphanus sativus* L.) seeds, *J. Biol. Chem*, 267, pp. 15301–15309.
3. Friis P., Kjaer A. (1966) 4-Methylthio-3-butenyl-isothiocyanate, the pungent principle of radish root, *Acta Chem. Scand*, 20, pp. 698–705.
4. Jones L.J.L., Thorpe J.P., Wallis G.P. (1982), Genetic divergence in four species of the genus *Raphanus*: Implications for the ancestry of the domestic radish *R. sativus*, *J. Linnean Society*, 18(1), pp. 35–48.
5. Suleiman A. and Maryam H.B. (2005), Volatile Constituents of *Raphanus sativus* L. var. *niger* Seeds, *J. Essential Oil Res.*, 17(4), pp. 440–441.
6. Iliana Kostova, Dimitar Dimitrov, Mihaela Ivanova, Radka Vlaseva, Stanka Damyanova, Nastya Ivanova, Albena Stoyanova, Oleksii Gubenia (2014), Studying the possibilities of using of essential oils in dairy products. 2. Dill (*Anethum Graveolens*), *Ukrainian Food Journal*, 3(4), pp. 516-523.
7. Teodora Atanasova, Miroslava Kakalova, Lyubomir Stefanof, Maya Petkova, Albena Stoyanova, Stanka Damyanova, Mykola Desyk (2016), Chemical composition of

- essential oil from *Rosa Damascena* mill., growing in new region of Bulgaria, *Ukrainian Food Journal*, 5(3), pp. 492–498.
8. Chernogorod L.B., Vinogradov B.A. (2006), Essential oils of some species of the genus *Achillea* L., containing fragranol, *Plant Resources*, 42(2), pp. 61–68.
 9. Kohlpaintner C., Schulte M., Falbe J., Lappe P., Weber J., Frey G. D. (2013), Aldehydes, Araliphatic, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, DOI:10.1002/14356007.m01_m03.pub2.
 10. Jonathan Clayden (2008), *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations*, Georg Thieme Verlag.
 11. Kulkarni L and Sohonie K. (1956), Non protein nitrogen in vegetables, *Indian J. Med. Res.*, 44, pp. 511–518.
 12. Eberhard Breitmaier. *Terpens*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
 13. Sandovala M, Okuhamaa N.N., Angelesam F.M., Melchora V.V., Condezob L.A., Laob J., Millera M.J.S. (2002), Antioxidant activity of the cruciferous vegetable Maca (*Lepidium meyenii*), *Food Chemistry*, 79, pp. 207–213.
 14. Eskin M NA and Tamir S. (2005), Functional foods and nutraceuticals, *Dictionary of Nutraceuticals and Functional Foods*, 1, pp. 377–378.

Purification of Raw Sugar Beet Juice by Electrocoagulation

Habibeh Azizi¹, Vahid Hakimzadeh¹, Hossein Alizadeh Golestani²

1 – Department of food science and technology, Quchan Branch, Islamic Azad University, Quchan, Iran

2 – Department of Chemical Engineering, Quchan Branch, Islamic Azad University, Quchan, Iran

Abstract

Keywords:

Sugar Bee
Electrocoagulation
Color
Purity
Turbidity

Article history:

Received
02.09.2016
Received in revised
form 14.11.2016
Accepted
27.12.2016

Corresponding author:

Vahid Hakimzadeh
E-mail:
v.hakimzadeh@
yahoo.com

DOI:

10.24263/2304-
974X-2016-5-4-6

Introduction. This research was carried out to study of electrocoagulation process as a new technique for removal of impurities and non-sucrose compounds from raw sugar beet juice.

Materials and methods. This study was performed in a batch chemical reactor equipped with a 5-liters tank containing 3 aluminium anode and 3 Iron cathode electrodes connected in parallel. Effects of voltage at 5, 10 and 15 volts; processing time at 15, 30 and 45 minute intervals; and pH value at 6, 7 & 8 levels on the purity, turbidity and colour of the sugar beet juice were investigated by the Box-Behnken response surface methodology statistical design on Minitab 17 statistical software.

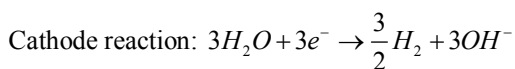
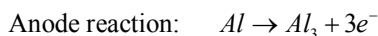
Results and Discussion. The results indicated that during the EC process, turbidity was reduced as the voltage increased. As the voltage rises, the solubility of the anodal electrodes also increases resulting in removal of a larger quantity of pollutants. Therefore, reduction in turbidity following the rise in voltage can be attributed to the increase in flake production, while changes in pH value had no significant effect on turbidity. Although the increase in voltage did not significantly effect the intensification of the colour, however it can be attributed to the increase in bubbles and the subsequent increase in enzymatic activity during floatation. It seems that the increase in enzymatic activity intensifies the melanin colour with the passage of time due to the openness of the reactor cell during floatation and aeration. Increase in the pH value, however, only slightly intensified the colour. The results indicated that the increase in voltage resulted in increase in the level of purity. The solubility of the anodal electrodes increases as the voltage rises and subsequently a higher quantity of impurities and polutants are removed by aluminium hydroxides produced. Increase in voltage also leads to production of greater quantity of bubbles which increase contact between aluminium hydroxides with the pollutants and impurities and facilitates the floatation of more of the produced sludge and thus removal of a greater quantity of the impurities. Increase in process time also resulted in an increase in the level of purity as an increase in reaction time results in more floating sludge is produced on the fluid surface. Increase in the pH value had no significant effect on the level of purity.

Conclusion. The results generally indicated that electrocoagulation process has positively affected on the turbidity reduction and increase the purity of the raw sugar beet juice during the process of purification though colour intensity was not so significantly influenced.

Introduction

Purification, removal of impurities, i.e. the non-sucrose compounds from sucrose, is one of the critical challenges facing the sugar industry. Raw sugar beet juice contains 50 non-sucrose and impurities such as reducing sugars, organic and non-organic acids, amino acids, proteins, starch, wax, resin, minerals such as potassium, magnesium, calcium, and silicon, colour and floating substances [7]. Obtaining a raw sugar beet juice with the highest degree of purity and least colour is the main objective in the purification stages. Purification by the conventional method (Liming – carbonization) requires a high degree of precision in the addition of lime and carbon dioxide as lack of precise control in the addition of these compounds can result in only partial separation of the impurities from the juice and the fragmentation of the colour compounds adsorbed from calcium carbonate crystals [8]. Traditional purification method also produces a large quantity of pulp due to high consumption of lime resulting in environmental problems. The most important disadvantage of this method is its high energy consumption [16]. Therefore, considering the abovementioned points, use of modern technologies such as the membrane process, electrocoagulation etc. in the sugar industry seems essential.

Electrocoagulation is a process in which suspended particles, emulsion or soluble pollutants are destabilized in an aquatic environment by an electric current. This process is beneficial in a wide range of water and sewage purification systems, and removal of mineral, pollutants and pathogens [5]. This process begins with the oxidation of anodes and the production of Al^{+3} and Fe^{+2} ions and continues with the combination of the metallic ions with hydroxyl ions resultant from water electrolysis in the proximity of the cathode and the production of metallic hydroxides which destabilize the pollutants and creates suspended particles or flakes. These flakes can float on the surface of the fluid aided by the hydrogen bubbles produced in the cathode due to the difference in density or be removed through precipitation [3]. In general, the impurities removal mechanism in the electrocoagulation process includes coagulation, adsorption, precipitation, and floatation which are performed in accordance to the reactions below in the electrodes thus follows:



The Al^{3+} and OH^- ions produced during above reactions are formed into monomers such as $Al(OH)^{2+}$, $Al(OH)_2^{+2}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ and or polymers such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{34}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$ which are eventually changed into $Al(OH)_3$ and become precipitated [9]. Insolubility of iron and aluminium hydroxides in water, availability and the low cost of these metals in comparison to metals with similar characteristics has resulted in their more widespread use in the process of electrocoagulation [10 & 11]. Other advantages of this method also include: use of simple equipment, low initial investment and operation costs, unnecessary of chemical substances, low sludge production, production of larger, more stable and acid resistant flakes, faster filtration, elimination of small colloidal particles, and low repair and maintenance care [4]. The research by Shivayogimath and his collaborator, where they

exploited electrocoagulation in the purification of the sugar industry wastewater, is among many examples of the application of this method. Their results indicated that the electrocoagulation process incorporating iron electrodes can be used as an affordable substitute for the traditional methods of purifying sugar industry wastewater [12]. Xu et al., (2002) also applied electrocoagulation in order to retrieve useful compounds from the wastewater produced by egg processing plants. Their results indicated that the use of this process in the egg processing industry can be very successful and lead to the recovery of fractions such as protein and highly digestible fat. Bazrafshan et al, (2013) used electrocoagulation in order to purify dairy wastewater and found that this is a suitable method for the removal of BOD₅, COD and other pollutants.

With regard to the high potential of EC process in removing impurities, the purification of raw sugar beet juice was investigated in this study through applying aluminium anode and iron cathode electrodes under the influence of parameters such as voltage, pH value, and process time in a batch chemical reactor.

Materials and methods

Material

The raw sugar beet juice was prepared from Chenaran sugar plant. Also, all the chemical material, component and reagent for determination of Turbidity, color and purity was purchased from Merck company.

Methods

EC process

This study was carried out in experimental form on a laboratory scale in a batch pilot. Properties of the raw sugar beet juice are given in Table 1. As shown in Figure 1, the electrocoagulation system consists of a 5 liter tank in which 3 aluminium electrodes as anode and 3 iron electrodes as cathode have been placed alternatively at a distance of 0.015m from each other with a lateral surface area of 0.01875m² for each electrode connected to an electrical power supply in a unipolar form. The tests were performed at three voltage levels (5, 10 and 15 volts), three pH levels (6, 7 and 8) and three time intervals (15, 30, 45 minutes). Firstly, pH of juice was adjusted with 0.1M NaOH, then five liters of raw sugar beet juice was poured into the electrocoagulation cell at each stage and the effects of the abovementioned parameters evaluated. At the end of the process, samples were taken from the mid-cell area and turbidity, colour, and purity of the raw sugar beet juice was tested after the precipitation of coagulums and filtration.

Table 1

Initial Properties of Raw Sugar Beet Juice

Variable	Unit	Value
Turbidity	NTU	166
PH	-	6
Colour	ICUMSA	10520
Pol	%	13.2
Brix	%	14.9
Degree of Purity	%	88.6

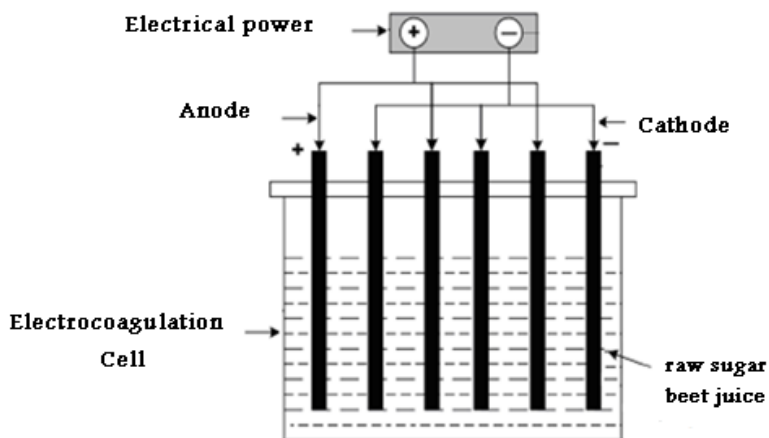


Figure 1. Electrocoagulation pilot schematic

Measuring the colour

The colour was measured following the absorption value reading taken at a wavelength of 420nm by the spectrophotometer model UNICO 2100 and evaluated according to the ICUMSA Standard using equation 1 below [15].

$$Color (ICUMSA) = 10^5 \times \frac{A}{L \times RDS \times \rho} \quad (1)$$

where:

A = Light absorption, L = Cell Length, RDS= Refractometric Dry Solid and ρ = Density

Turbidity

Turbidity of the raw sugar beet juice was directly measured using the turbidimeter (Aqualytic™ AL450T-IR model) according to the NTU unit [14].

Purity

Purity was determined using equation 2 following the evaluation of Pol (percentage of sucrose) by NIR W2 Saccharometer and the percentage of solid matter by NAR-1T Refractometer [13].

$$Q = \frac{pot}{Brix} \times 100 \quad (3)$$

Experimental design

Effects of independent variables: voltage, processing time, and pH value on the purity, turbidity and the colour of the raw sugar beet juice were examined in this study by the Box-Behnken response surface methodology statistical design subject the full quadratic model (equation 3) on Minitab 17 statistical software.

$$f = b_0 + b_1V + b_2V^2 + b_3T + b_4T^2 + b_5P + b_6P^2 + b_7VT + b_8VP + b_9PT \quad (3)$$

where:

V= Voltage, T= Time and P= pH

Run numbers, experimental treatments and replicate runs designed by RSM is summarized in Table 2.

Table 2

Experimental runs, independent variable levels and replicate runs in RSM (box-bhenken)

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Voltage (volt)	5	15	15	15	5	15	5	15	10	10	10	10	10	10	10
Time (min)	15	15	45	45	30	30	30	30	15	45	15	45	30	30	30
pH	7	7	7	7	6	6	8	8	6	6	8	8	7	7	7

Results and discussion

Investigation of the effect of independent variables on raw sugar beet juice turbidity changes

Turbidity is one of the most important factors that occurs in purification of the raw sugar beet juice. Turbidity can result from residual mud on the sugar beet, organic compounds, insoluble cellular compounds, beet plant fragments etc. As shown in Figure.2, the results indicated that during the EC process, turbidity was reduced as the voltage increased. As the voltage rises, the solubility of the anodal electrodes also increases resulting in removal of a larger quantity of pollutants. Therefore, reduction in turbidity following the rise in voltage can be attributed to the increase in flake production. In electrocoagulation process for the removal of seasonal turbidity from drinking water was found that the removal rate of turbidity significantly increased as the voltage increased.

Increase in EC process time also led to an increase in coagulation and a higher rate of impurity removal. Efficacy of impurity removal is directly dependent upon the concentration of the ions produced on the electrodes, and as the concentration of the metal ions and hydroxide coagulums increases along with time increase, their rate of such removal also rises [1].

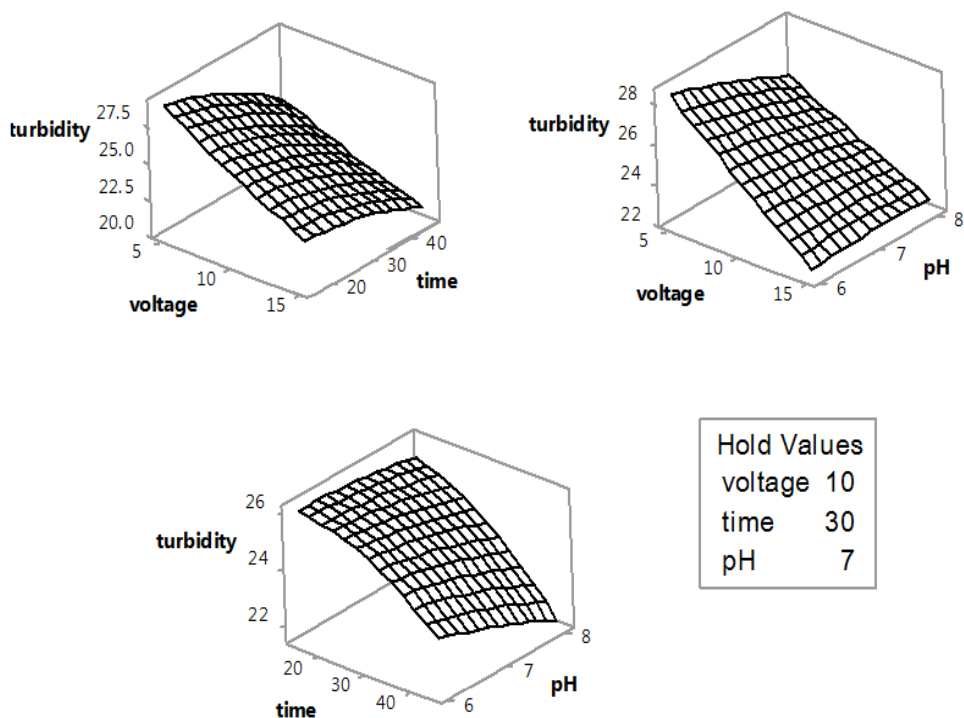


Figure 2. Effects of voltage, time and pH on variability of juice turbidity

Shivayogimath et al., (2012) found during the investigation of purification of the sugar industry sewage by electrocoagulation that the rate of removal of Turbidity increases with time and declared that the maximum amount of turbidity (92.4%) is achieved after four hours. Higher efficiency of the higher rate of turbidity removal can also be attributed to the Faraday law. According to the Faraday law, $m = \frac{MIt}{zF}$ the quantity of metal ions (m) is dependent upon the intensity of the applied current (I) and electrolysis time (t). So, concentration of coagulants increases along with an increase in the above parameters.

However, in this research no significant increase was observed in turbidity changes as the pH value increased. The Al^{+3} and OH^- ions produce various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2^{+}$ and polymeric species such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$ when the pH varies between 4 to 9 in value, which eventually transform into insoluble $Al(OH)_3$ flake through chemical reactions precipitation/polymerization. $Al(OH)_3$ coagulums

contain a larger surface which is suitable for the absorption of soluble organic compounds and trapping colloidal fragments. Therefore, the concentration of the coagulants such as $Al(OH)^{2+}$ and $Al(OH)_3$ are similar in this range of the pH value [6].

Investigation of the effect of independent variables on raw sugar beet juice colour changes

Colour is another one of the important factors in the purification of the juice. Melanins formed as the result of the enzymatic browning reactions are among the most important colour substances formed in the syrup by diffusion. Although these colour compounds are superficially absorbed by the calcium carbonate crystals during the later stages, the results however indicated that during electrocoagulation the colour intensifies as the voltage and time are increased (Figure 3).

Although the increase in voltage did not significantly effect the intensification of the colour, however it can be attributed to the increase in bubbles and the subsequent increase in enzymatic activity during floatation. It seems that the increase in enzymatic activity intensifies the melanin colour with the passage of time due to the openness of the reactor cell during floatation and aeration. Increase in the pH value, however, only slightly intensified the colour. These results correspond with the results of the research carried out on the elimination of colour from coloured wastewater through electrocoagulation [6].

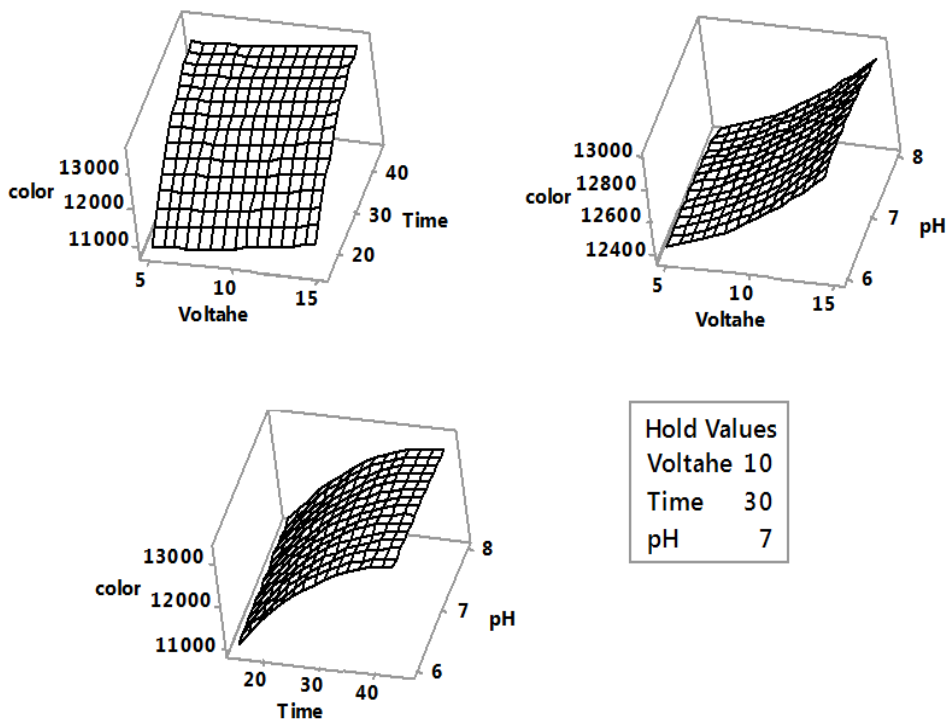


Figure 3. Effects of voltage, time and pH on variability of juice color

Investigation of the effect of independent variables on raw sugar beet juice purity changes

An increase in the purity level of the raw sugar beet juice during purification is indicative of desirable removal of the non-sucrose soluble and insoluble compounds. The results according to Figure 4 indicated that the increase in voltage resulted in increase in the level of purity. As explained previously, the solubility of the anodal electrodes increases as the voltage rises and subsequently a higher quantity of impurities and pollutants are removed by aluminium hydroxides produced. Increase in voltage also leads to production of greater quantity of bubbles which increase contact between aluminium hydroxides with the pollutants and impurities and facilitates the floatation of more of the produced sludge and thus removal of a greater quantity of the impurities. Increase in process time also resulted in an increase in the level of purity as the an increase in reaction time results in more floating sludge is produced on the fluid surface. Increase in the pH value had no significant effect on the level of purity.

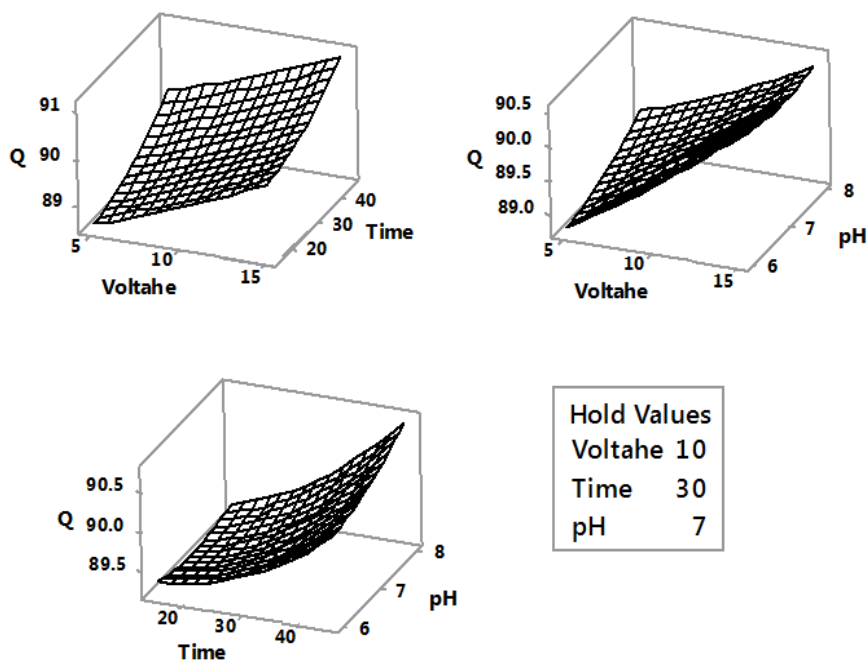


Figure 4. Effects of voltage, time and pH on variability of juice purity
Comparison EC process with traditional refining method

For the judgment of EC process performance to refining the sugar beet juice, the properties of obtained sugar juice by EC process was compared to properties of thin juice from Chenaran sugar plant by traditional method. As seen in the table 3 purity reached to the purity of thin juice approximately. EC process to removal of turbidity was very successful, too. But removal of color by this method not suitable because of flotation and Intensification of enzymatic browning. Although, it can hoped that color would removed by supplementary process as filtration.

Table 3

Compare the properties of refined sugar beet juice by EC process with thin juice (traditional method)

Properties	Raw sugar beet juice	EC process	Traditional process
Turbidity (NTU)	166	20	19
Color (ICUMSA)	10520	11500	1400
Purity (%)	88.6	91	91.5

Table 4

Analysis of operational parameter and coefficient of full quadratic model

Source	DF	Turbidity			Color			Purity		
		Ss	P-value	Coefficient	Ss	P-value	Coefficient	Ss	P-value	Coefficient
Model	9		74.9597	0.009		11091621	0		7.08433	0.018
Constant		24.9		0	12635.5		0	89.600		0.000
Linear										
V	1	-2.408	46.3685	0.001	276	609463	0	0.700	3.92	0.002
T	1	-1.648	21.7140	0.003	1092.2	9543664	0	0.575	2.645	0.004
P	1	-0.506	2.5088	0.130	-16.4	2155	0.461	0.125	0.125	0.317
Quadratic										
V·V	1	0.1	0.0369	0.835	71.4	18817	0.065	0.063	0.01442	0.721
T·T	1	-0.590	1.2853	0.252	-487.8	878715	0	0.213	0.16673	0.255
P·P	1	-0.145	0.0766	0.763	-29.2	3140	0.380	0.113	0.04673	0.527
Interaction										
V·T	1	0.460	0.8464	0.341	-43.9	7709	0.192	-0.025	0.00250	0.881
V·P	1	0.655	1.7161	0.195	1.3	7	0.967	-0.175	0.12250	0.321
T·P	1	-0.315	0.3969	0.504	-38.3	5868	0.245	0.125	0.06250	0.467
Residual	5		11.765			16395			0.50500	
Lack-of-fit	3		3.8295	*		16395	*		0.50500	*
Pure error	2		0.000			0.000			0	
Total	14		78.7892			11108556			7.58933	
R ² (%)			95.14			99.85			93.35	
Adj-R ² (%)			86.32			99.57			81.37	

Conclusion

The results generally indicated that electrocoagulation process has positively affected the reduction in turbidity and increase in the purity of the raw sugar beet juice during the process of purification though colour intensity was not so significantly influenced. Investigation of the independent parameters indicated that increases in the voltage and process time of coagulation significantly affected the reduction in turbidity and increase in purity such that the turbidity was reduced by 87% in comparison with the initial raw sugar beet juice while the purity increased by three units. Changes in the pH in the 6-8 range however, had no noticeable effect on Turbidity, colour, and purity. Although the results of this research indicated only a slight increase in the colour intensity of the raw sugar beet juice due to floatation and enzymatic browning, it is hoped that the colour produced can be removed by absorption on the surface of bentonite powder or active carbon by filtration. The operational parameters in this research were effective on the variations of color, turbidity and purity with appropriate R^2 . Analysis of operational parameters effectiveness subject the full quadratic model summarized in table 4. This process can be offered as an effective method in the purification of the raw sugar beet juice in combination with other purification methods.

Acknowledgements

The authors would like to thank Laboratory chef and university president of Islamic Azad University, Quchan branch for his assistance in this project.

References

1. Asgari G., Mohammadi A., Roshanaei G., Sharifi Z., Mehralipour J., Shabanloo A., Shabanloo M. (2013), Investigation of the performance of the electrocoagulation and electrocoagulation/floatation processes in the removal of seasonal Turbidity by using iron and aluminium electrodes, *Water and Wastewater Journal*, 24(2), pp. 62–69.
2. Bazrafshan E., Moein H., Kordmostafapour F., Nakhaie S. (2013), Application of Electrocoagulation Process for Dairy Wastewater Treatment, *J Chem*, 64013, pp. 1–8.
3. Chaturvedi S.I. (2013), Electrocoagulation: A Novel Wastewater Treatment Method. *International Journal of Modern Engineering Research (IJMER)*, 3, pp. 93–100.
4. Chen G. (2004), Electrochemical technologies in wastewater treatment. *Sep Purif Technol*, 38, pp. 11–41.
5. Emamjomeh M., Sivakumar M. (2009), Review of pollutants removed by electrocoagulation and electrocoagulation/floatation processes, *J Environ Manage*, 90, pp. 1663–1679.
6. Ghanbari F., Mazaheri A., Mehdipour F., Mir Shafian S., Moradi M., Sharifi Maleksari H. (2013), Investigation of the effect of the electrocoagulation on the removal of colour from coloured sewage by using aluminium/iron and aluminium/copper electrodes, *Journal of Sabzevar University of Medical Sciences*. 20(5), pp. 716–725.
7. Gil G.E and Wright P.H. (1994), Process for producing refined sugar from raw juices, *US Patent No. 5*, pp. 281, 279.

8. Hakimzade V., Razavi S.M.A., Piroozifard M. K., Shahidi M. (2006), The potential of microfiltration and ultrafiltration process in purification of raw sugar beet juice, *Desalination*, 200, pp. 520–522.
9. Kobya M., Can O.T., Bayramoglu M. (2003), Treatment of textile wastewaters by electrocoagulation using iron and aluminum electrodes, *J Hazard Mater*, 100, pp. 163–178.
10. Yousuf A.M., Schennach R., Parga J.R., Cocke D.L. (2001), Electrocoagulation (EC)_Science and applications, *J Hazard Mater*, 84, pp. 29–41.
11. Parga JR., Cocke DL., Valenzuela JL., Gomes JA., Kesmez M., Irwin G., Moreno H., Weir M., (2005), Arsenic removal via Electrocoagulation from heavy metal contaminated groundwater in La Comarca Lagunera Mexico, *J Hazard Mater*, 124(1-3), pp. 247–5.
12. Shivayogimath C.B., Jahagirdar R., (2013), Treatment Of Sugar Industry Wastewater Using Electrocoagulation Technique, *Int J Res Eng Technol*, 262–265.
13. The Official ICUMSA Method GS 1/2/3/9-1, (2011), *The Determination of the Polarisation of Raw Sugar by Polarimetry*.
14. The Official ICUMSA Method GS 2/3-18 (2013), The Determination of the Turbidity of White Sugar Solutions.
15. The Official ICUMSA Method GS 9/1/2/3-8 (2011), *The determination of sugar solution color at pH 7.0 by MOPS buffer method*.
16. Vaccari G., Tamburini E., Sgualdino G., Urbaniec K., Klemes J., (2005), Overview of the environmental problems in beet sugar processing: possible solution, *J Clean Prod*, 13, pp. 499–507.
17. Xu L.J., Sheldon B.W., Larick D.K., Carawan R.E., (2002), Recovery and Utilization of Useful By-products from Egg Processing Wastewater by Electrocoagulation, *Poult Sci*, 81(6), pp. 785–79.

Analysis on application of different grape varieties in the production of icewine. A review

Viktoriya Ostapenko

Odesa National Academy of Food Technologies, Odesa, Ukraine

Abstract

Keywords:

Icewine
Ice wine
Grapes
Late maturing
Climate

Article history:

Received 12.10.2016
Received in revised form
20.12.2016
Accepted 27.12.2016

Corresponding author:

Viktoriya Ostapenko
E-mail:
viktoriya_velass@mail.ru

DOI: 10.24263/2304-
974X-2016-5-4-7

Introduction. The choice of suitable vine cultivars to icewine production is exerting an increasingly influence on market supply expanding the premium segment of agricultural sector.

Materials and methods. Databases and international laws in winemaking were used to assessing the completed performance associated with application of different grape varieties for icewine production in different countries.

Results and Discussion. Current study illustrates the comprehensive range of grapes used by winemakers who decided to leave vines during low temperature in different producing countries among which are Germany, The Czech Republic, Austria, Slovenia and Canada. The states listed compose the most diverse grape groups for finished wines. Europe has the various grapes growing in winter to freeze but the total Icewine amount is lower compare to countries located in the North America including Canada and the United States of America.

Majority of countries largely adopt *Vitis vinifera* possessing thick-skin that offers better protection against winter damage, however, varieties of this class are relatively sensitive to weather than hybrids or autochthonous grapes. Riesling is the most common used for icewine processing due to appreciation of characteristics of vine during winter period.

Climate conditions are the main contributor to obtaining Icewine crops that can significantly decrease the expected volumes of harvest, thuswise grapes protective measures are provided before low temperatures.

Conclusions. The result obtained from review based on the determining of the use of various cultivars demonstrates the development and expansion of icewines within the world wine society.

Introduction

Harvest dates need to be considered carefully since they are based on subjective evaluations of optimum fruit composition in view of ulterior wine quality, whose definition is exposed to individual interpretation and trends, and may also depend on commercial targets, market constraints, processing capacity and other factors [1]. According to VQA in Canada grapes for Icewine¹ production must be harvested no earlier than November, picked while the air temperature is -8°C or lower and the optimal time for harvesting is -7°C in European countries [2]. The grapes must be harvested and pressed at these same temperatures. The grapes are harvested at $\leq -8^{\circ}\text{C}$ and pressed at low temperature to obtain the minimum juice 35° Brix required for icewine in Canada. During pressing, much of the water is retained with the grape skins as ice, while a juice is highly concentrated in sugars, acids and aroma compounds [3].

The choice of cultivar for icewine production is important as it can affect the sensory and chemical composition of the obtained wine. Generally, grape quality is the key characteristic for the production of quality wines. The total requirements for grapes used in icewine production are a resistance to rot and other diseases, the healthier structure, technological maturity and the chemical composition of grapes. Characteristics of a good variety for icewine production are that it has thick skin, be late maturing, possess a high natural acidity and be resistant to low winter temperatures, but should be noted yield of grape juice per tone of grapes is low [4]. According to Definition of the vitivincultural products by code sheet of OIV [5] all grapes used for Icewine production should come from the same region.

Recently many countries have used comprehensive number of varieties and styles for icewine production, yet to be characterized in the literature [23, 30–33, 43, 44]. The choice of variety plays one of the important roles in the production of icewine. A number studies are focused on searching of solutions for stability of grapevines during low winter temperatures in order to obtain the good harvest.

The objectives of this research were:

1. To determine the main cultivars using for Icewine production across the world;
2. To indicate the substantial reasons for selection of grapes appropriated to naturally freezing. Redistribution in wine production may occur within continents, moving from declining traditional wine-growing regions to novel suitable areas [6]. Thereby the interest about new types of wines and new cultivars has increased.

Materials and methods

Information about Icewine grapes was obtained from bibliographic sources including articles, researches [1–4, 8–11] and thesis [7, 52] from Canada and then summarized using statistic data [18–20] and wine reports [22–26, 41–43] from different countries. As the

¹ Icewine (title of wine bottle) is predominantly used by Americans. Canadian researchers in the articles mark premium wine as *Icewine*, always with capital letter. Most of producers determine sweet wines respectively to official languages, but according to acts belonged to OIV producers should indicate wines like Canadians make. Author of this article uses the name of wine in accordance with the marking of a particular country.

principal indicator climate influence on the production of icewine was studied [12–17]. Company's presentations [21, 44–46] were foundation for determination of used grape varieties for icewine production. In order to show possible grape cultivars appreciated for icewine production various vines possessing cold-resistant and disease-resistant originated from different wine areas were examined [27–29, 34–39]. The official sites of wine governments were the main basis to choosing enterprises having special dessert bottles in their shops. Statutes and official documents of International Organisation of Vine and Wine [5] and annual reports of The Vintners Quality Alliance [31, 56] were indicators for determination peculiarities of utilized grapes. Data for the climatic conditions of wine regions could explain the layout of icewine producers. Figures presented in current review were produced using Excel software (MS Office 2007, Microsoft Corporation, Seattle, WA).

Results and Discussion

1. Grape parameters for Icewine production

Icewine is the only wine type for which the soluble solids concentration at grapes maturity is irrelevant, because the harvest of grapes for its production is performed at temperature that is critical and leads to freezing of the water inside the berry and concentrating all its components [7].

The resistance of low winter temperatures, high natural acidity, late ripening, tough skins and stems and reasonable resistance to diseases have been identified as the most important characteristics of grape varieties used for Icewine production, and largely explains the predominance of Vidal and Riesling [8]. The production of this wine type always depends on weather. Bad weather seriously can affect the Icewine grape crop thereby many mass production companies hedge against changes in temperature that impact on supply. Warm winter temperatures can significantly limit the winter grape harvest and subsequently the volume of produced Icewine. For example, approximately 60% of Ontario grapes set aside for Icewine were diverted to late harvest wines in 2001 due to insufficient harvest hour temperatures. In addition to the lost opportunity costs of selling the harvested juice in the form of cheaper late vintage table wine or grape juice rather than icewine, an additional loss is the increased vulnerability of the vines to winter damage [9]. Later harvesting is usually associated with significant losses due to deterioration of harvest from wind, rot and other factors, and possibly lower sugar content levels in grapes. Due to this bad weather conditions, losses in the Icewine industry were estimated in the range of 10–15 million dollars [10].

Additionally, winter hardiness is influenced by vineyard terroir factors and that vines that are water stressed would not be resistant in comparison with non-water stressed vines [11]. The resistance of low winter temperatures is a genetically controlled characteristic and the full expression of that characteristic can be adversely affected by stresses such as over cropping, drought, and diseases. Furthermore, the duration of the cold weather in regard to the vine acclimation and the rate of temperature change can dramatically affect the sustained cold injury [12]. With new viticulture technology for creation of cold-resistant and disease-resistant hybrid grape varieties, the possibility of growing of vines with improved properties has expanded into cold areas.

Climate change-related increases of the temperature, pH and potassium levels, especially in conjunction with higher sugar concentrations, have a direct influence on wine

chemistry, as well. It is often believed that relatively low crop load and optimal plant nutrient status are necessary to maximize cold hardiness of grapevines [13]. Also black grape varieties need more sunlight and heat than white grape varieties, to ensure the physiological ripeness of the tannins in their skins. It follows, therefore, that the bigger part of white grape varieties grow in cold regions; for example, Germany, Alsace, Loire Valley [14].

Should be mentioned that grapevine genetics play an important role in the level of cold hardiness of the cultivar. The different vine cultivars have different abilities to withstand cold temperatures and that abilities are determined by evolutionary factors such as its area of origin. The lineage of a particular cultivar, especially a hybrid, can give clues as to its potential cold resistance. Many vine species have been used for hybridization. Most of the cold resistant genes come through American grapevine species such as *Vitis labrusca*, *Vitis aestivalis*, and *Vitis riparia* [15]. In addition to its genotype, the cold resistance of a specific cultivar is determined by environmental conditions, such as seasonal temperatures and their variation, and by vineyard management practices. It is important to remember that exposure to lower temperatures plays a major role in the ability of the vine to acquire its maximum cold resistance. The colder region, provides an opportunity for maximum potential of cold resistance [16].

Other American species (*Vitis rotundifolia*, for example) are not cold resistant at all. *Vitis vinifera* is the most common vine cultivar and originated of the Mediterranean areas of Europe. Its ability to withstand cold winter weather is not good. Also, it is highly susceptible to winter and spring temperatures. Therefore, knowledge of the genetic background of a cultivar is a key component to choosing genotypes that are adapted to a particular climate [17].

Vitis vinifera cultivars are more susceptible to cold injury and there is also much variability between them. For example, varieties such as Riesling and Chardonnay are much more cold tolerant than others such as Merlot, Syrah and Semillon. Hybrid varieties are generally more cold tolerant than *Vitis Vinifera*. Vidal blanc is more cold sensitive than most of the University of Minnesota hybrids such as Marquette that can withstand -30 °C.

Grapevines have varying levels of crop depending on variety, location, training system and end use of the grapes. Ontario is no exception and in some vineyard blocks, crop levels can be considerably higher than other blocks when used for Icewine production or target (plateau) priced for lower tier wines. Higher crop levels have been associated with lower cold tolerance in previous literature for some hybrid varieties. Furthermore, some Vidal Icewine blocks have had a tendency to show reduced bud survival following some years of Icewine production especially where they have been machine harvested or the block has been used in consecutive years for Icewine production [18]. In general, Chardonnay, Pinot noir and Merlot reduce maximum hardiness due to cropping level and/or timing of harvest. Heavier crop levels and later harvests reduced maximum hardiness especially in cooler, wetter and delayed seasons. For Cabernet franc, Sauvignon blanc and Riesling, crop level and/or harvest date did not generally impact the vine's ability to reach maximum hardiness levels. Over-cropping can reduce maximum hardiness but in poor growing seasons even a balanced vine may have slightly reduced hardiness. Pinot noir vines with more clusters/shoot reduce cold tolerance regardless of harvest date. For other varieties larger crop levels generally reduce cold hardiness throughout all of dormancy in some years. Riesling is more of an exception and do not respond strongly to crop levels but later harvests reduce cold hardiness. Therefore, Riesling vines used for Icewine production may be slightly compromised in some years.

2. Used cultivars for Icewine technology

Resistance to a wide range of diseases is needed, but the production of wine is almost exclusively based on *Vitis vinifera* cultivars and even new hybrids within *Vitis vinifera* are poorly accepted owing to the industry's reliance on traditional and easily marketed classic wine grape cultivars[19]. Initially, Icewine was produced only from white grapes, but recently winemakers start to leave vines of the red varieties during winter for expanding of their range. The most utilized kinds of grapes from white varieties are represented in Figure 1. Figure 1 highlights used dark grape varieties.

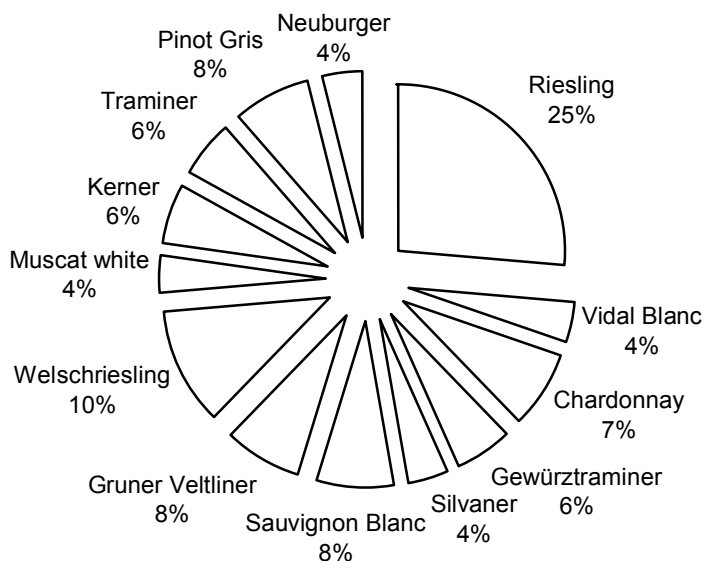


Figure 1. White grapes for icewine making by countries, %

Based on examined data the leaders are *Riesling* and *Welschriesling*. Evidenced for that fact is that the 26% and 11% relatively of total cultivars are appreciated by producing-countries due to their winter resistance and perhaps the possibility of growing on all grounds in deferent lands.

Welschriesling is a widely planted and well-known variety of Central and Eastern Europe. *Welschriesling* has many synonyms, including *Welsch Rizling* (Bulgaria), *Laski Rizling* (the former Yugoslavia), *Olasz Rizling* (Hungary), *Grasevina* (Croatia), and *Riesling Italico* (Italy). All central located European countries grow this white variety in order to produce exclusive type of wines.

Originated from the Bordeaux region of France *Sauvignon Blanc* is popular not only in Canada, also in Croatia, Slovenia and Russia for Icewine production. Austrian Icewine is often made from variety *Gruener Veltliner* that is estimated as terroir autochthonous grape of Österreich. The scientists suggest that it probably derives from a crossing with *Traminer* [20]. Dry and mild long autumn contribute to the optimum ripeness, juiciness and sugar content for *Gruener Veltliner* and *Silvaner*, a white grapes of uncertain origin that is planted in Alsace and more widely in Germany.

Chardonnay and *Sauvignon Blanc* are used by winemakers from the Czech Republic, Germany and Slovakia. Additionally, the Royal DeMaria 2000 Chardonnay Icewine is recognized as the most expensive Icewine in the world, retailing at \$250,000 a bottle [21].

Neuburger is chosen by companies landed on Austria and the Czech Republic. Moldavian, Croatian and Slovenian estates deliver Icewine crops through harvests of *Traminer*. The Russian Federation mostly sells *Riesling* and *Muscat Ottonel* dessert wines that are included to special category.

The most used cultivar is *Vidal Blanc* in Canada, grape hybrid possessing the appreciated characteristics for high quality wines. Originated from France the sort is widespread across provinces provided annually crop to wineries. Vidal has been widely planted in Eastern and Midwestern states due to its many positive attributes: moderate cold resistance (more than *Vitis vinifera* varieties), spring frost avoidance (due to late bud break), bunch rot resistance and especially its versatile and desirable wine style and quality [22]. It requires places with long growing seasons and moderate winter temperatures. Bud break is late, which reduces the risk of spring freeze injury. It is characterized by small berries on very large, loose, tapering bunches of grapes. Bunches of grapes thinning is sometimes required to prevent overcropping [12]. Also Chinese wineries adopting the experience of Canadian growers plant basically Vidal near own Huanglong Lake which promotes a cold and not too dry climate [23]. It is important to know that aged icewine from wine varieties Vidal of the Canadian Company "Inskillin" is defined as the best sweet wine of 2002. Vidal Blanc Icewine of 2013 made by Debonne Vineyards was just named best dessert wine at the 2015 *San Francisco Chronicle* Wine Competition, one of the largest contests in the United States.

The biggest amount of icewine from North America is produced using French-American hybrid, and European countries prefer *Riesling*. The first icewine in the world was a Riesling, made in British Columbia by Walter Hainle in 1973. Incidentally, Riesling is technical kind of grapes, identified on the banks of the River Rhine. The morphological features and biological properties of Riesling are related to ecological-geographic group to Western European varieties. Riesling is considered to be one of the world's greatest white grape varieties and some of the best white wines were obtained from it. It is a native variety of Germany, where it is believed to have been cultivated for at least 500 years and possibly as long as 2000 years, after all, over 22,000 hectares in German vineyards are planted with Riesling which is about 60 percent of all the Riesling in the world [24]. In addition, numerous comparative trials resulted in more than 80 Riesling clones registered in Germany developed by the breeding department of the Forschungsanstalt Geisenheim [25]. The Riesling grape's ability to retain its acidity while achieving high sugar levels is what creates wines with considerable aging potential [26]. Conclusively, as a result, Riesling can be identified as icewine king due to its good winter resistance and the most expanding across wine regions in the world. This variety is selected by 14 producing countries. On the basis of current researches most of states landed on Europe utilize especially above mentioned white variety. Such countries as Germany, the Czech Republic, Slovenia and Luxembourg basically create Riesling icewines.

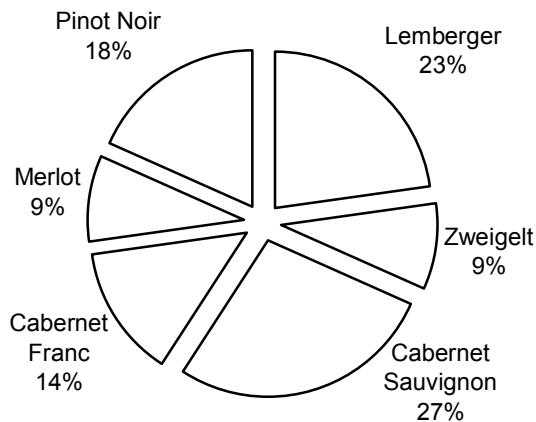


Figure 2. Dark grapes for icewine making by countries, %

Cabernet Sauvignon due to its relatively late maturing is viable grape cultivar for the places with low temperatures. Also this variety has high resistance to mildew and botrytis disease. Better than many other European sorts in the group is opposed to phylloxera and slightly is damaged by grape moth. The point to be emphasized is that many investigators are devoted to evaluate dormant bud cold hardiness of grapes among them scientists and winegrowers often explore parameters of *Cabernet Sauvignon* [27], [28], [29]. It is variety which was frozen in Brazil [30].

The second position of used red varieties belongs to *Lemberger*, having many synonyms: *Frankova* in the Czech Republic, *Frankovka modrá* in Slovakia, *Blauer Limberger* or *Blue Limberger* in USA, but Austrians call it *Blaufränkisch* like *Vitis vinifera* name. The most popular dark grape variety in Canada and United States of America is *Cabernet Franc*. According to data from Annual Report [31] in Canada there was a substantial 68% increase in the production of Cabernet Franc Icewine in 2015.

However, Canada is considered for the biggest Icewine producer by volumes. Wineries from Germany plant the significant number of diverse grapes for atypical technology. All aforementioned grapes varieties are included in Icewine production, except for Vidal and Traminer. Despite varieties shown in Figures 1 and 2, such grapes as *Muskat Trollinger*, *Trollinger*, *Gold Muscat*, *Huxelrebe*, *Ehrenfelser*, *Cabernet Mitos* are used by Germans to obtain of elite quality drinks. The last three grapes varieties were investigated by the Geisenheim Grape Breeding Institute. Exactly from *Huxelrebe* was produced first batch of Polish icewines at Jagiellonian University [32]. Anselmann Winery has icewines of the grape varieties *Silvaner*, *Chardonnay*, *Dornfelder*, *Cabernet Sauvignon*, *Pinot Noir* and *St. Laurent*.

The comprehensive range of current grapes varieties by countries is presented in Figure 3. From the analysis can be concluded that Germany, Austria and the Czech Republic have a diverse market of Icewine that is made from different grape varieties.

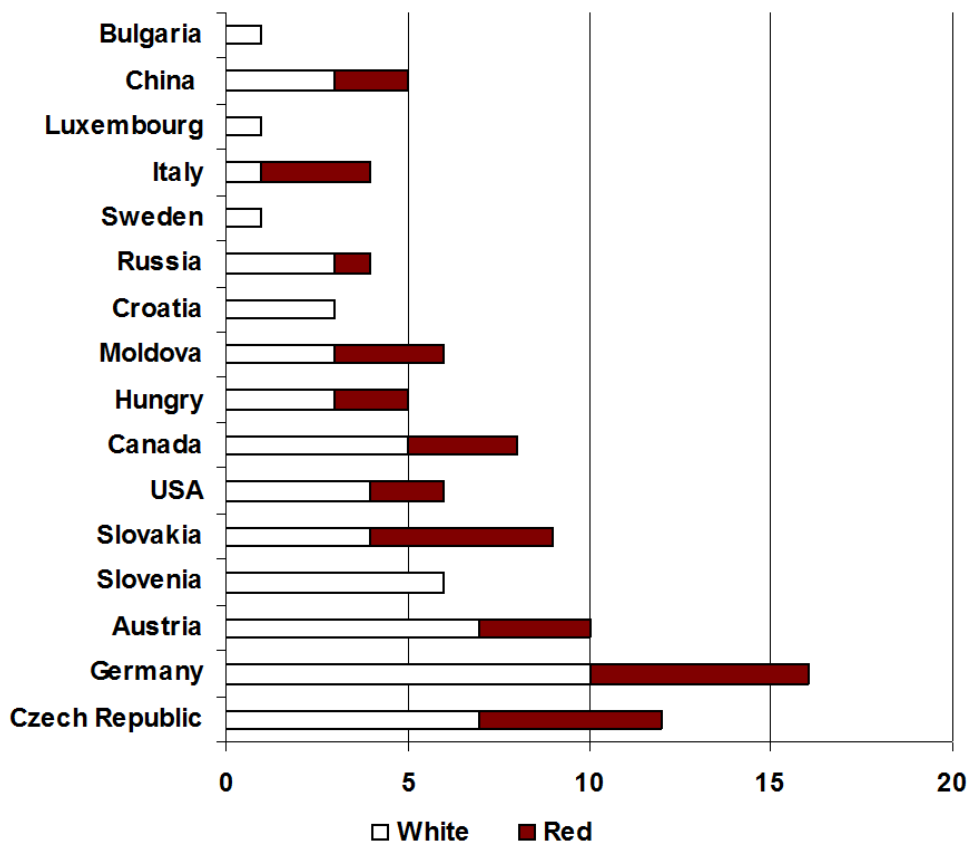


Figure 3. Range of grape varieties that used for production of icewine in different countries

Such countries as Luxembourg, Sweden, Slovenia and Croatia leave exclusively white berries on the vines to become shriveled. Icewine technology in Luxembourg is described in the law represented in official site of the Institute Viti-Vinicole Grand Duché de Luxembourg. According to it premium wines can be made from the varieties Pinot Blanc, Pinot Gris and Riesling[33]. The North Countries represented in this study have preference to Vidal. In the smallest European countries wines are produced from Riesling. It was found that Slovakia is only country that produces icewines by using more dark-skinned varieties than light. The majority of wineries prefer white frozen grapes. Germany, Austria, Canada and USA use the similar grapes including Kerner, Gewürztraminer, Cabernet Sauvignon and Riesling.

Figure 4 appoints the classification of made icewines by type of grape where the varietal exceeds the blended by 56%. It is possible to obtain sweet stable wine easily using one type of grapes than several. But mix icewines are yielded in Moldova, Italy, Austria, Russia and USA. In the last country concentrated grape must was blended with red raspberry wine in Arrowhead Wine Cellars, Pennsylvania. Pioneers of icewine usually use one variety.

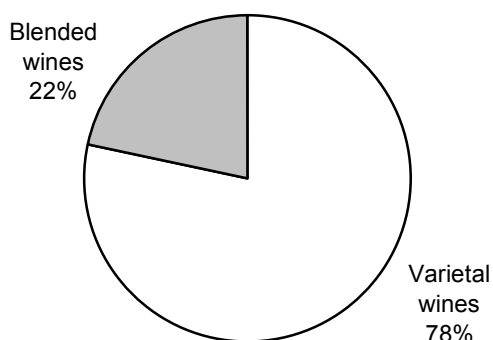


Figure 4. Percentage of icewines produced by type of wine

Nowadays breeding of the new cultivars is developed by growers with helping scientists. Hence, special programs for planting of cold resistant grape varieties were conducted based on further crosses using French hybrids, native American species, and *Vitis vinifera* varieties at Cornell University and University of Minnesota. Currently led by grape breeders and Professor Bruce Reisch, the Cornell Breeding Program at the New York Agricultural Experiment Station in Geneva has used interspecific hybridization to select wine grapes with cold resistance, high yield, disease resistance and high wine quality. ‘Cayuga White,’ ‘Melody,’ ‘Chardonel,’ ‘Marquis,’ and ‘Traminette’ were released based on the investigations of above mentioned university. «GR7» (Geneva Red 7) – is a highly healthy, productive and winter resistant grape cultivar, with moderate resistance to diseases. His red wines have a classical hybrid aroma, better tannin structure than Baco Noir and De Chaunac. It has a place in the traditional red hybrid blended wines, and it is already in limited commercial production. The University of Minnesota initiated its breeding program for wine grapes in the mid-1980 and, in 2000, completed a state-of-the-art enology lab and research winery. In the period from 1996 through 2006, the University of Minnesota breeding program developed and released four cold resistant, productive, moderate- to highly-disease resistant wine grape varieties—Frontenac, Frontenac Gris, La Crescent and Marquette [34].

Despite the high yields of icewines made from *Vitis vinifera*, hybrids and autochthonous grapes are often used possessing the highest resistance to impact of low temperatures. While there are many individual weather and climate factors that can affect grape growth and wine quality (e.g., solar radiation, heat accumulation, extreme temperatures, precipitation, wind, and extreme weather events such as hail). Growing season length and temperatures are critical aspects because of their major influence on the ability to grapes ripening with achievement of optimum levels of sugar, acids, and aromatic components in order to maximize of the wine quality [35]. Also training system can influence on bud survival in cool climates reviewed by [36] according to it the right choice of grapevine growing is useful to obtain successful crop. Large diameter canes are less winter resistant. Therefore, diverting or reducing vigour through management practices or using a divided canopy system may improve sunlight exposure of shoots and increase the resistance [18].

Having regard to investigates edited by Reisch Bruce I., Pool, & Peterson (1993) [37], the most susceptibility of grape varieties to low-temperature injury are Elvira, Saint Croix

and Ventura, American types derived from *Vitis labrusca*. But in common used varieties to obtain icewines is included *Vitis vinifera*, that were identified as the most cold sensitive [38]. Consequently, many producing countries step by step have switched to indigenous grapes.

Current study shows the first frozen grape varieties in different countries, among them are Italy, Hungary and Bulgaria produced premier icewines from indigenous grapes. It was noticed that Riesling had been commonly used for icewines by first producers due to its wide spread and winter hardiness. The Riesling grape has ability to retain its acidity while achieving high sugar levels. This creates wines with considerable aging potential. The main significance of aforementioned cultivar is its high acidity that harmonizes the final sweetness of the resulted icewine. The first icewine in Romania was obtained from *Traminer*. Slovakia obtained first icewines using *Gruner Veltliner*. China used *Vidal*. Chateau Pajzos became the first Hungarian winery for production of Tokaj Icewine that was yielded not from Riesling and from indigenous variety called *Furmint*. The Perico Winery, located in Brazil, firstly produced wines from *Cabernet Sauvignon* when temperature dropped to -7.5°C in Santa Catarina wine region [30].

Italians produce icewines using only domestic varieties – *Avanà*, *Becuet*, *Chatus* in mix. The *Prié blanc* is the only one native white-berried variety from Aosta Valley. It is employed by company Cave Mont Blanc Morgex. The Winery at Spring Hill located in Ohio, USA makes icewines from *Noiret* that is a product of the Plant Breeding Program at Cornell University. This variety results in a fine, full bodied red wine with characteristic of peppery notes. Therefore, Kiona Estate crafted icewines from variety *Chenin Blanc* and Cave B Estate Winery makes icewine from *Semillon* grapes in Washington. *Furmint* is widely used only for making sweet Tokaj, but Hungaria showed that white grape varieties also is intended for icewine production. Consumers can find icewines from Bulgaria that grows *Mavrud* to production of rare beverages. «Johanneshof-Reinisch», Austrian winery presented "Eiswein" utilizing *Zirfandler*, autochthonous cultivar that can find in the Thermenregion. *Alibernet (Odesskij Chernyj)* was bred in 1950 in the Ukrainian Scientific Research Institute of Wine and Vines in Odesa, but then announced grape was developed in former Czechoslovakia. Due to its late-ripening, it requires the best positions, harvests are regular and high. Such grape benefits were attracted by winegrowers in the Czech Republic to freezing. Winemakers from Slovakia plant own native grapes. Among them *Andre and Devin* are suitable for icewine production.

3. Harvest conditions

Weather conditions during the growing season and during the dormant period can have an impact on vine health and cold resistance to low winter temperatures. There are many factors which must be considered in selecting of icewine grape varieties. The most important factors are climate and topography of a prospective site. Other factors include slope-aspect and soil conditions [39]. In order to obtain certain amount of grapes and avoid the losses in such conditions winemakers should monitor temperature levels before harvest.

Monitoring of the temperatures in the vineyard is very important. Each site has specific characteristics – topography, soils, cultivars, cropping history and many others that influence vine resistance. The local or vineyard climate can vary within the vineyard from east to west and from north to south depending on the size and natural slope of vineyard. For this reason, multiple stations have been located throughout the grape growing regions of Ontario and have demonstrated that on a single night the lowest cold temperatures can differ by up to 5°C or more.

In order to obtain suitable crop for Icewine growers and winemakers should be sure in the area weather conditions whereby the wine volume always depends on winter season. Icewine is produced in all wine production regions of Canada; however, the main part of icewine production is in Ontario, principally the Niagara Peninsula, where the summers are warm and the winters are cold. This climate is suitable for optimal grow [40]. Although Ontario is not unique in producing of Icewines. It is the major wine region that has the climate capable to allow the icewine production almost every vintage.

The Niagara Peninsula region has cold climate. The region is situated near N43° latitude, with relatively high variation in day-night temperatures and substantial sunshine during the growing season. Three of the five Great Lakes of central North America – Lakes Huron, Erie and Ontario formed Ontario's wine regions. During winter the lakes do not freeze, their warmer water helping in the protection of their shoreline vineyards against vine-destroying deep freezes. This combination provides the development of more complex and intense grape flavours during ripening than warmer climates.

Lake Erie is a multi-state American Viticultural Area (AVA) in the Great Lakes region of the northern United States. As might be inferred from the title, most of the AVA's vineyards are located along the shores of this most southerly of the Great Lakes, stretching through New York and Pennsylvania before reaching the vineyards of northern Ohio. Most of the viticulture lands lie along the edges of the lake or near water, where the temperatures are moderated by the insulating capacities of the water. By the same token such distribution is suitable for cultivation of grapes widespread for Icewine making. This arrangement provides a unique micro climate where the large mass of lake water holds heat from the summer, moderates local temperatures and provides warm breezes through autumn to delay typical first frost into November and conversely the lake moderates winter low temperatures, but keeps the area cooler into the spring, delaying first budding until past the typical last frost date[41]. Thus, the biggest share of Icewine production and sales belongs to upstate the Finger Lakes located in the middle of New York State. The most of wineries centres on main lakes named Canandaigua, Keuka, Seneca and Cayuga. The climate of these areas provide temperate conditions suitable for viticulture. Furthermore, American native grapes varieties are established with the highest hardiness ratings compare to grape varieties obtained from *Vitis vinifera* [28]. Proof of that is estimation of the economic losses during winter season. They were conducted by The OSU Grape Team in Ohio State according to its average estimated crop loss, total estimated grape and wine value loss and average loss per acre of Vinifera Grape Varieties exceed than harms of American Grape and Hybrid Grape Varieties [42].

There is different type of climatic conditions which significantly influence grape growing of each country across Europe. The warmest wine-growing region is Moravia in the Czech Republic. It is the most favourable in temperatures in the comparison with the Mikulov and Velké Pavlovice regions for example. Cooler Bohemia region lays in the rain shadow of the Krušné Hory and České Středohoří Mountain ranges. The climate is continental, with the influence of cold invasions and moist air from the Atlantic Ocean or from Siberia. Summer is with intense temperatures. That fact significantly accelerates the grapes ripening [43]. The biggest company producing icewine in the Czech Republic «Znovín» is situated in The Znojmo Sub-region where cold climate contributes to planting *Müller Thurgau*, *Rhine Riesling*, *Grüner Veltliner (Veltlínské zelené)*. Although, icewine producers are situated too in all sub regions of the country where the climates are not considered as cold. Croatian winery «Bodren» located in winegrowing region Pregrada, Hrvatsko Zagorje is situated between Alps and Adriatic Sea on the southern foothills of the mount. The climate is continental-type. The microclimatic potential guarantees the

accumulation of high acids levels in grapes. This has been used as an advantage for production of dessert wines in which the acidity is well balanced against sweetness and reduces the sensation of weight [44]. The continental climate, which means warm summers and cold winters, is defining for wine regions of Germany and Austria. Yet even Germany and Austria underwent climate variations that caused the regular harvest and uncertain supply of icewine from year to year [45].

Besides countries which are commonly considered as areas with cold climates there are states providing icewine making due to its low winter temperatures. The moderate continental Moldovan climate boasts plenty of sunshine and warmth, and is characterized by a long warm period – 260–290 days, and a relatively short cold period that lasts only 75–105 days [46]. That make possible to growing of grape varieties for rare wine style.

The management to protecting grapes against winter damages plays the significant role in controlling of the harvest volumes. One of the methods to prevent potential decrease of grapes yields is netting of vines blocks [47]. Also noise makers and scaring devices ensure the saving vineyards from animals and birds attacks. There is also always the risk for grapes decay before the temperatures are cold enough for an Icewine harvest. Due to study created by [48] estates can indicate spatial and temporal patterns for bird damages on the wine grapes at the level of single vineyards. The potential employing of weather derivatives against temperature related risks is capable to save the grape harvest. This technology is widely used in various agricultural sectors. Consequently, in order to obtain favourable crop for Icewine processing the winemakers should focus on determination of the time for grapes harvest during low temperatures and to select resistant grape varieties.

4. Impact of grapes on sugar and alcohol content in Icewine

Icewine is a wine for which the harvest temperature is the most important to achieve the quality finished beverages. As a result, colder temperatures are required to freeze the berry and achieve the desired soluble solids concentration in the must later in the season and, thus, reducing yields [49]. It was noticed, that the date and time of harvest basically impact on composition of frozen grapes. The time period of harvest determines the main biochemical and chemical reactions in icewine. The most important among them are sugar levels and volatiles concentration. The ideal temperature is between -10 and -13 °C before picking. This provides the optimum sugar levels and good flavor in the grapes. The dependence of sugar content from temperature is highlight in Table 1. The data about sugar levels in grape must from Canada is presented in Figure 5.

Table 1

Dependence of sugar content from temperature

Temperature, °C	Sugar content, %
-6	29
-7	33
-8	36
-9	39
-10	43
-11	46
-12	49
-13	52
-14	56

Higher sugar concentration is observed during autumn season. Higher sugar levels occur in freezing grapes. Should be noted, that the optimal days for harvest were fixed in the middle of December, but wineries determine the final time for harvest based on current weather conditions when air temperature is appreciated. The latest dates of gather were defined as not favorable for icewine making due to low-quality grapes that had been rotten. But according to researches of Canadian winemakers and scientists the highest concentrations of aroma compounds were estimated from grapes harvested with increasing hang time. Unfortunately, the complete composition of the Icewines made from only *Riesling*, *Vidal* and *Cabernet Franc* from Canada are described in scientific literature.

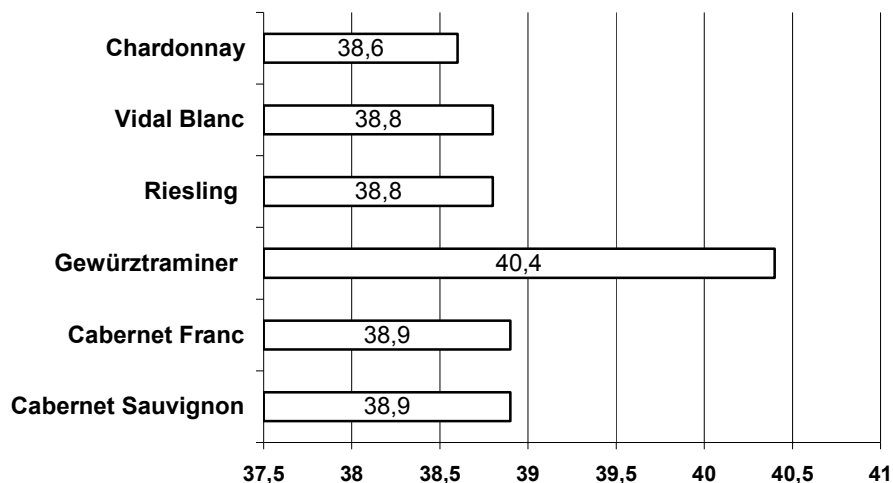


Figure 5. Sugar of must from frozen grapes in Canada, °Brix

The most concentrated grapes make challenges for providing of Icewine production: slow fermentation rates, difficulties in reaching 10–11% (v/v) ethanol in the wine before the yeast stop fermenting and overproduction of glycerol that influence higher concentration of volatiles predominantly acetic acid. Increasing Icewine juice concentration from 40 to 46°Brix decreases yeast growth, sugar consumption rate, the total amount of sugar consumed and the total amount of produced ethanol. Increasing The sugars in the grape must for Icewine production lead to raises of the proportion of yeast sugar metabolism diverted away from growth and towards glycerol and acetic acid production. This leads to increased osmotic stress. The acetic acid presented in Icewine at certain levels is not an indicator of microbial spoilage, but rather is a natural by-product of wine yeast fermentation under hyperosmotic stress that may be of benefit in the overall sweetness to sourness balance of the wine. In higher levels it exerts a negative influence overall wine quality [50].

It should also be emphasized that alcohol content differs among countries. Typically, premium wine contains 9–12% alcohol while icewine from Germany and most of European countries have 7–10% ethanol. This fact can be explained by the time of the harvest contributed largely on concentrating of grapes. In some parts of Europe, the vintage is done at a temperatures of minus 7 °C. Winery Klet Zorenč – Hohnjec from Slovenia offers premium wines contained more than 14% alcohol that represents the highly alcoholic

icewine among another types from other countries. Also enterprise Moravčikova vína from the Czech Republic produces icewine contain 14% alcohol. An ethanol concentration in icewines directly correlates with sugar levels and the use of yeast strains for fermentation.

The choice of yeast strain can contribute to the consistent production of high quality wines with unique styles and characteristics. Therefore, the most of articles, investigations and research works are dedicated to ascertaining of convenient yeast strains for providing fermentation [51], [43], [53], [54], [55]. The only weather condition required for a successful harvest is the amount of time between the desired temperature. Other climatic factors such as humidity or wind speed do not affect the quality of the harvested grapes [9].

Similar in character to Icewines, but with less pronounced sweetness and intensity are Late Harvest wines. They are made from grapes harvested after the regular fall harvest but before Icewine harvest. They range from Special Select Late Harvest (sweet and almost like Icewine) to Select Late Harvest to Late Harvest (usually just sweeter than an off-dry or medium table wine) [56].

5. Prices of Icewines made from diverse grapes

Quality signals are important price determinants. An objective quality measure is very difficult to define. Many of the sensory indicators that determine expert quality ratings are subjective. Additional indicators, such as labeling, bottle design, or the reputation of producers and regions may also advance or hinder the sale of a particular wine [57].

Bodren Icewine 2009 (Vrhunsko), Regional Decanter Award Winner 2011 from Croatia costs 63 euro per 250 ml bottle while price of Cuvee Ledeno Vino (Icewine) 2008 of this estate is 38 euro. Also Canadian company Inniskillin is considered as brand of Icewine selling their bottles of 0,375 ml priced more than 70 dollars. However, Icewine from *Riesling* is more expensive than wine made from *Vidal* of this winery. But evidenced fact that Oak aged *Vidal* Icewine is the most known premium beverage thereby has the highest price than another wines. Also with the same charges American wines are sold, but the highest values of icewine s were pointed in the New York state exactly in shops of wineries located in the Finger Lakes area.

The prices of German *Eiswein* are different depending on wine region, popularity of winery and historical roots of exclusive wine establishing. The white icewine s have bigger circle of customers and cost relatively higher while red Icewines are less common inside market. The analyzed data for current study shows that *Riesling* and *Chardonnay* Icewines are the most expensive contrary to wines produced from another cultivars. The prices of rare wines from ingenious varieties are quite different among countries. It was noticed that elite wines cost more in that case if adverse weather conditions occur during grape Icewine season.

Due to consolidation position including necessary characteristics suitable for Icewine production mentioned grapes are chosen mostly. Also marketplace of estate in ice category, management of advertisement and tax policy impact the price of premium wine bottle. The major of producers despite of used grapes from diverse countries have the similar price politic the mean score of which is 40 dollars of 0,375 l bottle. The bottles of 0,200 l and 50ml cost in average 25 and 10 dollars respectively. Additionally there are not true icewine s in market produced by alternative methods which have lower prices. However, company Znovin located in the Czech Republic sells their wines with price that is similar to icewine bottle made by non-real producers.

To conclude this part should be noted that choice of used grape do not contribute much to certain price per bottle. Small sizes of describing price about icewines prove the truth of different harvest time that make impossible to analyze bigger amount of wines per one

period. The significant role belongs to harvest time, reputation of winery and risks of producers. The above listed factors largely determine the management of pricing model of Icewines.

The findings reported here can be useful for growers and especially for further investigations related to icewine technology. As icewine making is not studied in whole aspects, the next researchers should be directed to discussion of the data confirmed based on the true choice of varieties for atypical technology in various producing-countries.

Conclusions

Weather conditions are the most important factor for Icewine production generally, thereby the grape choice plays useful role to achieve harvest for rare beverage. Despite of popular ascertainment of *Vitis vinifera* Icewine production basically from white cultivars, the hybrids and native varieties are still widely utilized because they tolerate much lower temperatures and break bud later in the winter season. Their resistance or tolerances to many of the common diseases that affect grapes also contribute to popularity between estates making premium wines. Only seven counties had used native grapes for obtainment of first premium wines bottles. White grapes used for production of Icewine are more diverse group. *Riesling* and *Welschriesling* are common used and that determine them as the leaders in whole category. The red Icewine production used predominately *Cabernet Sauvignon* and *Lemberger*. According to this review each country selects the most suitable varieties possessing the necessary grape characteristics for Icewine developing. Varietal choices made by individuals should be made in the context of climate, site quality, management, and the suitability of varieties from an agronomic and marketing perspective.

References

1. Hope-ross P. (2006), Analysis in Brief From the Vine to the Glass: Canada' s Grape and Wine Industry From the Vine to the Glass, *Canada ' s Grape and Business and Trade Statistics Field*, 11, pp. 1–11.
2. Reynolds A. G. (2010), *Managing Wine Quality. Volume 2: Oenology and Wine Quality*, Andrew G. Reynolds, ed., Woodhead Publishing, Oxford.
3. Nurgel C., Pickering G.J., Inglis D.L. (2004), Sensory and chemical characteristics of Canadian icewine s, *Journal of the Science of Food and Agriculture*, 84(13), pp. 1675–1684.
4. Ananicz M. (2011), Winter Gift in the Glass, *35th Annual New York Wine Industry Workshop*, pp. 27–35.
5. (2015)4. *Special wines. 4.7. Icewine – Eiswein (OENO 6/03)*, pp. 6–7.
6. Hannah L., Roehrdanz P. R., Ikegamib M., Shepardb A. V., Shaw M. R. et al. (2013), Climate change, wine, and conservation, *Proceedings of the National Academy of Sciences*, 110(17), pp. 6907–6912.
7. Bowen A.J. (2010), *PhD Thesis, Elucidation of Odour-potent Compounds and Sensory Profiles of Vidal blanc and Riesling Icewines from the Niagara Peninsula: Effect of Harvest Date and Crop Level*, Brock University, St. Catharines.
8. Soleas G.J., Pickering G.J. (2007), Influence of variety, wine style, vintage and viticultural area on selected chemical parameters of Canadian Icewine, *Journal of Food, Agriculture and Environment*, 5(3–4), pp. 97–102.
9. UrveyT., Weersink A.(2006), Pricing Weather Insurance with a Random Strike Price: the Ontario Ince-wine Harvest , *the American Agricultural Economics Association Annual Meeting Providence, Rhode Island(July 24–27, 2005)*, pp. 696–709.
10. Cyr D., Kusy M. (2007), Identification of Stochastic Processes for an Estimated Icewine

- Temperature Hedging Variable, *American Association of Wine Economists Editor*, (5), pp. 1–21.
11. Jasinski M., Reynolds A. (2011), The Terroir of Winter Hardiness, *Abstracts from Presentations at the ASEV Eastern Section 36th Annual Meeting & National Viticulture Research Conference*, Towson, p. 555A.
 12. Bordelon B. (2009), Grape Varieties for Indiana, *Purdure Extension*, pp. 1–10.
 13. Davenport J.R., Keller M., Lynn J.M. (2008), How Cold Can You Go? Frost and Winter Protection for Grape, *HortScience*, 43(7), pp. 1966–1969.
 14. Grainger, K., Tattersall, H. (2007), *Wine Production: Vine To Bottle*, Blackwell Publishing, Oxford.
 15. Fennell A. (2004), Freezing tolerance and injury in grapevines, *J. Crop Improv.*, pp. 201–234.
 16. Zabadal T., Dami I., Goiffinet M. (2007), Winter injury to grapevines and methods of protection, *Michigan University Extension*, pp. 15–18.
 17. Stafne E.T., (2004), Factors affecting cold hardiness in grapevines, *Department of Horticulture and Landscape Architecture, Oklahoma State University*, Stillwater.
 18. Willwerth J., Ker K., Inglis D. (2014), *Best Management Practices for Reducing Winter Injury in Grapevines*, Cool Climate Oenology and Viticulture Institute, Brock University, St. Catharines.
 19. Linda F Bisson, Waterhouse A. et al. (2002), The present and future of the international wine industry, *Nature*, 418(68), pp. 969–999.
 20. Steurer R. (2009), *Rebsorten des Straßfertailes*, Broidl, Berlin.
 21. Royal DeMaria, available at: <http://www.royaldemaria.com/>
 22. Dami I. (2014), Winter Survival of Vidal Blanc Vines for Icewine Production, *Wines & Vines*, pp. 78–81.
 23. Lu J. (2015), Grape Wine Today in China, *Analysis of China wine industry*, pp. 1–85.
 24. (2011), The magazine of the German wine institute Oechsle, *Deutsches Weininstitut*, pp. 1–71.
 25. Regner F., Wiedeck E., Stadlbauer A., (2000), Differentiation and identification of White Riesling clones by genetic markers, *Vitis*, 39(3), pp. 103–107.
 26. Liu L., Cozzolino D., Cynkar W.U., Damberg R.G., Janik L. et al. (2008), Preliminary study on the application of visible-near infrared spectroscopy and chemometrics to classify Riesling wines from different countries, *Food Chemistry*, 106(2), pp. 781–786.
 27. Wolf, T., Cook M.K. (1994), Cold hardiness of dormant buds of grape cultivars: Comparison of thermal analysis and field survival, *HortScience*, 29(12), pp. 1453–1455.
 28. Pool R.M., Reisch B.I., Welser M.J. (1990), Use of different thermal analysis to quantify bud cold hardiness of grape selections and clones, *Proceedings of the V. International Symposium on Grape Breeding*, Geneva, New York, USA, pp. 318–329.
 29. Wolf T. (2011), Cover Crop, Rootstock, and Root Restriction Effects on Cabernet Sauvignon Dormant Bud Cold Hardiness, *Abstracts from Presentations at the ASEV Eastern Section 36th Annual Meeting & National Viticulture Research Conference*, Towson, Maryland, p. 556A.
 30. Langman, J. (2009), Icewine produced in Brazil for the first time. *Decanter*.
 31. (2016), *Annual Report 2015 Vitners Quality Alliance*, available at: <http://www.vqoantario.ca>.
 32. Bednarczyk J. (2012), Jagiellonian University vineyard will make icewine, *Science and Scholarship in Poland*, pp. 25–29.
 33. (2016), The icewine has been harvested, *The official portal of the Grand Duchy of Luxembourg*, available at: <http://www.luxembourg.public.lu/en/actualites/2016/01/25-vinglace/index.html>
 34. Covert C. (2008), Cold Climate Grape Varieties From Eastern U. S. Breeding Programs, *Foundation Plant Services*, pp. 10–12.
 35. Jones G., White M. A, Cooper O.R., Storchmann K. (2005), Climate change and global wine quality, *Climatic change*, 73(3), pp. 319–343.
 36. Reynolds A.G., Vanden Heuvel J.E. (2009), Influence of grapevine training systems on vine growth and fruit composition: A review, *American Journal of Enology and Viticulture*, 60(3), pp. 251–268.
 37. Reisch Bruce I., Pool R., Peterson D. (1993), Wine and Juice Grape Varieties for Cool Climates, *A Cornell Cooperative Extension Publication*, 2, p.6.
 38. Dami I.E., Ennahli S., Zhang Y. (2012), Assessment of winter injury in grape cultivars and pruning strategies following a freezing stress event, *American Journal of Enology and Viticulture*,

- 63(1), pp. 106–111.
39. Perry R., Sabbatini P., Burns J. (2012), Growing Wine Grapes in Michigan, *Department of Horticulture*, Michigan State University, East Lansing, pp. 353–355.
 40. Bowen A.J., Reynolds A.G. (2015), Aroma compounds in Ontario Vidal and Riesling icewines. I. Effects of harvest date. *Food Research International*, 76, pp. 540–549.
 41. (2015), *Wine Catalog. Premier Award-Winning Wines Since 1968*, available at: www.piwine.com.
 42. Dami, I., Lewis D. (2014), 2014 Grape Winter Damage Survey, The Ohio State University, Columbus.
 43. (2006), *Wines from Moravia and Bohemia – Czech Republic*, available at: <http://www.wineofczechrepublic.cz>.
 44. (2011), *Notes on Bodren Ice and Sweet Wines from Continental Croatia*, available at: www.croatianfinewines.com.
 45. Jones G., Hirasawa J. (2011), Inniskillin and the Globalization of Icewine, *Harvard Business School*, (Mba 2005), pp. 1–27.
 46. Inkpen A., Phillips R. (2006), The Wine Industry, *Moldovan Investment and Export Promotion Organisation*, 44, pp. 1–17.
 47. Inglis D.L. (2011), Extreme Winemaking in the Canadian North. Sweet success and sour pitfalls in Icewine production, *Brock University*, St. Catharines.
 48. Somers C.M., Morris R.D. (2002), Birds and Wine Grapes : Foraging Activity Causes Small-Scale Damage Patterns in Single Vineyards, *Journal of Applied Ecology*, 39(3), pp. 511–523.
 49. Bowen A.J., Reynolds A.G. (2012), Odor potency of aroma compounds in Riesling and Vidal blanc table wines and icewines by gas chromatography-olfactometry-mass spectrometry, *Journal of Agricultural and Food Chemistry*, 60(11), pp. 2874–2883.
 50. Pigeau G.M., Bozza E., Kaiser K., Inglis D. (2007), Concentration effect of Riesling Icewine juice on yeast performance and wine acidity, *Journal of Applied Microbiology*, 103, pp. 1691–1698.
 51. Erasmus D.J. (2004), Impact of yeast strain on the production of acetic acid, glycerol, and the sensory attributes of icewine, *American Journal of Enology and Viticulture*, 55(4), pp. 371–378.
 52. Martin S.J. (2008), *PhD Thesis, The Osmoadaptive Response of the Wine Yeast Saccharomyces cerevisiae KI-VIII16 during Icewine Fermentation*, Brock University, St. Catharines.
 53. Pigeau G.M., Inglis D.L. (2005), Upregulation of ALD3 and GPD1 in *Saccharomyces cerevisiae* during Icewine fermentation, *Journal of Applied Microbiology*, 99(1), pp. 112–125.
 54. Inglis D. (2008), Make Icewine Easier, at Least for Yeast, *Vineyard Winery Management*, pp. 71–75.
 55. Synos K., Reynolds A.G., Bowen A.J. (2015), Effect of yeast strain on aroma compounds in Cabernet franc icewines, *LWT – Food Science and Technology*, 64(1), pp. 227–235.
 56. (2016), *Vitners Quality Alliance*, available at: <http://www.vqaontario.ca>.
 57. Schamel G., Universit L. (2003), International Wine Trade: Analyzing the Value of Reputation and Quality Signals, *the 2003 AAEA Annual Meeting*, pp. 1–16.

Chemical composition of *Salvia officinalis* l. essential oil from Bulgaria

Stanka Damyanova¹, Silvia Mollova²,
Albena Stoyanova³, Oleksii Gubenia⁴

1 - University of Russe, Branch – Razgrad, Bulgaria

2 - Institute of Rose, Kazanlik, Bulgaria

3 - University of Food Technologies, Plovdiv, Bulgaria

4 - National University of Food Technologies, Kyiv, Ukraine

Abstract

Keywords:

Salvia officinalis
Essential oil
Composition
Bulgaria

Article history:

Received 14.09.2016
Received in revised form
13.11.2016
Accepted 27.12.2016

Corresponding author:

Stanka Damyanova
E-mail:
sdamianova@uni-ruse.bg

DOI: 10.24263/2304-
974X-2016-5-4-8

Introduction. The objectives of this study is to present the chemical composition of *Salvia officinalis* essential oil from Bulgaria.

Materials and methods. The herb from salvia was used from the market. The essential oil was obtained by hydrodistillation for 3 h in laboratory glass apparatus. The chemical composition of the oil was determined chromatographically.

Result and discussion. The moisture of the plant was 12.16% and the yield of essential oil is 0.93%.

Twenty-eight components were identified in the oil.

The main compounds of essential oil were as follows: α -thujone (26.68%), (E)- β -caryophyllene (7.47%), 1,8-cineole (7.19%), α -humulene (6.11%), β -pinene (5.44%), β -thujone (5.35%), camphor (4.84%), allo-aromadendrene (4.55%), borneol (3.69%), and α -pinene (3.58%). Three groups of compounds were found in hydrodistilled sage oil. The total oxygen-containing monoterpenes constituted the highest percentage of the components of the essential oil constituting 59.15%, followed by sesquiterpene hydrocarbons (24.37%) and monoterpene hydrocarbons (14.66%). The oxygen-containing monoterpene fraction was most abundant in the oil and it was particularly rich in ketones (70.96% of this fraction)

Conclusion. It can be stated that a number of oxygen-containing monoterpenes, sesquiterpene hydrocarbons and monoterpene hydrocarbons were detected in *S. officinalis* essential oil.

Introduction

The family of Lamiaceae consist of about 230 genera. Many species from this family are considered of high importance because of their uses in medicine, culinary and cosmetics, and production of essential oil. Same of the major genera belonging to Lamiaceae family is *Salvia*.

About 900 species of the genus *Salvia* are cultivated throughout the world. The commercial oil is produced mainly by *S. officinalis* L. (sage) and *S. sclarea* L. (clary sage).

Sage (*Salvia officinalis* L.) is a common herbal plant widely cultivated in various parts around the world, but it is native in East Mediterranean region. It is typically cultivated in temperate climatic areas where is abundant sunlight.

The preparation of dried herb of sage is registered as a medicinal drug. Phytochemical investigation of sage revealed a great number of bioactive compounds, among which the most important are essential oil and polyphenol compounds.

A previous studies have revealed α -thujone, 1,8-cineole, β -pinene, β -thujone, camphor and borneol to be the major constituents of the sage essential oil [1, 2, 3, 4, 5, 6, 8, 11, 14, 15, 16, 18, 19, 20, 21].

Different chemotypes have been described for sage: 1. camphor > α -thujone > 1,8-cineole > β -thujone; 2. camphor > α -thujone > β -thujone > 1,8-cineole; 3. β -thujone > camphor > 1,8-cineole > α -thujone; 4. 1,8-cineole > camphor > α -thujone > β -thujone; 5. α -thujone > camphor > β -thujone > 1,8-cineole [9].

ISO 9909:1997 [10] for medicinal uses regulates the amounts of the following constituents in the essential oil: cis-thujone (18.0-43.0%), camphor (4.5-24.5%), 1,8-cineole (5.5-13.0%), trans-thujone (3.0-8.5%), α -humulene (\leq 12.0%), α -pinene (1.0-6.5%), camphene (1.5-7.0%), limonene (0.5-3.0%), bornyl acetate (\leq 2.5%) and linalool+linalyl acetate (\leq 1.0%).

Sage essential oil and extracts have been used for thousands of years in folk medicine [9].

Essential oil distinguishes itself by an olfactory bouquet with camphor and thujone-like notes. This kind of fragrance is highly appreciated in compositions with herbal and spicy character, and is especially favored in the creation of masculine-type perfumes. The characteristic aromatic-herbal complex of the oil is also of a particular interest to the development of aromatic compositions for food industry – typically for canned fish and meat products [9].

More recently, studies on the biological activity of sage showed that the essential oil and some of its constituents possess good antimicrobial activity with respect to bacteria, yeast and fungi involved in food spoilage [1, 2, 3, 11, 12, 13].

The aim of present study was producing of the sage essential oil and determination of their chemical composition.

Materials and methods

In the investigation was used herb from sage (*Salvia officinalis* L.) from the market.

The raw material moisture content was determined by drying up to constant weight, at 105 °C [17].

The essential oil was obtained from the cut (1-2cm) aerial parts (100g) by hydrodistillation for 3 h in laboratory glass apparatus of British Pharmacopoeia, modified by Balinova and Diakov [7]. The oil was dried over anhydrous sulfate and stored in tightly closed dark vials at 4 °C until analysis.

GC analysis was performed using gas chromatograph Agilent 7890A; column HP-5 ms (30m x 250µm x 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 as 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.

Results and discussion

The moisture of the plant was 12.16%.

The essential oil obtained from sage with a yield of 0.93% (in abs. dry mass) was a yellowish liquid with a warm camphoraceous, thujone-like odor and taste. The difference in the yield of the oil and the reported data may be due to the climatic conditions in the respective locality in which the plant is growing and the part of the plant processed.

The list of the compounds, in order of elution, and the quantitative data, expressed as area percentage, was reported in Table 1. As seen 28 components representing 88.75% of the total content were identified in the oil. Thirteen of them were in concentrations over 1% and the rest 15 constituents were in concentrations under 1%.

As seen the major constituents (up 3%) of the oil were as follows: α -thujone (26.68%), (E)- β -caryophyllene (7.47%), 1,8-cineole (7.19%), α -humulene (6.11%), β -pinene (5.44%), β -thujone (5.35%), camphor (4.84%), allo-aromadendrene (4.55%), borneol (3.69%), and α -pinene (3.58%).

The difference in the quantities of chemical composition of the our essential oil and the reported data may be due to environmental conditions under which the plant has grown as well as the variation in conditions of analysis.

The chromatographic profile showed a complex mixture of components. The classification of the identified compounds, based on functional groups, was summarized in Table 1. The total oxygen-containing monoterpenes constituted the highest percentage of the components of the essential oil constituting 59.15%, followed by sesquiterpene hydrocarbons (24.37%) and monoterpene hydrocarbons (14.66%). The percentage of aliphatic hydrocarbons, oxygen-containing sesquiterpenes and phenyl propanoids were under 1%.

The oxygen-containing monoterpene fraction was most abundant in the oil and it was particularly rich in ketones (70.96% of this fraction) (Figure 1).

The ketones and cyclic ethers were the main groups of compounds responsible for the characteristic odor of sage oil and their concentrations were similar to those regulated by ISO 9909:1997 [10].

Table 1

Percentage composition of the essential oil of
Salvia officinalis L.

N	Components	RI	Content
1	(Z)-salvene	849	0.39
2	(E)-salvene	858	0.11
3	α -Pinene	939	3.58
4	Camphene	953	0.75
5	β -Pinene	980	5.44
6	Myrcene	991	0.67
7	α -Terpinene	1018	0.29
8	<i>p</i> -Cymene	1026	0.18
9	Limonene	1030	2.02
10	1,8-Cineole	1032	7.19
11	γ -Terpinene	1061	0.26
12	α -Thujone	1098	26.68
13	β -Thujone	1112	5.35
14	Camphor	1141	4.84
15	(E)-Pinocamphone	1160	0.38
16	Borneol	1165	3.69
17	Terpinen-4-ol	1178	0.45
18	α -Terpineol	1189	0.29
19	Bornyl acetate	1284	3.62
20	(E)- β -caryophyllene	1418	7.47
21	α -Humulene	1455	6.11
22	<i>allo</i> -Aromadendrene	1465	4.55
23	γ -Muurolene	1477	0.43
24	Viridiflorene	1494	2.52
25	γ -Cadinene	1513	0.18
26	δ -Cadinene	1524	0.37
27	Ledol	1568	0.53
28	Caryophyllene oxide	1583	0.41
Total			88.75
Oxygen-containing monoterpenes			59.15
Sesquiterpene hydrocarbons			24.37
Monoterpene hydrocarbons			14.66
Aliphatic hydrocarbons			0.56
Oxygen-containing sesquiterpenes			1.06
Phenyl propanoids			0.20

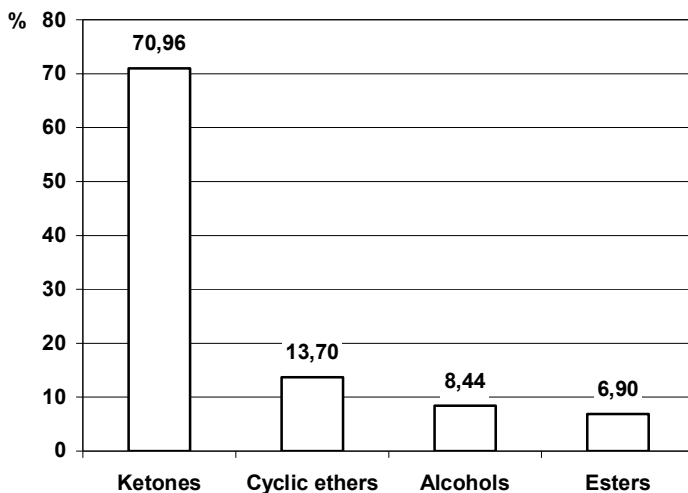


Figure 1. Oxygen-containing monoterpene fraction

Conclusion

It can be stated that a number of oxygen-containing monoterpenes, sesquiterpene hydrocarbons and monoterpene hydrocarbons were detected in *S. officinalis* essential oil.

References

1. Abu-Darwish M., Cabral C., Ferreira I., Goncalves M., Cavaleiro C., Cruz M., Al-Bdour T., Salguero I. (2013), Essential oil of common sage (*Salvia officinalis* L.) from Jordan: Assessment of safety in mammalian cells and its antifungal and anti-inflammatory potential, *BioMed Research International*, pp. 1–9.
2. Alizadeh A., Shaabani M. (2012), Essential oil composition, phenolic content, antioxidant and antimicrobial activity in *Salvia officinalis* L. cultivated in Iran, *Advances in Environmental Biology*, 6, pp. 221–226.
3. Altun M., Ünal M., Kocagöz T., Gören A. (2007), Essential oil compositions and antimicrobial activity of *Salvia* species, *Journal of Essential Oil Bearing Plants*, 10, pp. 251–258.
4. Archana P., Negi K., Dutta M. (2013), Variability in essential oil composition of sage (*Salvia officinalis* L.) grown under North Western Himalayan region of India, *Journal of Medicinal Plant Research*, 7, pp. 683–688.
5. Asllani U. (2000), Chemical composition of Albanian sage oil (*Salvia officinalis* L.), *Journal of Essential Oil Research*, 12, pp. 79–84.
6. Awen Z., Unnithan C., Ravi S., Kermay A., Prabhu V., Hemlal H. (2011), Chemical composition of *Salvia officinalis* essential oil of Libya, *Journal of Essential Oil Bearing Plants*, 2011, pp. 89–94.
7. Balinova A., Diakov G. (1974), On improved apparatus for microdistillation of rose flowers, *Plant Science*, pp. 79–85.

8. Bernotiene G., Nivinskiene O., Butkiene R., Mockute D. (2007), Essential oil composition variability in sage (*Salvia officinalis* L.), *Chemija*, 18, pp. 38–43.
9. Georgiev E., Stoyanova A. (2006), *A guide for the specialist in aromatic industry*, Plovdiv.
10. ISO 9909 (1997), Oil of Dalmatian sage (*Salvia officinalis* L.).
11. Miguel G., Cruz C., Faleiro M., Simões M., Figueiredo A., Barroso J., Pedro L. (2011), *Salvia officinalis* L. essential oils: effect of hydrodistillation time on the chemical composition, antioxidant and antimicrobial activities, *Natural Product Research: Formerly Natural Product Letters*, 25, pp. 526–541.
12. Miladinovic D., Miladinovic L. (2000), Antimicrobial activity of essential oil of sage from Serbia, *Physics and Technology*, 2, pp. 97–100.
13. Pop A.-M., Muste S., Mureşan C., Pop C., Salanta L. (2013), Comparative study regarding the importance of sage (*Salvia officinalis* L.) in terms of antioxidant capacity and antimicrobial activities, *Hop and Medicinal Plants*, 41, pp. 66–74.
14. Porte A., Godoy R., Maia-Porte L. (2013), Chemical composition of sage (*Salvia officinalis* L.) essential oil from the Rio de Janeiro state (Brazil), *A Revista Brasileira de Plantas Mediciniais*, 15, pp. 438–441.
15. Raal A., Orav A., Arak E. (2007), Composition of the essential oil of *Salvia officinalis* L., from various European countries, *Natural Product Research*, 21, pp. 406–411.
16. Rajabi Z., Ebrahimi M., Farajpour M., Mirza M., Ramshini H. (2014), Compositions and yield variation of essential oils among and within nine *Salvia* species from various areas of Iran, *Industrial Crops and Products*, 61, pp. 233–239.
17. Russian Pharmacopoeia. (11th Edition), (1990), Moscow.
18. Tsankova E., Konaktchiev A., Genova E. (1994), Constituents of essential oils from three *Salvia* species, *Journal of Essential Oil Research*, 6, pp. 375–378.
19. Tucker A., Maciarello M. (2011), Essential oils of cultivars of Dalmatian sage (*Salvia officinalis* L.), *Journal of Essential Oil Research*, 2, pp. 139–144.
20. Vera R., Chane-Ming J., Fraise D. (1999), Chemical composition of the essential oil of sage (*Salvia officinalis* L) from Reunion Island, *Journal of Essential Oil Research*, 11, pp. 399–402.
21. Vernin G., Metzger J. (1986), Analysis of sage oils by GC-MS data bank – *Salvia officinalis* L. and *Salvia lavendulifolia* Vahl., *Perfumery and Flavorist*, 11, pp. 79–84.

Effect of processing parameters on the proximate composition and sensory characteristics of breadfruit 'elubo'

Tijani Akeem Olumide¹, Bakare Henry Adegoke²,
Oke Emmanuel Kehinde³, Oyedeji Ajibola Bamikole⁴

1 – National Biotechnology Development Agency, Owode Yewa, Ogun state, Nigeria

2 – Department of Hospitality and Tourism, Federal University of Agriculture, Abeokuta, Nigeria

3 – Department of Food Science and Technology, Federal University of Agriculture, Abeokuta, Nigeria

4 – Department of Biotechnology and Food Technology, Durban University of Technology, Durban, South Africa

Abstract

Keywords:

Breadfruit
Elubo
Processing
Sensory

Introduction. Breadfruit is an underutilized fruit and its utilization as food can be improved by converting it to indigenous foodstuff like elubo that has an established processing technology.

Materials and methods. The breadfruit were washed in clean water to remove adhering latex and dirt, peeled manually and chopped. The chopped breadfruit was parboiled in water at 30, 50 and 60 °C for 90, 120 and 150 min. The parboiled breadfruit was steeped for 6, 12 and 18 hrs. The steeped breadfruit was drained, dried in the cabinet dryer at 60 °C for 2 days and milled into flour (elubo) while the breadfruit paste (Amala) produced from the breadfruit flour (elubo) was subjected to sensory analysis.

Results and discussion. The moisture content of breadfruit elubo varied between 9.07 and 12.20%. The moisture content of a food sample reflects the amount of solid matter in the sample. The high ash content of breadfruit elubo (BE) is an indicative of being a good source of mineral for the flour. The values of the ash content varied between 2.00 and 2.90%. The fibre content of the breadfruit elubo varied between 2.86 to 3.60%. Parboiling temperature, parboiling time and steeping time does not significantly ($p > 0.05$) affects the fibre content of the breadfruit elubo. The protein content of breadfruit elubo varied between 3.80 and 5.42%. The protein content of the breadfruit elubo decrease irrespectively of parboiling temperature, parboiling time and steeping time. The carbohydrate content for the breadfruit elubo varied from 73.67 to 78.33%. High carbohydrate content in food implies the food is a high in calorie. The carbohydrate content of the breadfruit elubo is not significantly ($p > 0.05$) affected by the parboiling temperature, parboiling time and steeping time. The Sensory parameters of breadfruit paste prepared from breadfruit elubo were significantly ($p < 0.05$) different from paste of yam elubo (t -value=2.523, degree of freedom=14, p -value=0.01, one tailed).

Conclusion. The result revealed that breadfruit elubo has high fibre and carbohydrate content which implies that breadfruit elubo can serves as high energy food.

Article history:

Received 16.10.2016

Received in revised
form 29.11.2016

Accepted 27.12.2016

Corresponding author:

Oke Emmanuel Kehinde
E-mail:
kennyoke35@gmail.com

DOI: 10.24263/2304-
974X-2016-5-4-9

Introduction

Elubo is obtained from the conversion of yam tubers into fine flour and the unit operations involved include harvesting, sorting, peeling, slicing, blanching, drying and milling. The resulting product is a white to cream flour, which can be stored for months [1]. The quality of *elubo* is dependent on the process parameters adopted for its production. Elubo can be processed into a thick consistency food popularly called “Amala” which is prepared by reconstituting (cooking and stirring with boiling water) fermented or unfermented yam flour (*elubo*) to achieve starch gelatinization [2, 3, 4]. Amala primarily contains carbohydrates and as a result, it does not provide adequate nutrition. Amala prepared from yam flour contribute more than 200 dietary calories per capita daily for more than 150 million people in West Africa and serve as an important source of income [5].

In Nigeria, yam is the second most important source of carbohydrate after cassava [6]. Nigeria is the highest producer of yam in the World [7] producing about 38 million tonnes per annum [8] which is well over half of the world’s yams [9]. It is a seasonal crop that has competing domestic culinary uses and therefore attracts relatively higher prices during off-season period. One way to minimize this higher price during off-season period is the use of under utilized crops in the production of *elubo*, for the purpose of providing cheap and unrestricted access to this staple food.

Breadfruit (*Artocarpus altilis*) is a tropical fruit native to Malaysia and countries of the South Pacific and the Caribbean and it is an important food in these areas [10]. Breadfruits are found from sea level to about 1550 m elevation. It has been reported that breadfruit yields in terms of food are superior to other starchy staples such as cassava and yam [11]. The mature fruit is a good source of carbohydrate (84%) with starch constituting more than 60% of the total carbohydrate [12]. The bread fruit pulps are made into various dishes; it can be processed into flour and used in bread and biscuit making [13]. Breadfruit has also been reported to be rich in fat, ash, fibre and protein [14]. Despite the importance of this fruit, its production is faced with several problems including short shelf life and poor yield due to diseases [15]. The fruits are utilized in Nigeria within 5 days of harvesting because of their short shelf lives. One way to minimize post-harvest losses and increase the utilization of breadfruit is by processing into flour, which is a more stable intermediate product. Its utilization can be enhanced by converting it to *elubo*, which is the starting material for processing through reconstitution with hot water to form a paste or dough. In Nigeria, breadfruit is regarded as the poor man’s substitute for yam (*D. Rotundata* or *D. Alata*), because it can be used in the preparation of several foods for which yam was a traditional crop of choice. It also costs less than one third the price of procuring yam [16].

Extensive research from yam and cassava for “*elubo*” have been reported by several authors [17, 3, 18, 4, 19]. Information is however scanty on the use of breadfruit for “*elubo*” production. Also, if the existing technology for the production of *yam elubo* (YE) is to be adapted for breadfruit *elubo* (BE), it would be necessary to explore the effect of critical processing parameters on the some quality attributes of the *elubo* and the paste made from its reconstitution. This study therefore investigated the optimum processing conditions required for the production of breadfruit *elubo* using response surface methodology (RSM), and the sensory acceptability of the breadfruit *elubo* (BE) paste (Amala) compared to the one made from yam *elubo* (YE).

Materials and methods

Materials

Freshly harvested matured breadfruits were purchased from a local market in Idiroko, Ogun State, Nigeria. Equipment used include cabinet dryer, laboratory milling machine, mechanical sieve, digital weighing balance, stirrer, knife, bucket and stainless steel perforated tray, stainless steel pot, electric cooker were obtained from the Food processing Laboratory of Department of Food Science and Technology, Federal University of Agriculture, Abeokuta, Nigeria.

Methods

Production of breadfruit flour (“elubo”)

The method described by [4] for the production of yam flour *elubo* was adopted, with variation in parboiling time, parboiling temperature and steeping time. The fruits were washed in clean water to remove adhering latex and dirt, peeled manually and chopped. The chopped breadfruit was parboiled in water at 30, 50 and 60 °C for 90, 120 and 150min. The parboiled breadfruit was steeped for 6, 12 and 18hrs. The steeped breadfruit was drained and dried in the cabinet dryer at 60 °C for 2 days. The dried breadfruit was milled using laboratory milling machine (Fritsch, D-55743, Idar-oberstein-Germany). The milled sample was sieved using 250µm screen and stored in air-tight polyethylene bags.

Preparation of Breadfruit Paste (Amala)

“Amala” was prepared from breadfruit flour using the method described by [20]. Breadfruit paste (Amala) was prepared by adding 200g of breadfruit flour (elubo) to 200 ml of boiling water in a stainless pot. The paste was stirred manually with a wooden spoon over a low flame until a smooth consistency was attained.

Experimental design and process optimization

Box-Behnken design [21] was used for the experiment. The three independent variables used for the process optimisation were parboiling temperature (X_1), parboiling time (X_2) and steeping time (X_3). Design Expert software version 7.00 (Stat Ease Inc., Minneapolis, MN, USA). The three levels established for each of the independent variables based on a series of preliminary experiments were coded as -1, 0, and 1 with their actual values in Table 1. The design consists of 17 experimental runs to which the dependent variables (Responses) were fitted after the laboratory experiments. The measured responses were the proximate composition (Moisture, ash, protein, fibre and carbohydrate)

Experimental data were fitted to a second order polynomial model and regression coefficient the various responses were obtained. The generalized second-order polynomial used in response surface analysis was.

Where Y is the response, β_0 is the intercept, where β_1 , β_2 and β_3 are linear, quadratic and interaction coefficients respectively, x_1 , x_2 , x_3 are the various independent variables and ϵ is the error. The statistical significance of the terms in the regression equations was examined by analysis of variance (ANOVA) for each of the responses. The design expert software was used to generate response surfaces models graphs showing the relationship between the independent variable and the responses while holding a variable constant. The parameters were optimized by using the numerical method of RSM based on desirability concept to obtain range of optimised solutions which were used for the verification experiments to determine the validity of the model.

Table 1

The coded values for the independent variables

Processing Variables	Variable	-1	0	+1
Parboiling temperature (°C)	(X1)	45	30	60
Parboiling time (min)	(X2)	120	90	150
Steeping time (h)	(X3)	6	12	18

Table 2

Response surface analysis different experimental runs

Experimental Runs	Parboiling temperature (X1) °C	Parboiling time (X2), min	Steeping time (X3), h
1	60	150	12
2	45	90	6
3	60	120	6
4	30	150	12
5	45	90	18
6	45	120	6
7	30	120	6
8	45	120	12
9	30	90	12
10	45	150	18
11	45	120	12
12	30	120	18
13	60	12	18
14	45	120	12
15	45	150	6
16	45	120	12
17	60	90	12

Determination of proximate composition of breadfruit elubo

Moisture content and crude fibre content of breadfruit elubo were determined by AOAC method. Crude protein was determined by the standard kjeldahl method, AOAC method. Fat content of the samples were measured using Soxhlet extraction method according to AOAC method. Ash content was determined by igniting 5g of sample in a furnace for 4hours at 550 °C until light grey ash colour and constant weight was achieved by [22].Carbohydrate content were determined by difference method. The analyses were carried out in triplicates.

Sensory evaluation of breadfruit paste (Amala)

Simple paired comparison was used to compare the difference between *amala* made from breadfruit elubo (BE) and yam elubo (YE). Thirty untrained panelists were asked to rate the colour, mouldability, taste, aroma, smoothness, elasticity, stickiness and hardness of the respective *amala* samples

Statistical analysis

Apart from the statistical method used as an integral part of the RSM. Independent t-test was also used to evaluate the result of the sensory analysis conducted on the amala.

Results and discussion

Effect of process variables on moisture content of breadfruit elubo (BE)

In Table 3, the regression coefficients of the quadratic models for the response variable, along with the corresponding p-value are presented. Coefficient values less than 0.05 indicated that the model was significant. In this case, the linear coefficient of parboiling temperature (X_1), steeping time (X_3) had a significant impact on the moisture content. The quadratic effects of the parboiling temperature, time and steeping time had negative significant ($p < 0.05$) effect on the moisture content. However, the interactive effects of all the process variables except for parboiling temperature and steeping time (X_1X_3) had no significant ($p > 0.05$) impact on the moisture content. Moisture content of breadfruit elubo varied between 9.07 and 12.20%. The moisture content of a food sample reflects the amount of solid matter in the sample. The higher the moisture content, the higher the rate of spoilage. Adebowale *et al.*, [23] stated that moisture content is a measure of the water content and also an indicator of shelf stability. Figure 1 shows the effect of the process variables on the moisture content of breadfruit elubo. From the figure, increase in parboiling temperature (PT) and parboiling time (Pt) brought about an increase in moisture content at constant steeping time (ST). A similar trend was observed when increasing ST and PT using a constant level of Pt. From the results, at a higher ST and Pt, there was an increase in moisture content of the breadfruit elubo. This may be as a result of decrease in porosity which will lead to an increase in moisture content. The higher moisture content observed for breadfruit elubo may be due to the thick slices (50–60 mm) used. Babajide *et al.*, [4] earlier reported that thick slices (30–50 mm) had significant higher moisture content than slices less than 30mm. Increase in moisture content can enhance microbial growth which leads to deterioration in foods. FAO [6] recommended a safe level of 12 to 14% moisture content for flour or powdered food

Table 3

Regression Coefficients for moisture content of BE

Factors	Coefficient Estimate	Standard error	p-values
Constant	12.16	0.078	< 0.0001
Parboiling Temp(x_1)	0.096*	0.061	0.1605
Parboiling Time(x_2)	0.14	0.061	0.0547
Steeping Time(x_3)	1.37*	0.061	< 0.0001
P Temp·P Time(x_1x_2)	0.013	0.087	0.8894
P Temp·S Time(x_1x_3)	-0.25*	0.087	0.0236
P Time·S Time(x_2x_3)	0.030	0.087	0.7395
P Temp·P Temp(x_1^2)	-0.81*	0.085	< 0.0001
P Time·P Time(x_2^2)	-1.03*	0.085	< 0.0001
S Time·S Time(x_3^2)	-0.52*	0.085	0.0004

*Significant at $p < 0.05$, P=parboiling, x_1 =parboiling temperature, x_2 =parboiling time and x_3 =steeping time

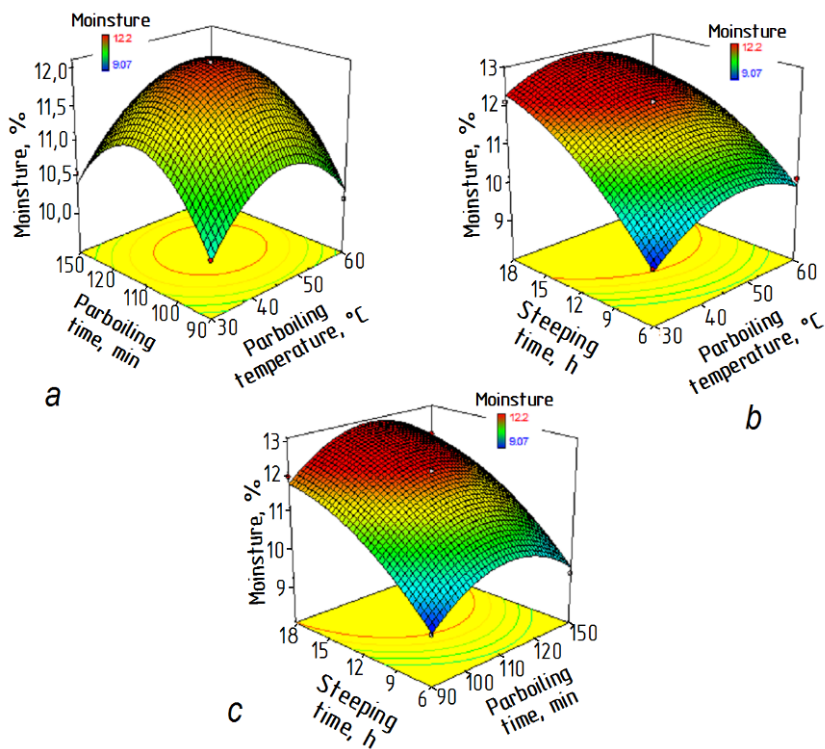


Figure 1. Response surface plot for Moisture content (%) of BE
 (a – steeping time = 12; b – parboiling time – 120; c – parboiling temperature = 45)

Effect of process variable on protein content of breadfruit elubo (BE)

An acceptable second-order polynomial regression equation (2) as a function of parboiling temperature, time and steeping time was generated for the protein content after the removal of non-significant terms as follows:

$$Y = 4.41 + 0.04X_2 - 0.77X_3 + 0.36X_1^2 - 0.36X_2^2 - 0.19X_3^2 \quad (2)$$

where X_1 , X_2 and X_3 represent coded values of parboiling temperature and steeping time, respectively and Y is the response variable (BE protein content).

In table 4, the regression coefficients of the quadratic models for the response variable, along with the corresponding p-value were presented. Coefficient values less than 0.05 indicate that the model is significant. In this case, the linear coefficient of parboiling time (X_2), steeping time (X_3) had a great impact on the protein content. The quadratic effects of the parboiling temperature, time and steeping time had negative significant ($p < 0.05$) effect on the protein content. However, the interactive effects of all the process variables had no significant ($p > 0.05$) impact on the protein content. The protein content of the breadfruit *elubo* varied between 3.80 and 5.42%, within the experimental conditions. The response surface plots for protein content at different experimental conditions are presented in Figure 2. From the figures, it can be observed that increasing PT and Pt at constant ST decreases protein content at constant Pt increase in ST and PT results in low protein content. Also, increasing ST and Pt when PT is constant lowers the protein content of the breadfruit *elubo*.

The effect of parboiling and steeping on the protein content of the breadfruit *elubo* probably maybe due to the denaturation of protein caused by the effect of heat on the breadfruit slices during parboiling. This is an indication that protein content of breadfruit flour can be influenced by using appropriate set of processing parameters. This shows that protein content will decrease irrespectively of parboiling temperature, parboiling time and steeping time [27].

Table 4

Regression coefficient for protein content of BE

Factors	Coefficient Estimate	Standard error	p-values
Constant	4.41	0.018	< 0.0001
Parboiling Temp(x_1)	0.02	0.014	0.3186
Parboiling Time(x_2)	0.04*	0.014	0.0313
Steeping Time(x_3)	-0.77*	0.014	< 0.0001
P Temp·P Time(x_1x_2)	0.00	0.020	1.0000
P Temp·S Time(x_1x_3)	-0.02	0.020	0.3451
P Time·S Time(x_2x_3)	-0.03	0.020	0.1727
P Temp·P Temp(x_1^2)	0.36*	0.019	< 0.0001
P Time·P Time(x_2^2)	0.36*	0.019	< 0.0001
S Time·S Time(x_3^2)	-0.19*	0.019	< 0.0001

*Significant at $p < 0.05$, P=parboiling, x_1 =parboiling temperature, x_2 =parboiling time and x_3 =steeping time

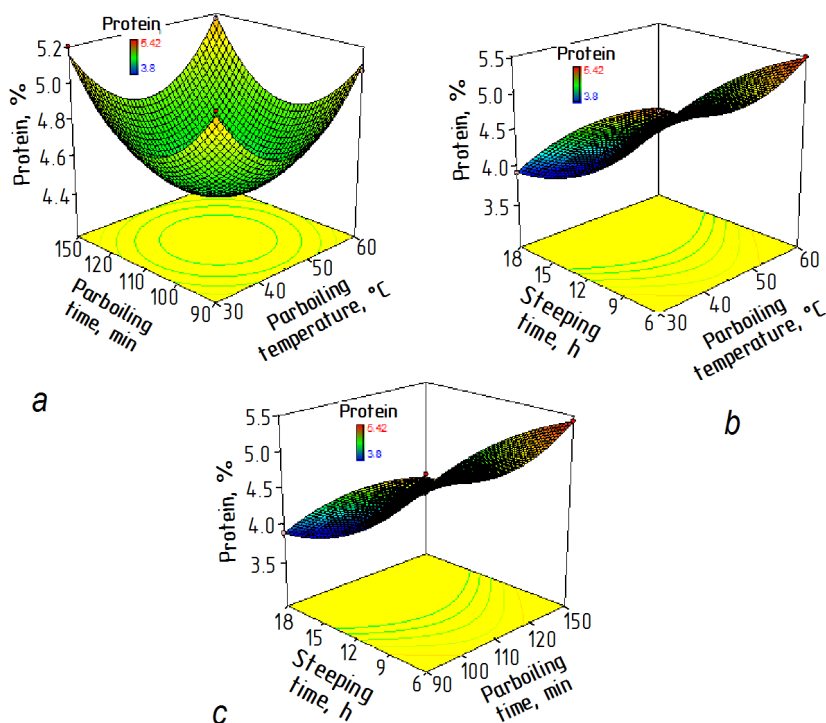


Figure 2. Response surface plot for Protein (%) content of BE
(a – steeping time = 12; b – parboiling time – 120; c – parboiling temperature = 45)

Effect of process variable on ash content of breadfruit elubo (BE)

In table 5, the regression coefficients of the quadratic models for the response variable, along with the corresponding p-value were presented. Coefficient values less than 0.05 indicate that the model is significant. The quadratic, interactive and the linear effect has no significant effect on the ash content. The values of ash content for breadfruit *elubo* varied between 2.00 and 2.92%. Ash content is a reflection of mineral status, even though contamination can indicate a high concentration in a sample. The ash content of breadfruit *elubo* (BE) was higher than 2.07% reported for sweet potatoes *elubo* by Fetuga *et al.*, [20] and 2.03% reported by Babajide *et al.*, [24] for yam *elubo*. The high ash content of the flour is indicative of being a good source of minerals. Breadfruit *elubo* would therefore, be a better source of minerals than sweet potatoes and yam *elubo*. Figure 3 shows the effect of the process variable on the ash content of breadfruit *elubo*. From the figure, It was observed that increasing PT and decrease in Pt when ST is constant increases ash content while decreasing ST and increasing PT at constant Pt increases ash content. At a constant PT, increase in ST and Pt decreased the ash content of the breadfruit *elubo*. This maybe because of the leaching of soluble minerals from the breadfruit [4]

Table 5

Regression coefficient for ash content of BE

Factors	Coefficient Estimate	Standard error	p-values
Constant	3.09	0.081	0.2391
Parboiling Temp(x_1)	-0.07	0.064	0.8072
Parboiling Time(x_2)	-0.01	0.064	0.3275
Steeping Time(x_3)	0.11	0.064	0.1194
P Temp·P Time(x_1x_2)	0.04	0.064	0.9153
P Temp·S Time(x_1x_3)	-0.13	0.091	0.6916
P Time·S Time(x_2x_3)	$-2.5 \cdot 10^{-3}$	0.091	0.0496
P Temp·P Temp(x_1^2)	0.11	0.091	0.1826
P Time·P Time(x_2^2)	-0.14	0.088	0.1658
S Time·S Time(x_3^2)	-0.06	0.088	0.3146

*Significant at $p < 0.05$, P=parboiling, S=steeping, x_1 =parboiling temperature, x_2 =parboiling time and x_3 =steeping time

Effect of process variable on crude fibre content of breadfruit elubo (BE)

The quadratic effect linear effect and the interaction effect of the parboiling temperature, parboiling time and steeping time does not significantly ($p > 0.05$) affects the fibre content of the BE. The fibre content of breadfruit *elubo* varied between 2.86 to 3.60%. The fibre content of breadfruit *elubo* was higher than yam *elubo* (1.65%) reported by Babajide *et al.*, [24], but lower than 3.2% reported by Fetuga *et al.*, [20] for sweet potato *elubo*. Fibre is reported to plays a significant role in the prevention of several diseases such as; cardiovascular diseases, diverticulosis, constipation, irritable colon, cancer and diabetes [25, 26]. Figure 4 shows the response surface plots for the crude fibre at different experimental condition. From the figure, it was observed that increasing PT and Pt when steeping time is constant decreases fibre content while increasing ST and PT at constant Pt increases fibre content. At a constant PT, increase in ST and Pt increases the fibre content of the breadfruit *elubo*. It was shown that parboiling temperature, parboiling time and steeping time does not significantly ($p > 0.05$) affects fibre content of the breadfruit, this was in accordance with Adejumo *et al.*, [27].

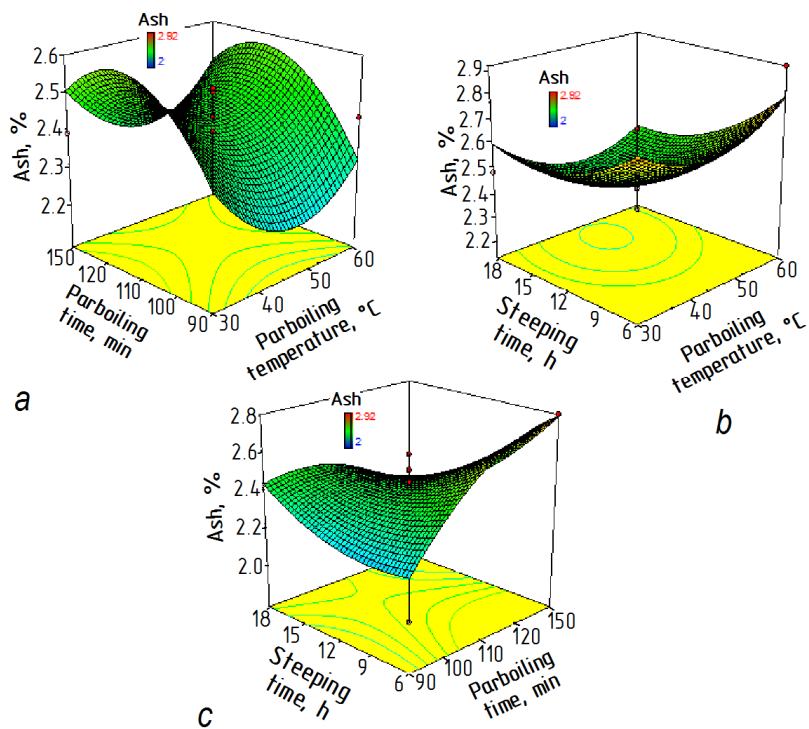


Figure 3. Response surface plot for Ash (%) content of BE
 (a – steeping time = 12; b – parboiling time – 120; c – parboiling temperature = 45)

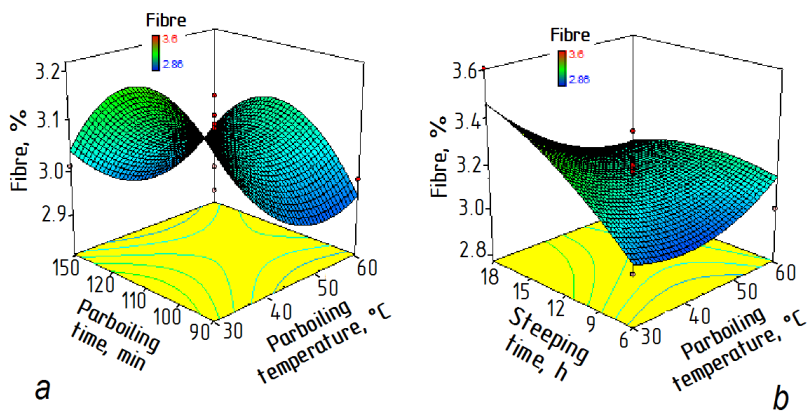


Figure 4. Response surface plot for Fibre (%) content of BE
 (a – steeping time = 12; b – parboiling time = 120)

Effect of process variable on carbohydrate content of breadfruit elubo (BE)

The main effect and the interaction effect of the parboiling temperature, parboiling time and steeping time does not significantly ($p>0.05$) affects the carbohydrate content of the BE. The carbohydrate content for the *breadfruit elubo* ranged from 73.67 to 78.33%. High carbohydrate content in food implies the food is a high in calorie. The carbohydrate of the breadfruit *elubo* in this research is lower than Fetuga *et al.*, [20], which reported a value of 87.68% for sweet potatoes *elubo*. The response surface plots for carbohydrate content at different experimental conditions are presented in Figure 5. It was observed that increasing PT and Pt at constant ST resulted in decrease in carbohydrate content increasing ST and PT at constant Pt decreases carbohydrate content. At a constant PT, increase in ST and Pt decreases the carbohydrate content of the breadfruit *elubo*. The carbohydrate content of the breadfruit *elubo* is not significantly ($p>0.05$) affected by the parboiling temperature, parboiling time and steeping time. The result obtained in this work is similar to the findings of Akissoe *et al.*, [28], which reported that different cultivars have varied carbohydrate content of yam *elubo*.

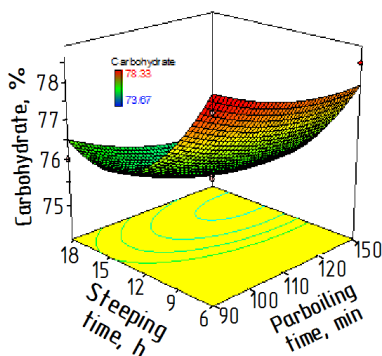


Figure 5. Response surface plot for Carbohydrate (%) content of BE (parboiling temperature = 45)

Comparison of amala made from breadfruit elubo and yam elubo

The mean difference between conditions was 5.00 and the 95% confidence interval for the estimated population is between 0.68 and 6.57. The independent t-test showed that the difference between conditions were significantly different ($t\text{-value}=2.523$, degree of freedom=14, $p\text{-value}=0.01$, one tailed). This implies that the sensory attribute of cooked paste prepared from breadfruit elubo were different from paste of yam flour. This could be due to the familiarity of the panel to traditionally processed yam paste (amala) which is free from odour, stickier, and darker in colour than breadfruit amala.

Conclusion

It can be inferred from this study that breadfruit elubo can be developed into a cooked paste (*Amala*). Response surface methodology was successfully utilized for optimization of the proximate composition of breadfruit *elubo*. However, the breadfruit elubo has high fibre and carbohydrate content which implies that breadfruit elubo can serve as high energy food and can be used to improve the health benefit of the consumer.

Reference

1. Adediji K.K. (2010), *Physical, functional and sensory properties of yam flour 'elubo' obtained from Kuto- market, Abeokuta*. B.Sc Thesis, Federal University of Agriculture, Abeokuta.
2. Akingbala J.O., Oguntimien T.B, Sobande A.O. (1995), Physio-chemical properties and acceptability of yam flour substituted with soy flour, *Plant Food for Human Nutrition*, 48, pp. 73–80.
3. Akissoe N., Hounhouigan D.J., Bricas N., Vervier P., Nago C.M, Olorunda A. (2001), Physical, chemical and sensory evaluation of dried yam (*Dioscorea cayenensis rotundata*) tubers, flour, and amala a flour-derived product, *Tropical Science*, 4, pp. 151–155.
4. Babajide J. M., Henshaw F.O, Oyewole O.B. (2006), Effect of Processing Variables on the Quality of Traditional Dry Yam Slices, *European Journal of Science*, 14, pp. 102–113.
5. Babaleye T. (2003), *Raising the status of the yam, a major food crop in West Africa*, Anbba supplement issue/edition, No. 463.
6. F.A.O. (1994), *Tropical root and tuber crops. In: Production, perspectives and future prospects. FAO plant production and protection paper*, 126, Rome, Italy.
7. F.A.O. (2008), *Food and agriculture organisation. Action programme for the prevention of food losses, improving post-harvest handling, storage and processing of root and tuber crops*, Rome, Italy.
8. F.A.O. (2012), *Production yearbook, vol. 55, collection FAO statistics, No. 170. FAO*, Rome, Italy.
9. Onwueme I.C. (1978), *The tropical root crops*, John Wiley and Sons, New York.
10. Taylor M.B, Tuia V.S. (2007), Breadfruit in the pacific region, *Acta Horticulturae*, 757, pp. 43–50.
11. Singh H. (2009), *Tapping into breadfruit's bounty*, Available at: http://www.universityaffairs.ca/tapping-into-breadfruits_bounty.aspx
12. Oladunjoye I.O., Ologhobo A.D, Olaniyi C.O. (2010), Nutrient composition, energy value and residual anti-nutritional factors in differently processed breadfruit (*Artocarpus altilis*) meal, *African Journal of Biotechnology*, 9(27), pp. 4259–4263.
13. Amusa N.A., Kehinde I.A, Ashaye O.A. (2002), Bio-deterioration of breadfruit (*Artocarpus communis*) in storage and its effects on the nutrient composition, *African Journal of Biotechnology*, 1(2), pp. 57–60.
14. Ragone D. (1997), *Breadfruit (Artocarpus altilis): Promoting the conservation and use of underutilized and neglected crops*, Institute of plant genetics and crop plant research, Gatersleben International Plant Genetic Resources Institute, Rome.
15. Olaoye O.A., Onilude A.A, Oladoye C.O. (2007), Breadfruit flour in biscuit making: Effects on product quality, *African Journal of Food Science*, pp. 20–23.
16. Olutayo M.M., John O. A., Gail S.O., Baccus H.T, Sydney T.O. (2003), Evaluation of breadfruit (*Artocarpus communis*) in traditional stiff porridge foods, *Food, Agriculture and Environment*, 1(2), pp. 54–59.
17. Oyewole O.B, Odunfa S.A. (1988), Microbiological Studies on Cassava Fermentation for Lafun Production, *Food Microbiology*, 5, pp.125–133.
18. Mestres C., Dorthe S., Akissoe N, Hounhouigan J.D. (2004), Prediction of sensorial properties (colour and taste) of amala: A paste from yam chips flour of

- West Africa, through flour biochemical properties”, *Plant Foods Human Nutrition*, 59, pp. 93–99.
19. Nwabueze T.U, Odunsi F.O. (2007), Optimization of process conditions for cassava (*Manihot esculenta*) lafun production, *African Journal of Biotechnology*, 6, pp. 603–611.
 20. Fetuga G.O., Tomlins K., Bechoff A., Henshaw F.O., Idowu M.A, Westby A. (2014), Effect of variety and processing method on functional properties of traditional sweet potato flour (elubo) and sensory acceptability of cooked paste (amala), *Food Science and Nutrition*, 2(6), pp. 682–691.
 21. Box G.E.P, Behnken D.W. (1960), Some New Three Level Designs for the Study of Quantitative Variables, *Technometrics*, 2, pp. 455–462.
 22. AOAC. (2000), *Official methods of analysis. 17th edn.*, The Association of Official Analytical Chemists, Virginia.
 23. Adebowale A.A., Sanni L.O, Awonorin S. O. (2005), Effects of texture modifiers on the physicochemical and sensory properties of dried fufu, *International Journal of Food Science and Technology*, 11(5), pp. 373–382.
 24. Babajide J.M., Oyewole O.B, Obadina A.O. (2005), An assessment of the microbiological safety of dry yam (gbodo) processed in south west Nigeria, *African Journal of Biotechnology*, 5(2), pp. 157–161.
 25. Slavin J.L. (2005), Dietary fibre and body weight, *Journal of Nutrition*, 21, pp. 411–418.
 26. Elleuch M., Bedigian D., Roiseux O., Besbes S., Blecker C., Attia H. (2011), Dietary fibre and fibre-rich by-Products of food processing: characterization, technological functionality and commercial applications: A Review, *Food Chemistry*, 124, pp. 411–421.
 27. Adejumo B.A., Okundare R.O., Afolayan O.I, Balogun S.A. (2013), Quality attributes of yam flour (elubo) as affected by blanching water temperature and soaking time, *The International Journal of Engineering and Science*, 2(01), pp. 216–221.
 28. Akissoe W.H., Hounhouigan J.D., Mestres C., Nago M. (2003), How blanching and drying affects the colour and functional characteristics of yam (*D. cayenensis rotundata*) Flours, *Food Chemistry*, 82, pp. 257–264.

Usage of the nut raw materials and chia seeds to improve fatty acid composition of the smoothies

Andgela Dyakonova, Victoria Stepanova

Odesa National Academy of Food Technologies, Odesa, Ukraine

Abstract

Keywords:

Nut
Chia
Fatty acid
Drink
Smoothies

Article history:

Received 12.10.2016
Received in revised
form 21.12.2016
Accepted 27.03.2016

Corresponding author:

Victoria Stepanova
E-mail:
upiu@ukr.net

DOI: 10.24263/2304-
974X-2016-5-4-10

Introduction. Today, the ways of using nut, seed raw materials and its combinations as a source of essential fatty acids for healthy products are not sufficiently investigated.

Materials and methods. We have investigated the composition of ingredients of the universal base for the beverage industry. The content of proteins, fats, carbohydrates, ash and caloric of product was determined. With the help of the gas chromatography method, fatty acid structure of the prescription components was investigated and the ratio of ω -3 and ω -6 fatty acids in ready-made product was found out. We studied the amino acid content of the developed composition, its viscosity and storage stability.

Results and discussions. The authors suggested 9 recipes of smoothies drinks with different organoleptic characteristics. The results show, that 250 cm³ of the investigated drinks can satisfy daily need of the healthy person in linolenic and linoleic acids on 30 %, because their content in the prepared drinks is accordingly at least 0,5 g and 2 g. Such drinks are recommended to all groups of population, especially to people, who have a disease of cardiovascular system or wish to support its work in normal state.

Usage of chia seeds and walnuts significantly increase the content of biologically valuable substances in beverages. Chia seeds significantly affect on the rheological parameters of smoothies, increasing density and viscosity of drinks due to mucous substances of seeds' grains and also provides stability of fatty system at storage. The ability of chia seeds to create sliminess is explained by content of water-soluble polysaccharide – pentozans, which constituted to 8 % weight of grain seed. The findings suggest that the usage of chia seeds as part of a universal base maintains its stability by 100 % during 24 hours, which fully meets the needs of public catering establishments. Proteins which are a part of walnut – seed basis for smoothie drinks production have perfect composition. The limiting amino acids are lysine, methionine + cysteine, treonin and valin.

Conclusions. For the first time the possibility of using chia seeds as a structurant of smoothie drinks and ingredients composition for the production of universal bases for beverages, which has a balanced content of ω -3 and ω -6 fatty acids were studied.

Introduction

The analysis of statistical researches of physicians demonstrates that for the last year thousands people died because of cardiovascular system diseases [1]. These indexes show the necessity of disease prevention of such a type. One of the aspects of cardiovascular system diseases is the healthy nutrition and the usage of products which have positive influence on cardiovascular system.

In solving the problem of a large number of human diseases is important to providing the population with products of healthy food. A creation and implantation in the structure of foodstuffs which contains physiologically valuable natural ingredients that are capable to renew the content of scarce essentially nutrients and to weaken negative technogenic influence of environment on a human body is necessary. The market of products of healthy food constantly develops, but the main part of such products in our country is replenished by foreign producers.

Usage of various technologies of processing of food raw materials is accompanied by considerable decrease of content of native foodstuffs in diet of modern people. Technological operations deprive food of the important biologically active substances which are necessary for normal functioning of human organism which leads to different diseases that are called "diseases of civilization".

That's why the creation of multicomponent products of healthy food on the basis of natural raw materials, that contains biologically and physiologically necessary ingredients for human health recovering and expansion of their range, belongs to actual problems of the present day. With the help of combination of various natural raw materials and product recipe modeling, it is possible not only to weaken the influence of external negative factors on a human constitution, but also to get a product of new generation, which will prevent from alimentary-related conditions and diseases.

Formulation of the task. Design of functional food fat-containing products provides for the creation of the structures balanced by optimum composition of irreplaceable fatty acids and fat-like substances that have the corresponding functional and improving properties. For the correction of food diets and optimization of fatty balance, various fatty seasonings, such as pastas and sauces are included which usually have high caloric content and are not recommended as a food for certain diseases.

The previous researches showed us the necessity of creation of products for the daily use which have the low caloric content and the balanced fat and acid structure.

Now a considerable popularity as the products of healthy food, have got smoothie drinks that are prepared from fresh fruits, vegetables and berries. Smoothies are the drinks with stiff consistence that are more like desserts. Some consumers replace with this product one meal that's why the biological value of smoothie should be high and has healthy properties.

Analysis of scientific works

Prevention of cardiovascular system diseases demands the adequate balanced food. One of the main causes of such diseases is insufficient intake of polyunsaturated fatty acids, which are responsible for a lipoid metabolism in human organism. The main sources of these substances are products with high content of fat, especially of vegetable origin.

Within the last two decades fatty products became the object of close attention of both foreign and native scientists. It is connected with the fact, that fats are included into the

main three feedstuffs with proteins and carbohydrates and contain functional ingredients – polyunsaturated fatty acids, phospholipids and fat-soluble vitamins. Non-saturated fatty acids such as ω -3, ω -6 and ω -9 play an important role in maintaining the health of each person and are involved in metabolism. They influence favorably on immune, cardiovascular and nervous systems of an organism. These fatty acids are very important for the person, but they are not synthesized or synthesized in our organism in small quantities. A lot of authors singled out the so-called vitamin F, which contains essential linoleic and linolenic acids, which are the main components of ω -6 and ω -3 fatty acids.

The majority of the foodstuff that is widely used around the world contains ω -3 and ω -6 fatty acids in the unbalanced ratio. The balanced content of ω -3 and ω -6 fatty acids in food is required to support the balance of hormonal, cellular and other metabolic processes in organism. It is well known that for the best digestion of fatty acids such as ω -3 to ω -6, the ratio of 1 to 4 is necessary. Today, according to the World Health Organization in the majority of food diets of people the ratio is of 1:10 to 1:20 depending on age and eating habits of interviewed persons [2].

Despite these data, foods balanced with fatty acid composition produced in a small amount. For example, most of the healthy foods take drinks, and very popular healthy drink is smoothies. Usage of smoothie drinks grows every year, but there is not a smoothies with balanced fatty acid composition. Today smoothies are prepared and suggested almost in all public catering establishments, but the investigation of their physical and chemical indicators and their influence on human organism is not complete and it is paid not so much attention to the study of such a question.

Now the researches of European countries found that high active acidity of smoothie leads to the formation of tooth enamel erosion [3]. In Europe, the production technology of smoothie is created for gerodietetic food products, smoothie of radio protection effect on a grain basis and smoothie which is prepared on the basis of feijoa for people who have lack of iodine in organism [4, 5, 6].

The purpose of the work is studying of possibility to use of walnuts and chia seeds as a source of essential fatty acids in the universal basis for drinks.

Materials and methods

Investigated materials

Fruit, berry or vegetable raw materials are carefully crushed in a mashed state during preparing of smoothie drinks. Such mashed sauces are very dense and viscous that's why the producers adjust their consistence by the adding of water, crushed ice, juice, ice cream or milk. In addition to enrich the product with biologically valuable substances and to make the smoothie with juice spice taste, we proposed to use a liquid universal basis in the form of walnut-seed composition, which is made of vegetable milk and chia seeds.

To increase the content of polyunsaturated fatty acids particularly ω -3 and to ensure the desirable rheological properties of the product chia seeds are used by us. 100 g of chia seeds contain more than 20 g of protein and about 35 g of fat and 38 g of carbohydrates [7]. Chia seeds are valued as natural product which have curative properties because polyunsaturated fatty acids of chia seeds are presented in 41–59 % alpha-linolenic (ω -3) fatty acid and 18–25 % linoleic (ω -6) fatty acid.

In this research chia seeds are chosen as the object of the research that are cultivated in Paraguay and bought in ecomarket; vegetable milk of own production which was derived

from a Walnuts kernel according the technology that was suggested by us and created smoothie drinks.

Milk from a Walnuts kernel can be prepared in two ways: the first way includes frying of the Walnut kernel, separation of the Walnut shell, soaking of the kernel in 7 fold volume of water with further soaking and careful crushing with the help of blender. A prepared mixture is sustained at the room temperature within 30 minutes and then crushed to the state of emulsion and filtered.

Preparation of vegetable milk by the second way allows using crude Walnut kernels which are presoaked in water for 6–8 hours, and then they are carefully washed out, boiled and mixed up in 7 fold volume of water and crushed. The prepared mixture is filtered and subjected to fine-dispersed grinding again. For the basics, which is recommended to be used for the smoothie drink production, vegetable milk from the Walnuts kernel is mixed up in a certain proportion with chia seeds. For this purpose chia seeds are weighted and added to the nut milk and carefully mixed up and sustained for swelling.

Depending on what technology vegetable milk was prepared, the difference in organoleptic indicators of ready drinks is observed. Milk from the roasted kernel has more expressed nutty flavor and creamy color and milk from crude nuts has white color and more neutral flavor.

It should be noted, that substitution of milk of an animal origin by vegetable nut milk significantly increases a number of consumers of the created smoothies. Vegetarians, people who are not capable to take milk proteins and lactose in, can use this product and it also can be used during a post.

We used in our research the first way of preparing vegetable milk from a Walnut kernel.

Description of the methods and facilities

For the definition of physical and chemical indicators of products, standard methods described in special literature are used. Determination of viscosity of liquids was carried out by Ostwald's method [8]. The moisture, fat and ash contents were determined using standard methods [9]. Protein content was determined by Kjeldahl [10,11].

Isolation and separation of emulsion visually evaluated in a static beaker test method after a certain period of time (eg, 4 hours). Further statistical test is performed in a separatory funnel by measuring changes in concentration. In this case, change in the concentration of emulsion at the bottom of the separating funnel after a predetermined time is also determined and compared to the initial concentration of the emulsion immediately after mixing [12].

Determination of the total fat content [13]. To determine fatty acid content in the created products of gas chromatography method is used [14, 15]. Researches were conducted on the gas chromatograph Shimadzu GC chromatograph-14a with a flame ionizing detector according to the ISO 5508-2001 standard.

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

Results and discussions

Scientists have proved, that daily intake of ω -3 and ω -6 fatty acids for the healthy person depending on age and body weight is accordingly an average of 1,4 and 5,6 g [16]. To give smoothie healthy effect on cardiovascular system, the content of polyunsaturated fatty acids in drinks should be raised for creating required ratio of ω -3 and ω -6 fatty acids, that's why these criteria were chosen as the main ones during modeling fatty basis for the production of smoothie drinks. The content of basis recipe components for the production of smoothie is given in the Table 1.

Table 1
Formulation of the basis for the production of smoothies

Raw materials	Components content	
	Brutto, g	Netto, g
Walnut kernels	20	15
Chia seeds	1,67	1,67
Drinking water	150	150

According to the standard methods, the content of some biologically valuable substances in the created basis of smoothie drinks was determined. The research results are shown in Table 2.

Table 2
Chemical composition of bases

Name	Content g / per serving (150 g)
Proteins	2,89 ± 0,2
Fats	5,0 ± 0,2
Carbohydrates	2,85 ± 0,1
Ash	0,63 ± 0,02
Dietary fiber	2,46 ± 0,05
Calorie, kcal	119,3

If to compare chemical composition of the developed basis with a composition of ice cream sundae or creamy ice cream [17], which is often used as a basis for production of smoothies, we can conclude, that our basis has almost 2 times less calories, contains almost identical amount of protein, but at the same time contains 8 times less carbohydrates and twice less fats and also it contains all the necessary for our organism vitamins and dietary fibers. It should be pointed out, that ice cream fats are presented by saturated fatty acids the number of which in the diet of modern person is more than the daily need in contrast with the created composition.

For substantiation of healthy properties of drinks and the appropriateness of the use of the created smoothies for the prevention of cardiovascular diseases, the research of the content of the main polyunsaturated fatty acids was made; the quantity of ω -3, ω -6, ω -9 fatty acids and their ratio in the created basis for smoothie drinks is counted. Results of the research are given in Table 3.

Table 3

The content of essential fatty acids in the developed compositions

Fatty acid name	Fatty acid Lipid formula	Content in portion (150 g), g	Content in portion (150 g), %
Alpha-linolenic	18:3	0,56 ± 0,01	11,2
Linoleic	18:2	2,14 ± 0,05	42,8
Oleic	18:1	0,65 ± 0,01	13,0
∑ω-3		0,69 ± 0,01	13,9
∑ω-6		2,77 ± 0,05	55,4
∑ω-9		0,8 ± 0,01	16,0
∑ω-3: ∑ω-6			1:4

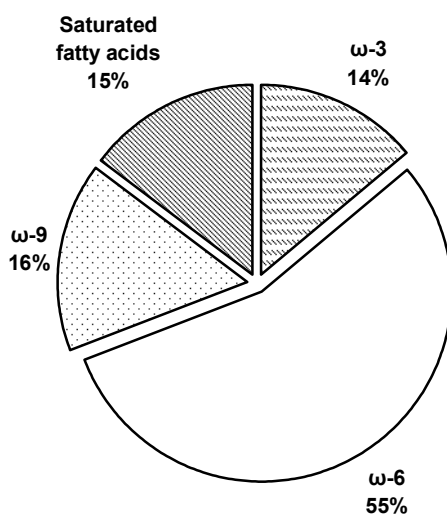


Figure 1. The content of fatty acids in the developed based

Taking into consideration the fact that walnuts and chia seeds contain a significant number of proteins the research of qualitative composition of proteins of the created composition was made and its amino-acid structure is determined. Results of research are presented in Figure 2.

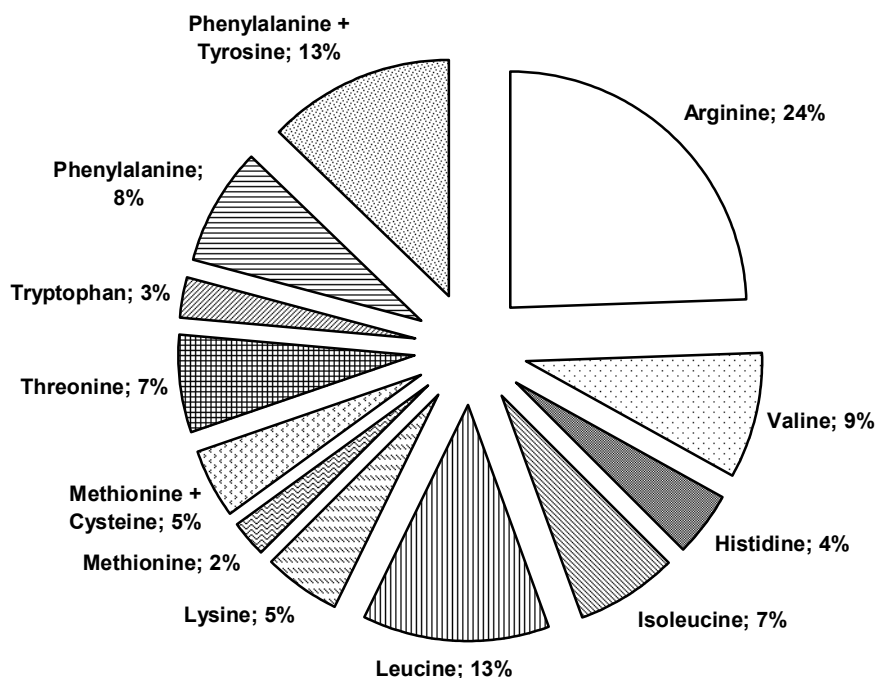


Figure 2. Amino acid composition of the nut-seeds bases for the production of the smoothies

For determination of biological value of proteins of the created walnut and seed composition amino-acid is counted. Calculation of amino acid score is reduced to calculating the percentage of each amino acid in the test protein relative to their content in the protein as a reference, according to this formula:

$$AS = \frac{AKh}{AKc} \cdot 100\%$$

where AKc – contents of amino acids in standard protein;
 AKh – contents of amino acids in the researched protein.
 Proteins of chicken egg are taken for a standard.

Limiting are those essential acids, amino acid score of which is less than 100%.

From the results of the research we can make a conclusion that proteins which are a part of walnut – seed basis for smoothie drinks production have perfect composition. The limiting amino acids are lysine, methionine + cysteine, treonin and valin.

Samples of the created smoothies belong to the non-Newtonian pseudo-plastic liquids, the increasing shear rate of which influences on falling of effective viscosity. Viscosity of vegetable milk is caused mainly by its proteinaceous and mucous components. It should be

pointed out, that during the contact of chia seeds with liquid on a surface of each grain of seed the gel cover is appeared, which is characterized by high content of soft and soluble food fibers. The ability of chia seeds to create sliminess is explained by content of water-soluble polysaccharide – pentozans, which constituted to 8 % weight of grain seed. These gels significantly affect on the structural and mechanical properties of the developed smoothies, provide the necessary structure and prolong the stability of the system.

Table 4

Amino-acid score of universal bases for the production of smoothies

Amino acid	Amino acid score, %
Isoleucine	102,79
Leucine	102,32
Lysine	54,11
Methionine + Cysteine	76,37
Phenylalanine + Tyrosine	118,94
Treonine	92,34
Tryptophan	150,52
Valine	96,02

From the results of the research we can make a conclusion that proteins which are a part of walnut – seed basis for smoothie drinks production have perfect composition. The limiting amino acids are lysine, methionine + cysteine, treonin and valin.

Samples of the created smoothies belong to the non-Newtonian pseudo-plastic liquids, the increasing shear rate of which influences on falling of effective viscosity. Viscosity of vegetable milk is caused mainly by its proteinaceous and mucous components. It should be pointed out, that during the contact of chia seeds with liquid on a surface of each grain of seed the gel cover is appeared, which is characterized by high content of soft and soluble food fibers. The ability of chia seeds to create sliminess is explained by content of water-soluble polysaccharide – pentozans, which constituted to 8 % weight of grain seed. These gels significantly affect on the structural and mechanical properties of the developed smoothies, provide the necessary structure and prolong the stability of the system.

Table 5

Change of rheological parameters of the bases for the production of smoothies, during storage

Indicator	Storage life, h			
	4	8	12	24
Viscosity, Pa·s	1,497	1,530	1,535	1,550
Stability, %	100	100	100	100

To expand the range of smoothies recipes of three drinks types – berries, fruits and vegetables were developed. Recipes of the developed beverages are presented in Table 6.

Table 6

Content of formulation components in smoothies

Ingredients	Berries smoothie			Fruits smoothie			Vegetables smoothie		
	The content of components, g								
	1	2	3	4	5	6	7	8	9
Bases for the production of the smoothies	150	150	150	150	150	150	150	150	150
Blueberries	50								
Strawberries		70							
Cherry			70						
Peaches				70		70			
Apricots					70				
Frozen melon pulp						50			
Cucumbers							90	80	80
Lemon	2						10	10	
Mint								30	
Spinach							30		50
Frozen banana	50	50	50	50	50				
Optional									
Sugar	5		5	5	5	5			
or fructose	2,8		2,8	2,8	2,8	2,8			
or honey	3,3		3,3	3,3	3,3	3,3			

For justification of expediency of use of the created basis for the production of smoothie drinks we compared the content of polyunsaturated fatty acids in the created basis and in smoothie that was made without its usage, but on the basis of drinking water. Drinks that are made according to the developed recipes, but on water basis contain from 0 to 0,068 g of polyunsaturated fatty acids in the ready drink and haven't preventive effect on cardiovascular system of the person. While drinks on the basis of walnut - seed composition contain from 2,58 g of polyunsaturated in ready smoothie and satisfy daily need in these functional ingredients at least for 30%.

Conclusion

The results of analytical and experimental researches confirms that the nut oils and fats in chia seeds, which are taken in the right proportions, providing the right balance of polyunsaturated fatty acids in universal composition which should be used as a basis for smoothie drink production. The basis is like liquid of emulsion type with impregnation of chia seeds, which has neutral taste, nutty flavor and combines well with any raw material.

Usage of this composition in smoothie drink gives an opportunity to raise the content of essential fatty acids in the product thanks to what the drinks according to the suggested basis satisfy need of healthy person in polyunsaturated fatty acids at least for 30%.

For the first time the authors scientifically substantiated the expediency of the combination of chia seeds with walnuts to obtain the necessary ratio ω -3 and ω -6 fatty acids. Also for the first time the universal basis for smoothie drinks production with the set content of nutrients is created. Authors proved that chia seed can be used in food products as a structurant. Usage of various prescription components confirms the universality of elaborated composition.

References

1. Kovalenko V. N., Dolzhenko M. N., Niecukai E.G., Dyachenko Ya.S., Nudchenko A. O. (2015), The Comparative characteristic of prevention of cardiovascular diseases in Ukraine and Europe according to the research EUROASPIRE IV: hosp. line, *Ukrainian cardiological magazine*, 4, pp. 17–24.
2. Lewis E. J. H. (2015), 21 days of mammalian omega-3 fatty acid supplementation improves aspects of neuromuscular function and performance in male athletes compared to olive oil placebo, *Journal of the International Society of Sports Nutrition*, 12 (1), pp. 1–11.
3. Tahmassebi J., Kandiah P., Sukeri S. (2014), The effects of fruit smoothies on enamel erosion, *European Archives of Paediatric Dentistry*, 15(3), pp 175–181.
4. Dyakonov A.G., Toryanik A. I., Svidlo K. V., Lipovoy D.V. (2013), Project technology of gero-dietetical smoothie on basis of oat seed grit and cellulose moisture content estimation, *Scientific journal NRU ITMO Series "Processes and Food Production Equipment"*, 1, pp. 15–18.
5. Kalugina I. M., Nenova A. V. (2014), Development of technology iodinated smoothie on the basis of a feijoa, *Journal of «Research works» published by Odesa national academy of food technologies*, 46(2), pp. 129–133.
6. Peresichnyy M., Neilenko S. (2010), Smoothie technology of radio protective action, *Commodities and Markets*, 2(10), pp. 48–55.
7. Ixtaina V. Y., Nolasco S. M. (2008), Physical properties of chia (*Salvia hispanica* L.) Seeds, *Industrial Crops and Products*, 28(3), pp. 286–293.
8. Viswanath D. S., Ghosh T., Prasad D. H. L., Dutt N. V. K., Kalipatnapu Y. Rani, (2007), *Viscosity of Liquids: Theory, Estimation, Experiment and Data*, Springer, Dordchert, The Netherlands, available at: <https://books.google.com.ua/books?id=TD3TeErQDoC&pg=PA17&lpg=PA17&dq#v=onepage&q&f=false>
9. AOAC Association of Analytical Chemists (2000), *Standard Official Methods of Analysis Chemists. 17th edition*, S.W Williams (Ed), Washington D.C.
10. Magomya A.M, Kubmarawa D., Ndahi J.A, Yebpella G.G. (2014), Determination of plant proteins via the kjeldahl method and amino acid analysis: a comparative study, *International journal of scientific & technology research*, 3 (4), pp. 68–72.
11. Pillay D., Mehdi, R. (1970). Separation of amino acids by thin-layer chromatography, *Journal of Chromatography*, 47, pp. 119–123.
12. Schaafsma G. (2005), The protein digestibility corrected amino acid score (PDCAAS) – A consent for describing protein quality in foods and food ingre dients, *A critical review j AOAS International*, 88(3), pp. 988–94.

13. Jensen W. B. (2007), The Origin of the Soxhlet Extractor, *J. Chem. Education*, 84(12), pp. 1913–1914, DOI:10.1021/ed084p1913.
14. Dieffenbacher A., Pocklington W.D. (1992), *Standard Methods for the Analysis of Oils, Fats, and Derivatives. 1st supplement to the 7th edn*, Blackwell Science, Oxford.
15. Iliana Kostova, Dimitar Dimitrov, Mihaela Ivanova, Radka Vlaseva, Stanka Damyanova, Nastya Ivanova, Albena Stoyanova, Oleksii Gubenia (2014), The possibilities of using of essential oils in dairy products. 2. Dill (*Anethum Graveolens*), *Ukrainian Food Journal*, 3(4), pp. 516–523.
16. Levitsky A.P. (2002), *Ideal formula of fatty food*, Odesa biotechnology, Odesa.
17. Skurikhin I.M., Tutelyan V.A. (2002), *Chemical composition of the russian foodstuff, The reference book*.

Effect of collagen based protein isolate «Belkozine» on biological value of boiled sausages

Anatolii Ukrainets, Vasyl Pasichniy,
Maksym Polumbryk, Maniefa Polumbryk

National University of Food Technologies, Kyiv, Ukraine

Abstract

Keywords:

Sausage
Protein
Pepsin
Trypsin
Belkozine

Article history:

Received 30.09.2016
Received in revised form
29.11.2016
Accepted 27.12.2016

Corresponding author:

Maksym Polumbryk
E-mail:
mx_pol@yahoo.com

DOI: 10.24263/2304-
974X-2016-5-4-11

Introduction. We have done comparative investigations of indispensable amino acids score of the proteins of boiled sausages, formulated with «Belkozine» and rate of tyrosine accumulation in the dynamic model of their digestion in human gastrointestinal tract in order to establish digestion level of the sausages .

Materials and methods. Hydrolysis has carried out in a special chamber consisted internal and external reservoirs. Internal part has a glass stirrer, which provided continuous mixing both fermented mass and dialysis of hydrolysis products. Duration of the two-step fermentation is 3 hours of each stage. Pepsin action was done on the first stage, whereas trypsin impact – on the second. Amino acids in protein containing foods have analyzed by ion-exchange chromatography of protein hydrolysates.

Results and discussion. The comparative investigations of enzymatic hydrolysis of boiled sausages, made from thigh chicken meat and cooled to 0-4 °C have carried out. Trypsin has a positive effect on tyrosine formation. We were investigated the amino acids profile of the boiled sausages. It was found that, «Belkozine» inclusion into formulations of the boiled sausages didn't cause significant changes in the amino acids content. Increase of «Belkozine» content resulted in the rise of tyrosine formation due to high availability of sausages proteins which has argued that this hydrocolloid has a positive impact on the ingestion degree of boiled sausages. The relationships between duration of hydrolysis and concentration of tyrosine, which is being formed during hydrolysis, has been established on the basis of experimental data.

Conclusions. Increase of this hydrolysate concentration from 6 to 12 % in the formulation give rise tyrosine formation as a result of sequential enzymatic hydrolysis in the pepsin-trypsin system, which in vitro simulates ingestion processes occurring in humans bodies. Therefore, «Belkozine» utilization in boiled sausages formulations allows to increase their biological value.

Introduction

Increased food production often resulted in loss of biological value of the final products due to concentration decrease of several important nutrients, such as essential fatty and aminoacids, macro- and microelements and others [1]. Thus, improvement of food technologies in order to increase their biological value is a still relevant for the manufacturers and consumers. Meat technologies take an important place in the diet for some specific groups, since products made from meat are the main source of amino acids in a human diet [2]. However, meat products, especially boiled sausages vary in their stability to provide all of the essential amino acid in amounts needed to meet human requirements. It has been shown, that boiled sausages can provide relatively complete proteins.

The methodology to measure the quality of dietary proteins for humans has been discussed for a long period of time. Protein Digestibility Corrected Amino Acid Score (PDCAA Score) was recommended by FAO/WHO as the preferred method to evaluate dietary protein quality [3,4]. Unfortunately, the true digestibility of the proteins is always higher, than apparent value since digestibility measurements take into account the fecal protein [5]. Thus, several gastrointestinal models, simulating gastrointestinal transit of food and digestive processes in the stomach and small intestine have been proposed [6, 7]. In this work we were applied dynamic *in vitro* amino acids digestibility model, which has been validated for the digestion of a broad range of food products, including dairy, wheat and fish products [5, 8, 9].

Inclusion of collagen containing protein «Belkozine» in the boiled sausages formulations can improve sensory and functional properties of the final products as well as partly compensate loss of essential aminoacids, which is usually occurs at the partial meat content decrease in the formulation [10]. We have used enzymatic hydrolysis method to investigate *in vitro* the effect of using «Belkozine» on ingestion degree of proteins of boiled sausages. This method can simulate the processes which occur in gastrointestinal tract of humans [11-13]. According to the method, protein containing samples were subjected to the proteolytic enzymes action, which were included pepsin and trypsin at the constant release of hydrolysis products by dialysis [11, 12].

Materials and methods

Materials

HCl, NaOH, Na₂CO₃, NaHCO₃, Na₂C₄H₄O₆, CuSO₄·5H₂O, Na₂WO₄·5H₂O, Na₂MoO₄·5H₂O were offered from Sigma-Aldrich. Unless specific notifications, all the chemicals were analytical reagent grade without further purification. Crystalline pepsin and trypsin were obtained from Biopharm Co. (Kyiv, Ukraine). The semi-permeable (cut-off of 5-7 kDa, surface area 0,7 m²) was introduced in the bottom part of the digestibility compartment.

The chicken thigh meat was obtained from “Nasha Ryaba”. The thigh meat was deboned and skinned before being stored under vacuum at -20 °C and was used within a 10 days of storage. Dry beef isolate «Belkozine» was obtained from Belkozine Co. (Pryluky, Ukraine) Carboxymehtylcellulose (CMC), Xanthan gum, guar gum, soybean isolate, whey protein isolate, soybean isolate, salt, sodium nitrite were obtained from Roeper Co. (Germany). Silicagel A300 was sourced from Shandong Sinchem Silica Gel (China). Aromatizer “Frankfurter`s sausages” was obtained from local supermarket “Auchan”.

Set-up of the in vitro digestion experiments

Hydrolysis has carried out in a special chamber consisted internal and external reservoirs. Internal part has a glass stirrer, which provided continuous mixing both fermented mass and dialysis of hydrolysis products. Duration of the two-step fermentation is 3 hours of each stage. Pepsin action was done on the first stage, whereas trypsin impact – on the second [11].

The ingestion procedure was modified [12]. The sample, containing approximately 150 mg of protein was subjected into internal vessel, having semipermeable membrane in the bottom part. After that, 15 ml of 0,02 M hydrochloric acid (pH=1,7) was added into the internal vessel and external vessel was filled with 60 ml of 0,02 M HCl in order to maintain ionic potential similar to that of internal vessel. Further, internal vessel has put into external vessel, so as the level of both liquids were the same. The samples were incubated at 37 °C. Crystalline pepsin (15 mg) was added into the internal, when temperature will reach this value. Thus, pepsin concentration (1µg/ml) in the internal vessel was similar to that of gastric juice at the ingestion of food. The reaction mixture was constantly stirred at 60 rpm. Duration of enzymatic hydrolysis in acidic conditions was 3 hours. After that, solution of external vessel was changed from acidic to base by 0,02 M NaHCO₃ addition, whereas protein containing slurry in the internal vessel was neutralized by means of 2 M NaOH solution addition, pH value should be 8,2. Further, internal vessel was diluted by 15 ml of 0,02 M NaHCO₃ solution which provided an opportunity to obtain buffer solution and 15 mg of trypsin was added. The procedure of incubation by trypsin was similar to that of pepsin and terminated after 3 hours. The samples were taken from external solution each hour of enzymatic hydrolysis [12].

Tyrosine concentration in these samples was determined photometrically at the appropriate absorbance wavelength ($\lambda = 750$ nm) according with the procedure, which is widely used for this purpose [14]. The calibrating plot of standard solution of tyrosine versus optical density, when values of optical density of the standard solutions was measured and finally concentration of tyrosine has determined.

Amino acids profile analysis and PDCAA score calculation

Amino acids in protein containing foods have analyzed by ion-exchange chromatography of protein hydrolysates. The procedure of hydrolysis was the following: the sample of boiled sausage (2mg) was placed into the thermo resistant flask and 1 ml of 6 M HCl was added. After that, flask was hermetically sealed and retained at 110 °C during 24 hours with nitrogen blanketing. Following hydrolysis, the ion exchange chromatography was used with post column ninhydrin derivatization for detection. Cystine was oxidized to cysteic acid by the sample treating with performic acid solution at for 0 °C for 16 hours. After that, the sample was hydrolyzed with 6M HCl at 110 °C during 18 hours. Cysteic acid was separated on an ion-exchange column post-column ninhydrin derivatization.

Amino acids results were converted to mg/ 100 mg protein using nitrogen to protein conversion factor of 6.25. Amino acid ratios (milligrams of an IAA (indispensable amino acids) in 1.0 g of test protein per milligram of the same IAA in 1.0 g of reference protein 100) for IAA are calculated by using the FAO/WHO suggested pattern of amino acid requirements as the reference protein for all ages except for infants. This pattern contains, in milligrams per gram of protein: histidine, 19; isoleucine, 28; leucine, 66; lysine, 58; methionine + cystine, 25; phenylalanine .tyrosine, 63; threonine, 34; tryptophan, 11; and valine, 35 [1, 3, 4].

Amino acids content was measured according with Moor and Stein method by means amino acids analyzer T 339 (Czech Republic) [15]. Eluted amino acids were measured by

reaction with ninhydrin and spectrophotometric determination at 570 nm for α amino acids and 440 nm for proline.

The values of Amino acids score and tyrosine concentration were obtained with statistical significance set at $P < 0.05$.

Results and discussion

The boiled sausages with different «Belkozine» content in the Protein Stabilizer (PS) were manufactured in order to evaluate effect of this additive on digestion degree. The developed composition of PS has the following components, %: carboxymethylcellulose – 5, guar gum – 10, xanthan gum – 5, whey isolate – 20, collagen containing protein «Belkozine» – 60. The functional and technological properties of the sausages were improved by silica dioxide (A300) addition into the formulation in the form of nanocomposite at the level of 0,3% to the total mass of mixture [10].

We have done comparative investigations of enzymatic hydrolysis of boiled sausages, made from chicken meat and cooled to 0-4 °C. In our previous works we have developed formulations of boiled sausages with different PS content. Formulations of these boiled sausages are given in the Table 1.

Table 1

Content of the forcemeat systems, %

Raw materials	Sample 1	Sample 2
Chicken thigh meat	80	60
Protein Stabilizer	10	20
Soybean isolate	10	20
Water, to the total mass	30	30
Salt, to the total mass	2,2	2,2

Since 20 % of the developed PS are not the proteins and 20 % is a soybean isolate, the health benefit of the developed compositions and final sausages may at first sight appear questionable. Thus, comprehensive research of digestibility of the developed sausages is necessary.

Table 2 compares the amino acids profile. The data shown in the table have suggested, that «Belkozine» inclusion into formulations of the boiled sausages didn't cause significant changes in the amino acids content. The sample of boiled sausages, contained 10 % of protein stabilizer has similar amino acid score with the control sample. In other words, decrease of meat content in the formulation has no negative impact on essential amino acids score in the final sausages. Taking to account these data, we have concluded about noticeable compatibility between thigh chicken meat and dry beef collagen containing protein «Belkozine» in the technology of boiled sausages. Further increase of PS level resulted in the negligible decrease of valine score, which is a limiting amino acid in the samples of sausages. Therefore, further increase of «Belkozine» content in the formulations is not desirable due to possible negative effect on amino acids profile.

Table 2
Protein content and Indispensable Amino Acids compositions of the samples of boiled sausages

Amino acid	Control		Sample with 10% PS		Sample with 20% PS	
	%	IAA Score, %	%	IAA Score, %	%	IAA Score, %
Lysine	8,55	155,0	8,46	154,0	8,44	153,0
Histidine	2,71	—	2,73	—	2,75	—
Arhinine	6,18	—	6,25	—	7,13	—
Aspartic acid	9,51	—	9,45	—	8,99	—
Threonine	4,78	118,0	4,68	117,0	4,48	112,0
Serine	5,26	—	5,32	—	5,33	—
Aminoglutaric acid	18,6	—	18,66	—	18,78	—
Proline	6,48	—	6,40	—	5,58	—
Glycine	4,88	—	4,90	—	5,02	—
Alanine	6,34	—	6,24	—	6,10	—
Cystine	1,2	114,0	1,22	114,0	1,34	114,0
Valine	3,65	72,0	3,60	72,0	3,53	71,0
Methionine	2,86	—	2,76	—	2,63	—
Isoleucine	3,08	79,0	3,16	79,0	3,26	82,0
Leucine	8,11	116,0	8,15	116,0	8,27	118,0
Tyrosine	3,75	133,0	3,80	134,0	3,92	139,0
Phenilalanine	4,12	—	4,22	—	4,45	—
Total	100,0	—	100,0	—	100,0	—

The data shown in the table 2 has been used in the next step of our investigations, there we were studied digestibility of sausages in the dynamic *in vitro* model. As it can be seen from the table 2, increase of the «Belkozine» content in the formulated sausages cause rise of tyrosine residue content. Thus, we were expected that it would be mirrored in the data, obtained from this model.

It is well known that the peptides and free amino acids being released into solution as a result of hydrolysis of protein containing products [1, 3, 9, 10]. Therefore, the total quantity of amino acids is determined in the processes, which modeling *in vitro* ingestion of foods [10, 11]. According to the Lowry protein assay, tyrosine concentration was determined by means of spectrophotometric devices.

We were compared an impact of way of protein stabilizer addition on the ingestion degree of proteins. PS was mixed with the forcemeat emulsion in hydrated form and as a dry powder. It has been found that the enzymatic hydrolysis rapidly proceeded in the sausages, formulated with dry PS, especially at the stage of trypsin action (Figure 1 and 2). In our opinion it may related to the formation of the more dense texture due to the rapid swelling of collagen in the sausages made with hydrated «Belkozine» based stabilizer.

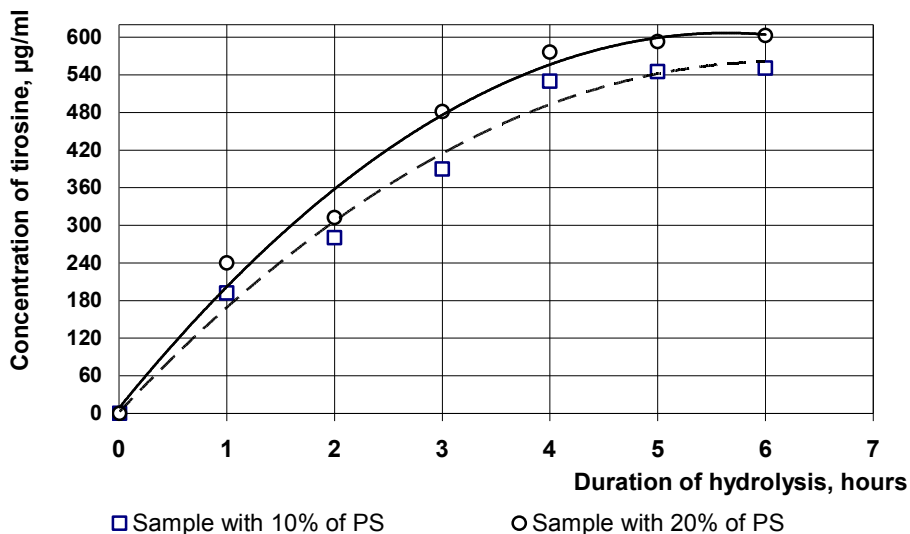


Figure 1. Tyrosine accumulation during enzymatic hydrolysis of boiled sausages, manufactured with dry PS

Relatively high quantity of tyrosine at the initial stage of pepsin enzymatic hydrolysis has observed in the sausages made with dry PS. It can be explained by the primary hydrolysis at the surface of the sausages, whereas trypsin reacted with low molecular peptides.

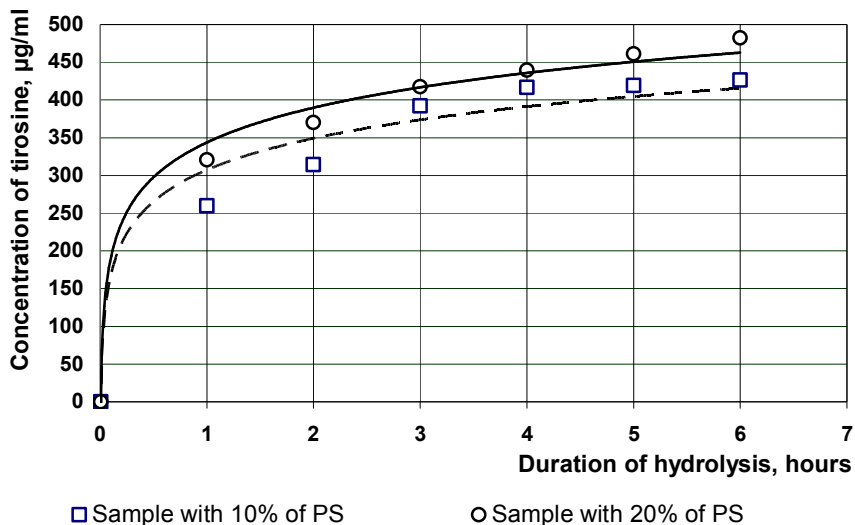


Figure 2. Tyrosine accumulation during enzymatic hydrolysis of boiled sausages, manufactured with hydrated PS

As it can be seen from Figure 1 and 2, rise of «Belkozine» content resulted in the increase of tyrosine formation due to high availability of sausages proteins which has argued that this hydrocolloid has a positive impact on the ingestion degree of boiled sausages. These results were explained by the greater tyrosine residues content in collagen containing protein «Belkozine» compared with those in raw meat and soybean isolate.

The relationship between duration of hydrolysis (t) and concentration of tyrosine (C), which is being formed during hydrolysis, has been established on the basis of experimental data. It can be described by the following equations:

$C = 60,6\ln(t) + 307,2$ (for the boiled sausages, formulated with hydrated PS at a level of 10 %)

$C = 66,4\ln(t) + 343,7$ (for the boiled sausages, formulated with hydrated PS at a level of 20 %)

$C = -14,7 t^2 + 181,3t + 1,7$ (for the boiled sausages, formulated with dry PS at a level of 10 %)

$C = -18,8 t^2 + 212,3t + 1,7$ (for the boiled sausages, formulated with dry PS at a level of 10 %); $r^2 = 0,9991$

Conclusions

Thus, on the basis of results of investigations, we have concluded about significant improvement of ingestion degree of boiled sausages manufactured with dry beef protein «Belkozine». Increase of this hydrolysate concentration from 6 to 12 % in the formulation give rise tyrosine formation as a result of sequential enzymatic hydrolysis in the pepsin-trypsin system, which in vitro simulates ingestion processes occurring in humans gastrointestinal tract. Therefore, «Belkozine» utilization in boiled sausages formulations allows to increase their biological value.

References

1. Caballero P., Finglas L., Trugo S., et.al. (2004), *Encyclopedia of food sciences and nutrition, 4th edition, 2004*, Academic Press, Oxford.
2. Jakobsen L., Kondrup J., Zellner M. (2011), Effect of a high protein meat diet on muscle and cognitive functions: A randomised controlled dietary intervention trial in healthy men, *Clinical Nutrition*, 30, pp. 303–311.
3. FAO/WHO. (1991), *Protein Quality Evaluation; Report of a Joint FAO/WHO Expert Consultation, United Nations; Rome, Italy, [Text]*, available at: www.fao.org/ag/humannutrition/35978-02317b979a686a57aa4593304ffc17f06.pdf.
4. Hughes H., Ryan D., Mukherjea R., Schasteen C. (2011), Protein digestibility-corrected amino acid scores (PDCAAS) for soy protein isolates and concentrate: criteria for evaluation, *J. Agricultural and Food Chemistry*, 59, pp. 12707–12712.
5. Havenaar R., Maathius A., De Jong A., et.al. (2017), Herring roe protein has a high digestible indispensable amino acid score (DIAAS) using a dynamic in vitro gastrointestinal model, *Nutrition Research*, (in press).
6. Moreno F.J., (2007), Gastrointestinal digestion of food allergens: effect on their allergenicity, *Biomedical Pharmacotherapy*, 61, pp. 50–60.

7. Wickham M., Faulks R., Mills C. (2009), In vitro digestion methods for assessing the effect of food structure on allergen breakdown, *Molecular Nutrition and Food Research*, 53, pp. 952–958.
8. Nabil S., Gauthier S., Drouin R., Poubelle P., Pouliot Y. (2011), In vitro digestion of proteins and growth factors in a bovine whey protein extract as determined using a computer-controlled dynamic gastrointestinal system (TIM-1), *Food Digestibility*, 22, pp. 13–22.
9. Framroze B., Savard P., Gagnon D., Richard V., Gauthier S. (2014), Comparison of nitrogen bioaccessibility from salmon and whey protein hydrolysates using a human gastrointestinal model (TIM-1), *Functional Foods and Health Disorders*, 4, pp. 222–231.
10. Ukrainets A.I., Pasichniy V.M., Zheludenko Y.V., Polumbryk M.M. (2016), Influence of protein containing compositions with high amount collagen containing stabilizer on boiled sausages quality, *scientific and practical journal «Food science and technology»*, 10(3), pp. 50–55.
11. Antipova L., Glotova I., Rogov I. (2001), *Research methods in meat and meat products*, Kolos, Moscow.
12. Pasichnyi V., Yastreba Y. (2010). Investigations of enzymatic ability of the plant protein containing fillers for canning patties manufacturing, *Scientific bulletin of Gzhytsky LNUVCMIB*, 3(45), pp. 50–53.
13. Kananen A., Savolainen J., Makinen J. (2000), Influence of chemical modification of whey protein conformation on hydrolysis with pepsin and trypsin, *International Dairy Journal*, 10, pp. 691–697.
14. Olson B., Markwell J. (2007), *Assays for determination of protein concentration, Current Protocol in Protein Science*. [Text], available at: onlinelibrary.wiley.com/doi/10.1002/0471140864.ps0304s48.
15. Spackman D., Stein H., Moore S. (1958), Automatic recording apparatus for use in chromatography of amino acids, *Analytical Chemistry*, 30, pp. 1190–1206.

Relaxation behavior of aqueous dispersion polysaccharides

Valerii Mank, Oksana Tochkova,
Oksana Melnyk, Oleksandr Bessarab

National University of Food Technologies, Kyiv, Ukraine

Abstract

Keywords:

Polysaccharide
Starch
Dispersion
Relaxation
Structure

Article history:

Received 12.10.2016
Received in revised
form 30.11.2016
Accepted 27.12.2016

Corresponding author:

Oksana Tochkova
E-mail:
tochka-ov@i.ua

DOI: 10.24263/2304-
974X-2016-5-4-12

Introduction. Rheological properties of aqueous solutions of polysaccharides showed thixotropic behavior in the destruction of their partially well-maintained structure that occur during physical or thermal effects.

Materials and methods. For experiments prepared 3–15% dispersion of native potato and corn starches in distilled water. These dispersions kept in an incubator for 30 min at a temperature 20 °C. The specimens loaded in a cylindrical container reotest at room temperature. After receiving the rheological curve of the sample aqueous dispersion of starch, its left in reotest for 3 hours and then received the rheological curve.

Results and discussion. A new method of relaxation in starch mixtures is that the structural relaxation of polymer units of the polysaccharides in time is slow and long.

According to the literature, only polysaccharides of molecular weight greater than 1 million, for example potato starch, is characterized by the slow relaxation of the structure. Physic-chemical characterization of polysaccharides - relaxation, is due to a partially ordered structure with the mutual arrangement of individual chains in a spatial grid.

Under the action of shear stress to reotest destroyed pseudo plastic structure of aqueous dispersions of starch is gradually restored to equilibrium with the system state. The recovery time of the structure is 17 hours.

The slow process of recovery, or structural relaxation of the spatial structure of aqueous dispersions of polysaccharides is due to the adjustment of the spatial grid of the polymer, which is formed due to the existence of transverse chemical bonds.

Similar behavior with a little time structural relaxation typical of other polysaccharides, in particular xanthan, the relaxation time which is about 3 hours.

Conclusion. These characteristics of colloidal systems affect its quality, structural, mechanical and technological properties that must be considered when choosing rational modes of equipment, development of optimal process conditions, the design of automated production control systems.

Introduction

Raw materials, semi-finished products and finished products of food processing industries have different structural and mechanical properties such as elasticity, flexibility, strength, creep, thixotropy, relaxation. These properties of food systems depend on temperature, humidity, pressure, mode of transportation, means and timing of storage. These factors affect the behavior of the structure during its deformation when machining: grinding, forming, stamping and others [1, 2, 12, 13].

To improve the organoleptic, structural, mechanical, physical and chemical characteristics of food products used polysaccharides. They provide some form of products such as sauces, puddings, confectionery, comminuted meat, fish products, and low fat dairy products. In a food system, the roles of polysaccharides are to stabilize the structure and interact with other components to deliver or maintain nutrient and flavor. For example, polysaccharides can serve as thickening agents for sauces, cream soups, and pie fillings; colloidal stabilizers for salad dressing; moisture retention for cake toppings; gel-forming agents for gum confections; binders for wafers and ice cream cones; and coating and glazing agents for nut meats and candies.

Among natural polysaccharides starch occupies a unique position. It has a wide range of applications in many industries and technology. This is what causes the large number of studies state starches of different botanical origin in conditions the action of various factors that appear in the literatures recently.

Natural polysaccharides, unlike synthetic, are characterized by a partially order structure which is formed in the process of synthesis and growth. This feature of biological macromolecules polysaccharides is due, primarily, their chiral structure, paired with the existence of hydrogen bonds included water molecules in their structure [1].

As you know, there is change in the nature of intermolecular interactions in biomacromolecules starch in a temperature range of 40–70 °C and converts it ordered structure [1, 2]. This is also confirmed by experiments in the dehydration process gelatinized starch [3].

The structural features of starch reflected in the rheological behavior of its aqueous dispersions. During processing, starch dispersions will be subjected to combined high heating and shearing that affect their rheological change as well as the final characteristics of the product. Starch gelatinization, especially granular swelling, changes the rheological properties of aqueous dispersions. The subsequent retrogradation will further modify the rheological properties of dispersions. Depending on the starch source and concentration, the final structure of starchy products will give a thickened solution or a gelled structure. Thus, the rheological curves of starch dispersions are characteristic of non-Newtonian fluid while at low shear stresses dispersions behave as elastoplastic system. Increasing the tension is the destruction structural formations and the system behaves as a classical fluid. These properties of the system due to the presence of intermolecular interactions and chaotic thermal motion of molecules [4–6].

It is suggested that after the removal of the applied stress to the system is slow restoration of the original structure, i.e. relaxation. Relaxation period is characterized by the speed system transition from a non equilibrium thermodynamic condition caused by external influence, in the state of thermodynamic equilibrium.

To confirm this assumption studied the rheological behavior of starch aqueous dispersions after a certain period of time after receiving another rheological curve.

Materials and methods

Materials. For experiments prepared 3–15% dispersion of native potato and corn starches in distilled water.

Method. These dispersions kept in an incubator for 30 min at a temperature 20 °C. The specimens loaded in a cylindrical container reotest at room temperature. After receiving the rheological curve of the sample aqueous dispersion of starch, its left in reotest [14] for 3 hours and then received the rheological curve [1, 2, 4].

Results and discussion

Rheological curves with time become more nonlinear and approaching in shape to the original curve (Figure 1, curve 1). This indicates that the destroyed under shear stress resistor pseudo plastic structure aqueous dispersions of starch gradually restored to equilibrium at the given conditions of the system.

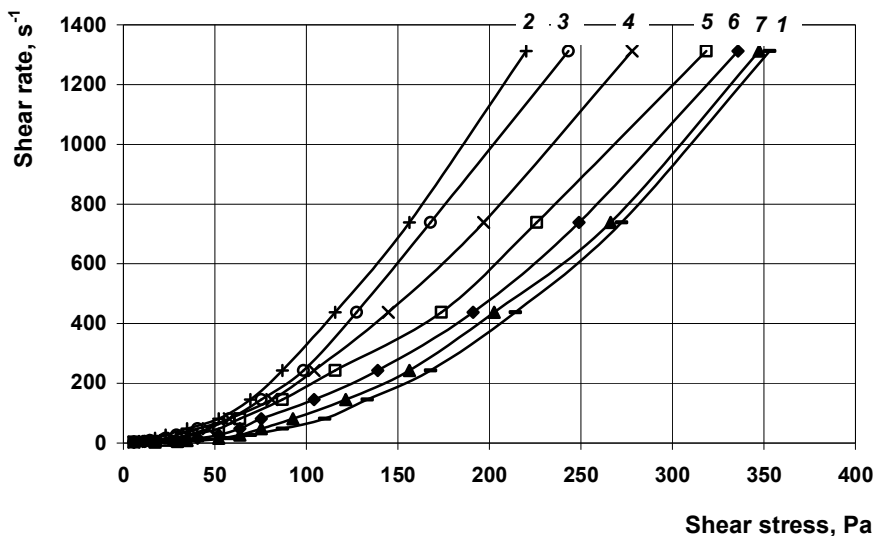


Figure 1. Rheograms for 5% dispersion of potato starch, heat treated at 20 °C (1) taken every 3 hours (2-7)

In general, the deformation that occurs as a result of shear stresses consists of elastic and viscous components. Elastic component are on Hooke's law [4, 7]:

$$\left(\frac{d\gamma}{d\tau}\right)_{el} = \frac{dP}{(Gd\tau)} \quad (1)$$

where P – shear stress, G – modulus of elasticity.

Any structured system described by Hooke's law only to a certain limit, above which comes the new state of deformation.

Viscous component is determined from the equation Newton [4, 7]:

$$\left(\frac{d\gamma}{d\tau}\right)_v = \left(\frac{P}{\eta}\right), \quad (2)$$

where η – viscosity.

Summing up two components obtained the Maxwell equation [4, 7]:

$$\frac{d\gamma}{d\tau} = \frac{dP}{\left(Gd\tau + \frac{P}{\eta}\right)} \quad (3)$$

As is known [4, 5, 7], unauthorized restoration structure of aqueous dispersions of various substances occurs exponentially to confirm this model, analyzed the rheological behavior of starch aqueous dispersions at regular intervals after the complete destruction of their structure. It was assumed that the value of shear rate that is fixed for each intermediate rheological curve in Figure 1 at shear stress of 200 Pa, also varies exponentially depending on the recovery time structure.

The dependence of shear rate of starch structure, ν on time at fixed shear stress 200 Pa can be represented by the following expression [7]:

$$\gamma = \gamma_0 e^{-\frac{\tau}{\tau_p}}, \quad (4)$$

where γ and γ_0 are shear rate s^{-1} , for observation τ and relaxation time, τ_p .

Studies to determine the 5% dispersion of potato starch presented on Figure 2.

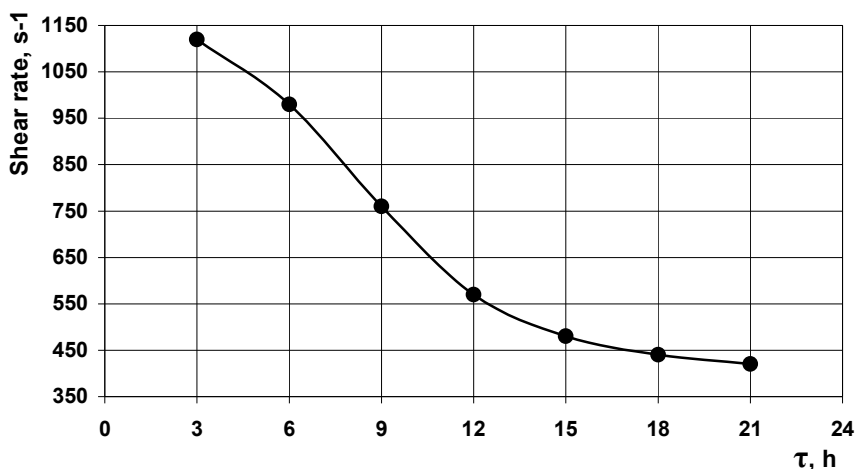


Figure 2. The dependence of shear rate on time at fixed shear stress (200 Pa) for 5% dispersion of potato starch, heat treated at 20 °C

To determine the period of relaxation structure constructed dependence $\ln \gamma - \tau$ (Figure 3).

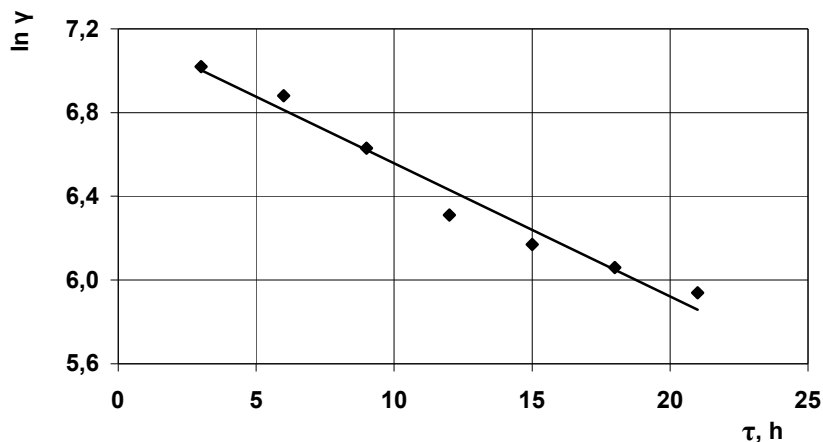


Figure 3. The dependence of shear rate on time at fixed shear stress

Relaxation period was calculated as $t_g = \frac{1}{\tau_p}$ the slope angle of the line $\ln \gamma = f \tau$. The relaxation period is 17 hours.

Linear dependence of the logarithm of shear speed from time observed the restoration of equilibrium in the system shown in Figure 4. It confirms the proposed mechanism of restoring equilibrium in the system after mechanical excitation. The rate of structure relaxation decreases evaluates from equation (1) is 17 hours, which indicates very slow process of restoring equilibrium of the sequence moving individual units of the polymer in a more convenient location moving individual units of the polymer in a more convenient location.

It is natural to assume that the recovery rate of equilibrium will depend on the complexity of the structure of the polymer. This is confirmed by similar experiments with simpler polysaccharides with a molecular weight of less than 1 000 000, while the molecular weight of starch 1 000 000. As an example, in Figure 4 shows the experimental determination of relaxation in aqueous solutions of the xanthenes gum. Time structural relaxation of the xanthenes gum is 210 minutes (Figure 4).

Very slow relaxation process spatial patterns are characteristic of cross-linked polymers in highly elastic state where the relaxation process is due to the restructuring of the spatial networks formed by intermolecular chemical bonds.

In the studied of polysaccharides aqueous dispersions maybe similar relaxation process that caused flexible friction a large areas of polymer chains.

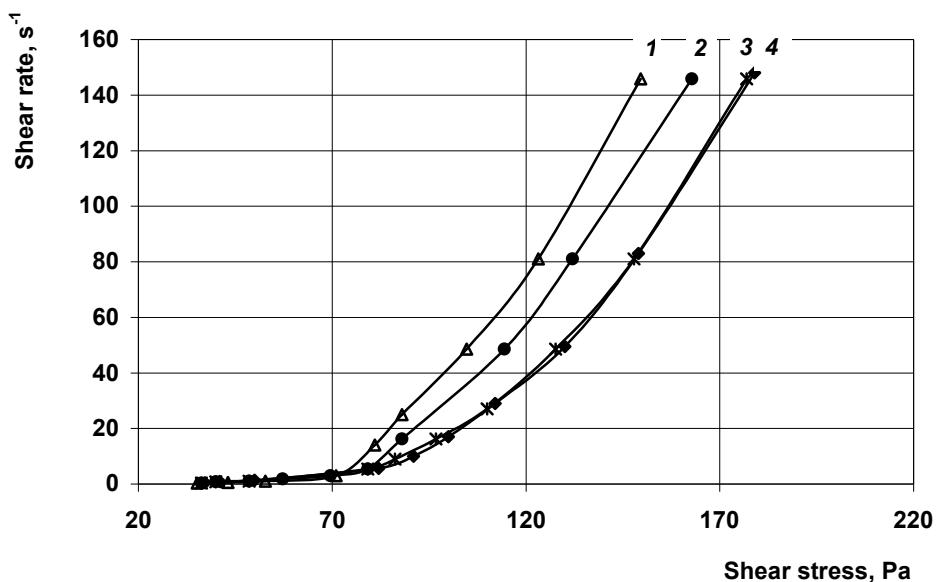


Figure 4. Rheograms for 5% dispersion of xanthenes, heat treated at 70°C (1) taken every 3 hours (2–4)

Conclusions

Study rheology behavior of aqueous starch dispersions in various stages of restoration non-Newtonian liquids structure and consideration possible model of their relaxation have confirmed the existence of ordered structures formed by interaction with water molecules surrounding hydrocarbon chains of biopolymers.

Under the influence of shear stresses in rheostat, the structural elements in starch mixtures are destroyed. Dispersion system became into a state of Newtonian liquid. Rebalancing to the original state in the second complex systems is slow enough.

Developed method of changing the times of the structural relaxation of the carbohydrate chains of the polymer.

This behavior aqueous dispersions of polysaccharides must be considered when considering the intermolecular interactions and structure of polymer solutions, as well as the development of technology using polysaccharides as food additives.

References

1. Mank V., Melnyk O., Bakhmach V. (2014), Anomalous properties in aqueous solutions of polysaccharides, *Ukrainian Journal of Food Science*, 2 (2), pp. 236–243.
2. Bertolini C.A. (2010), *Starches: characterization, properties, and applications*, Taylor and Francis Group, New York.

3. Xiaowen L., Wu L., Wang J., Li J., Qin Y. (2011), Characterization of Water Binding and Dehydration in Gelatinized Starch. *J.Agric.Food Chem.*, 59(1), pp. 256–262.
4. Malkin A. J., Askadskyi A.A., Kovryga V.V. (1978), *Metody izmereniya mekhanicheskikh svoistv polymerov*, Khimiya, Moscow.
5. Gorbatov A.V., Machykhyn S.A., Maslov A. M., (1982), *Strukturno-mechanicheskie kharakterystyky pischevukh produktov, Lehkaya i pischevaya promyshlenost*, Moscow
6. Xue T., Yu L., Xie F., (2008), Rheological properties and phase transition of starch under shear stress, *Food Hydrocolloids*, 22, pp. 973–978.
7. Padokhyn V.A., Kokina N.P., (2007), *Fiziko-mekhanicheskie svoistva suria i pischevukh produktov*, Ivanovo.
8. Flad E. (1999), *Interphase boundary gas-solid*, Moscow, pp. 129–147.
9. Olga Rybak (2013), Some aspects of the formation of emulsions and foams in food industry, *Ukrainian Journal of Food Science*, 1(1), pp. 41-49.
10. Akselrud G.A., Articular M.A. (1993), *Introduction to capilano-chemical technology*, Moscow.
11. Schrader M. E., Yariv S. (1990), Wettability of Clay Minerals, *Ibid*, 136(1), pp. 85–94.
12. Lugovska O., Sydor V. (2014), Effect of starch as hydrocolloids for formation of a stable emulsion system in food, *Ukrainian food journal*, 3(2), pp. 202-210.
13. Ai Y., Jane J.I. (2016), Starch: Structure, Property, and Determination, *Encyclopedia of Food and Health*, Academic Press, pp. 165–174.
14. Natalia Dacka, Olena Podobii (2014), The sour milk drink with antioxidant properties, *Ukrainian Journal of Food Science*, 2(2), pp. 205-212.

Fouling of polymer and organic-inorganic membranes during filtration of corn distillery

Yurii Zmievskii¹, Yuliia Dziazhko², Valerii Myronchuk¹,
Ludmyla Rozhdestvenska², Alexander Vilenskii³, Ludmyla Kornienko¹

1 – National University of Food Technologies, Kyiv, Ukraine

2 – V.I. Vernadsky Institute of General and Inorganic Chemistry of the National Academy of Science, Kyiv, Ukraine

3 – A.V. Shubnikov Institute of Crystallography of the RAS, Moscow, RF

Abstract

Keywords:

Distillery
Membrane
Nanoparticle
Separation
Modification

Article history:

Received 10.11.2016
Received in revised
form 18.12.2016
Accepted 27.12.2016

Corresponding author:

Yurii Zmievskii
E-mail:
yrazm@meta.ua

DOI: 10.24263/2304-974X-2016-5-4-13

Introduction. Baromembrane separation is the most commonly used method for processing of corn distillery. In order to prevent fouling, polymer membranes are hydrophilized modified with particles of inorganic ion-exchangers. The aim of the investigation was to establish and compare the mechanism of fouling for polymer and composite membranes.

Materials and methods. Polyethyleneterephthalate track microfiltration membrane was modified with aggregates of nanoparticles of zirconium hydrophosphate, the materials were examined with a method of scanning electron microscopy. The pressure test was performed using deionized water as a working liquid. Corn distillery was filtered at 1-4 bar and 60 °C.

Results and discussion. The models of pore blockage, pore constriction and cake formation were applied, particularly to water filtration through the composite membrane. Pore blockage and pore constriction were shown to be possible during pressure test at 60°C, this can be caused by transformation of porous structure of the polymer and fragmentation of the modifier. Regarding corn distillery, the composite membrane demonstrates higher stability against fouling than the pristine separator. Depending on time of filtration, the composite material obeys Darcy's law or shows the maximal flux at 3 bar. The flux of permeate through the pristine membrane decreases with pressure growth due to accumulation of organics. A linear increasing of productivity under similar conditions is characterized for modified membranes. It means that substances, which polluted the membranes, have a smaller hydrodynamic resistance. The mechanism of pore blockage is valid both for the pristine and composite membranes. Increasing in pressure enhances pore constriction (pristine membrane) and cake formation (all separators). Composite membranes have higher resistance to fouling that allows to use smaller amount of chemicals for regeneration, reduce time of regeneration and volume of wastewater.

Conclusions. The inorganic ion-exchanger allows us to improve stability against fouling with components of corn distillery: no fouling has been found at 1 bar. In order to prevent blockage under higher pressure and facilitate the membrane cleaning, location of ZHP particles just near the outer surface is necessary. Organic-inorganic membranes can be applied to other objects of food industry, especially under room and lower temperatures.

Introduction

More than 80 licensed plants of alcohol industry operates in Ukraine at present time, [1]. They are able to process 900 000 tons of grain per year and obtain 32 millions decalitres of alcohol. Their annual demand of beet molasses is 1.1 million tons, 30 millions decalitres of alcohol are produced from this feedstock. During the alcohol manufacture, a large amount of liquid wastes, such as grain distillery, is produced. These wastes are characterized by high chemical oxygen demand (COD), biological oxygen demand (BOD) and dark brown color [2]. In order to reduce ecological risks, processing of grain distillery is necessary. Baromembrane separation is the most commonly used technique for this purpose [3-7]. Permeate is returned to the fermentation process increasing ethanol yield [8]. This product could be also applied to extraction of proteins [9]. Concentrate is dried and used further as supplements to food for domestic animals [10] and even for production of bread and cookies [11].

Very important problem of baromembrane separation is fouling of polymer membranes with organic species [12]. Modification of the membrane with inorganic constituent allows us to overcome this difficulty [13, 14]. Hydrophilic inorganic particles inside pores of the membrane are a barrier against fouling with organics [14]. Moreover, in the case of synthetic ion exchangers [15-17], ion exchange membranes [18] or fibrous biomaterials [19], this approach allows us not only to protect them from organic species, but also to improve functional properties [15-19].

The method of polymer modification with hydrated zirconium phosphate (ZHP), functional properties of the membrane and its testing for practical application were considered earlier [14]. Regarding the application to baromembrane processing of grain distillery, further enhancement of the membrane is impossible without knowledge of fouling mechanism. Establishment of this mechanism is a purpose of the investigation.

Materials and methods

Polyethyleneterephthalate track membrane produced by A.V. Shubnikov Institute of Crystallography of the RAS (RF) was used for the investigations. Through pores of this porous polymer are regular and rather straight [14]. The membrane was modified with ZHP (4.7 mass %) as described in [14].

Both the pristine (further PM) and composite (CM) membranes were tested. A divided cell was used for baromembrane separation (effective area of the membrane was $2.1 \cdot 10^{-3} \text{ m}^2$), the stack elements are listed in [14]. Deionized water and corn distillery (pH 4.1, total solids – 73 g dm^{-3} , COD – 64) was used for investigations. The biological liquid was centrifuged and filtered through the paper filter.

Preliminarily the membranes were pressed (at 1 bar and further at 3 bar) in deionized water at 25°C , then the same procedure was performed at 60°C . After the pressure test, water was filtered through the membranes again at 1 bar and 60°C . Then the cell was filled with corn distillery, which circulated through the concentration compartment without filtration for 1 h at 60°C . Further deionized water was filtered at 1 bar and 60°C . After this, corn distillery was filtered at 1 bar and 60°C , than water was filtered again. The next procedure was filtration of corn distillery at 3 bar and 60°C followed by water filtration at 1 bar and 60°C . At last, corn distillery was filtered at 4 bar and 60°C .

Results and discussion

Pressure test

For example, Figure 1 shows cumulative volume (V) of permeate (deionized water) through the PM and CM as a function of time (τ). As seen, increasing in pressure drop (ΔP) causes intensification of water transport in accordance to Darcy equation [20]:

$$J = \frac{\Delta P}{\eta R_m} \quad (1)$$

Here J is the flux ($J = \frac{dV}{d\tau} \frac{1}{A}$, where A is the membrane area), η is the dynamic viscosity of a liquid, R_m is the hydrodynamic resistance of a membrane. The modified membrane is less sensitive to pressure than the pristine separator. As shown in [14], aggregates of ZHP particles block macropores (about 300 nm) of the polymer increasing hydrodynamic resistance. Similar phenomenon has been found for ceramic membrane containing incorporated particles of inorganic ion-exchangers [21, 22].

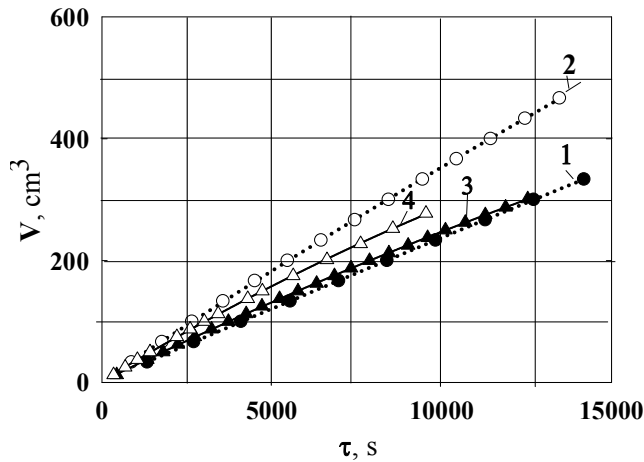


Figure 1. Filtration of deionized water at 60 °C: cumulative volume of permeate through PM (1, 2) and CM (3, 4) as a function of time. Pressure drop: 1 (1, 3) and 3 bar (2, 4).

In the case of modified membranes, the inorganic particles can be considered as contaminants. According to known theory of fouling, the fouling mechanism is pore blockage (primary particles or their aggregates are comparable with pores of polymer), if the $J - V$ curve is linear [21]. Pore constriction (deposition of particles on pore walls) is realized, when the $\frac{\tau}{V} - \tau$ curve is approximated by linear polynomial. At last, linearity of the $\frac{\tau}{V} - V$ curve indicates the cake model (precipitation on the outer surface of the membranes).

Regarding water filtration through CM, only pore constriction and pore blockage models can be applied. No fouling model is suitable for the process at 25 °C (practically no change of flux at 1 bar and no linearity of the $\frac{\tau}{V} - \tau$ curve). At the same time, pore blockage and pore constriction models are applicable at 60 °C (Figure 2). It could be explained by polymer squeezing and pore deformation (formation of their narrowings-widenings). This leads to an increase of hydrodynamic resistance. On the other hand, partial fragmentation of ZHP aggregates is possible. The primary particles, which leave the aggregates, can block voids between the next aggregate. On the other hand, the particles are deposited on walls of pores due to turbulence of water flow inside pores (centrifugal force appears as a result of vortex).

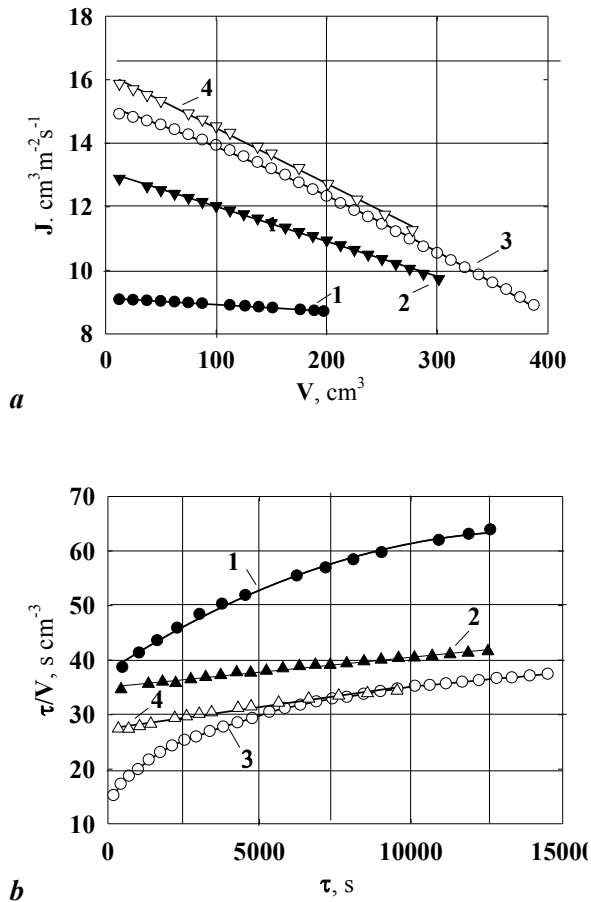


Figure 2. Application of pore blockage (a) and pore constriction (b) models to water filtration through CM.

Filtration was carried out at 1 (1, 2) and 3 (3, 4) bar, at 25 (1, 3) and 60 °C (2, 4).

The last assumption is confirmed by Figure 3, which illustrates water flux for different stages of water filtration. CM shows more rapid decrease of water flux than PM during water filtration at 1 and 3 bar (60 °C), though the inorganic particles should prevent deformation of the polymer. In the case of PM, decrease of the J value is due to polymer deformation. After the pressure test, both the pristine and composite membranes show lower flux of water due to transformation of porous structure on the one hand and lower temperature on the other hand. No sufficient change of the flux has been found after adsorption of corn distillery.

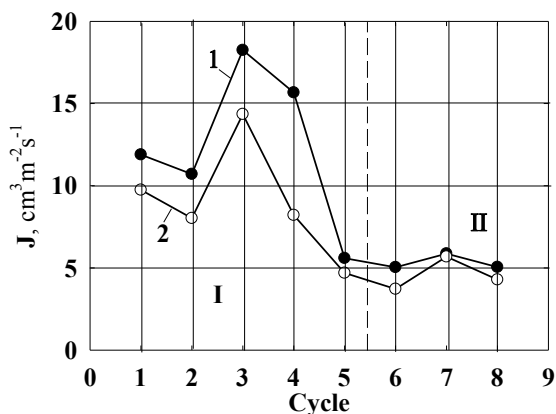


Figure 3. Water flux for different cycles of water filtration (numbers of abscissa axis): beginning (1) and end (2) of the process at 60 °C and 1 bar, beginning (3) and end (4) of the process at 60 °C and 3 bar, further filtration at 25 °C and 1 bar (5), after distillery adsorption without filtration (6), after distillery filtration at 60 °C and 1 bar (7) or 3 bar (8). The region I corresponds contact of membranes with distillery, the region II is related to water filtration after the processes that involve distillery. Curve 1 is related to PM, curve 2 is for CM

Filtration of corn distillery

In opposite to PM, the flux of permeate through CM remains without changes (CM, 1 bar) indicating stability of the composite membrane against fouling. In the other cases, the flux decreases over time. This values reduces slower for CM than for PM at 3 bar. Alternatively CM shows faster decrease of the flux at 4 bar probably due to stronger pressing of the, which occurs simultaneously with filtration. On the other hand, fragmentation of ZHP aggregates can be reinforced under these conditions. Regarding CM, the initial flux obeys Darcy law (Figure 5). However, the final one demonstrates a maximum at 3 bar. Both the initial and final flux fall with pressure in the case of PM evidently due to fouling. No sufficient change of water flux has been found after filtration of corn distillery (see Figure 3).

The model of pore blockage can be applied to all membranes, since approximation of the curves with linear polynomial gives the same correlation coefficient as for quadratic polynomial (Table 1, see also Figure 4). In the case of pristine membrane, increasing in pressure drop enhances the tendency to pore constriction and cake formation. Three these mechanisms are valid simultaneously at 4 bar. Regarding CM, only pore blockage and cake formation are realized under these conditions.

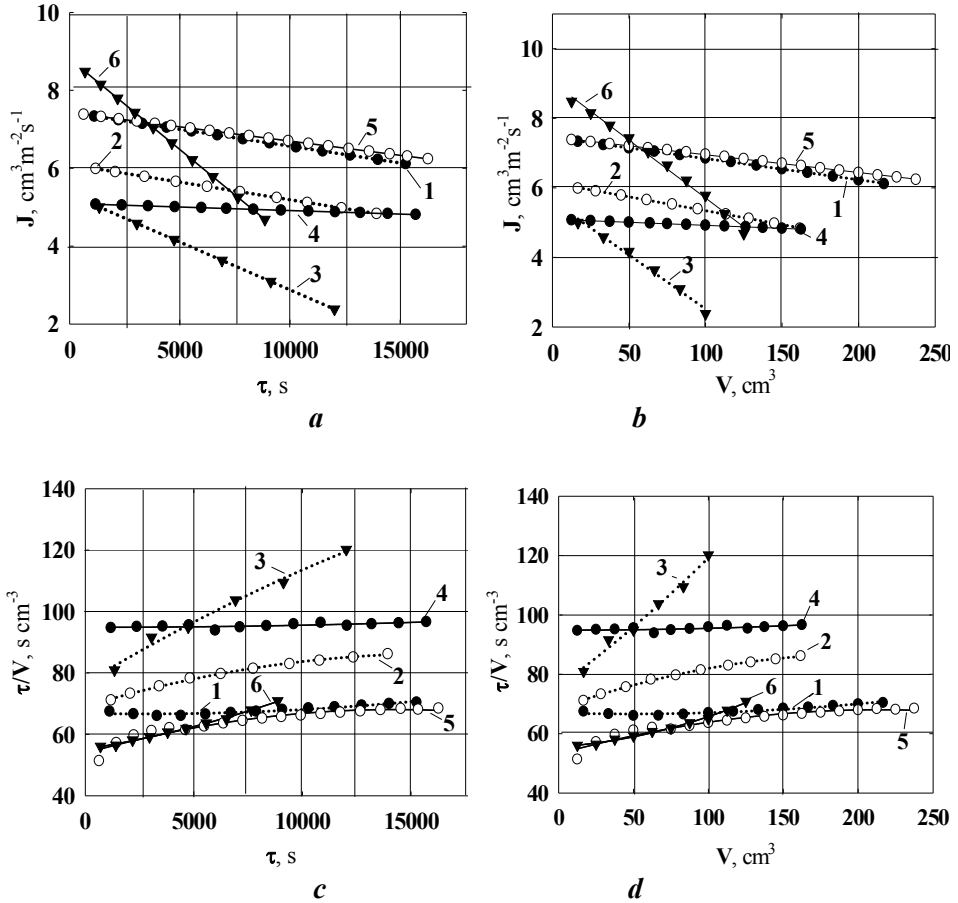


Figure 4. Filtration of corn distillery at 60 °C: permeate flux as a function of time (a), models of pore blockage (b), pore constriction (c) and cake formation (d); Membranes: PM (1–3), CM (4–6); Pressure: 1 (1, 4), 3 (2, 5), 4 (3, 6) bar.

Table 1
Application of different models to filtration of corn distillery at 60 °C

Membrane	Pressure, bar	Pore blockage, R^2		Pore constriction, R^2		Cake formation, R^2	
		Linear polynomial	Quadratic polynomial	Linear polynomial	Quadratic polynomial	Linear polynomial	Quadratic polynomial
PM	1	0.99	0.99	0.81	0.92	0.80	0.93
	3	0.99	0.99	0.95	0.99	0.97	0.99
	4	0.98	0.99	0.98	0.99	0.98	0.98
CM	1	—	—	—	—	—	—
	3	0.99	0.99	0.53	0.57	0.83	0.93
	4	0.98	0.99	0.82	0.92	0.99	0.99

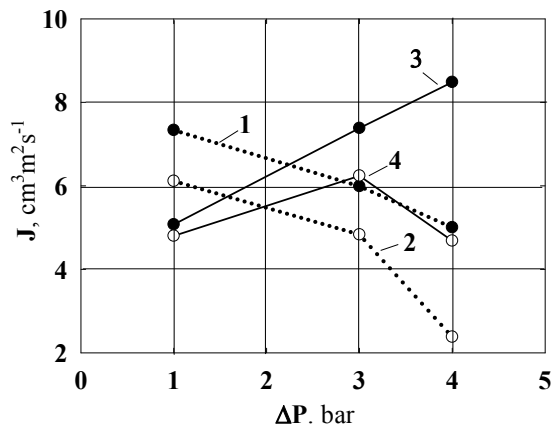


Figure 5. Filtration of corn distillery at 60 °C trough PM (1, 2) and CM (3, 4): initial (1, 3) and final (2, 4) permeate flux as a function of pressure drop

Since no sufficient change of water flux after filtration, the "corks" of organics occupy insignificant volume of pores of the polymer. Regarding CM, organics can block pores between ZHP nanoparticles of the aggregates.

Conclusions

ZHP affects permeability of the track membrane. During pressure test under elevated temperature, the flux of deionized water can be caused by not only transformation of porous structure of the polymer, but also by fragmentation of the modifier aggregates. This phenomenon is not observed under room temperature. The inorganic ion-exchanger allows us to improve stability against fouling with components of corn distillery: pore constriction is not realized for CM in opposite to PM. Moreover, no fouling has been found at 60 °C and 1 bar. In order to prevent blockage under higher pressure and facilitate the membrane cleaning, location of ZHP particles just near the outer surface is necessary. The improvement of the modification technique is a subject of further investigations.

Increasing in pressure leads to intensification of cake formation. However, the precipitate can be easy removed from the outer surface of the membrane by means of hydrodynamic pulsations.

Due to stability against fouling, organic-inorganic membranes can be applied to other objects of food industry, especially under room and lower temperatures.

References

1. Shamanska O. I., Palamarenko Y. V (2014), Modern trends in the alcohol industry of Ukraine, *Efectyvna ekonomica*, 4, available at: <http://www.economy.nayka.com.ua/?op=1&z=2903>

2. Bustamante M.A., Paredes C., Moral R., Moreno-Caselles J., Perez-Espinosa A., Perez-Murcia M.D. (2005), Uses of winery and distillery effluents in agriculture: characterization of nutrient and hazardous components, *Water Science and Technologies*, 51(1), pp. 145–151.
3. Vasic V. M., Sciban M. B., Prodanovic J. M., Kukic D. V. (2013), Characterization and utilization of the permeate and retentate obtained after “dead-end” ultrafiltration, *Acta Periodica Technologia*, 44, pp. 163–170.
4. Wu Y. V. (1988), Recovery of stillage soluble solids from corn and dry-milled corn fractions by high-pressure reverse osmosis and ultrafiltration, *Cereal Chemistry*, 65(4), pp. 345–348.
5. Lapisova K., Vlcek R., Klozova J., Rychtera M., Melzoch K. (2006), Separation techniques for distillery stillage treatment, *Czech Journal of Food Science*, 24(6), pp. 261–267.
6. Kornienko L., Zmievskii Yu., Myronchuk V. (2015) Investigation of ultrafiltration of grain stillage, *Ukrainian Food Journal*, 4(1), pp. 131–138.
7. Prodanovic J.M., Vasic V.M. (2013), Application of membrane processes for distillery wastewater purification—a review, *Desalination and Water Treatment*, 51(16–18), pp. 3325–3334.
8. Kim J.-S., Kim B.-G., Lee Ch.-H., Kim S.-W., Jee H.S., Koh J.-H., Fane A.G. (1997), Development of clean technology an alcohol fermentation industry, *Journal of Cleaner Production*, 5(4), pp. 263–267.
9. Mojovic L., Pejcin D., Rakin M., Pejcin J., Nikolic S., Djukic-Vukovic A. (2012), How to improve the economy of bioethanol production in Serbia, *Renewable and Sustainable Energy Reviews*, 16, pp. 6040–6047.
10. Ratanapariyanuch K., Tyler R.T., Shim Y.Y., Reaney M.J.T. (2012) Biorefinery process for protein extraction from oriental mustard (*Brassica juncea* (L.) Czern.) using ethanol stillage, *AMB Express*, 2, pp. 5.
11. Tsen C.C., Eyestone W., Weber J. L. (1983), Evaluation of the qualities of cookies supplemented with the distillers' dried grain flours, *Journal of Food Science*, 47, pp. 484.
12. Lee S.J., Kim J.H. (2014), Differential natural organic matter fouling of ceramic versus polymeric ultrafiltration membranes, *Water Research*, 48(1), pp. 43–51.
13. Safarpour M., Khataee A., Vatanpou V. (2015), Effect of reduced graphene oxide/TiO₂ nanocomposite with different molar ratios on the performance of PVDF ultrafiltration membranes, *Separation and Purification Technology*, 140, pp. 32–42.
14. Dzyazko Yu. S., Rozhdestvenskaya L.M., Zmievskii Yu. G., Vilenskii A.I., Myronchuk V.G., Kornienko L.V., Vasilyuk S.L., Tsyba N.N. (2015), Organic-inorganic materials containing nanoparticles of zirconium hydrophosphate for baromembrane separation, *Nanoscale Research Letters*, 10, pp. 64–75.
15. Dzyazko Yu.S., Ponomaryova L.N., Volfkovich Yu.M., Sosenkin V.E., Belyakov V.N. (2013) Polymer Ion-Exchangers Modified with Zirconium Hydrophosphate for Removal of Cd²⁺ Ions from Diluted Solutions, *Separation Science and Technology*, 48(14), pp. 2140–2149.
16. Dzyazko Y.S., Ponomaryova L.N., Rozhdestvenskaya L.M., Vasilyuk S.L., Belyakov V.N. (2014), Electrodeionization of low-concentrated multicomponent Ni²⁺-containing solutions using organic-inorganic ion-exchangers, *Desalination*, 342, pp. 52–60.
17. Dzyazko Yu. S., Ponomaryova L. N., Volfkovich Yu. M., Trachevskii V.V., Palchik A.V. (2015) Ion-exchange resin modified with aggregated nanoparticles of zirconium

- hydrophosphate. Morphology and functional properties, *Microporous and Mesoporous Materials*, 198, pp. 55–62.
18. Dzyazko Yu., Rozhdestveskaya L., Zmievsii Yu., Volkovich Yu., Sosenkin V., Nikolskaya N., Vasilyuk S., Myronchuk V., Belyakov V. (2015) Heterogeneous Membranes Modified with Nanoparticles of Inorganic Ion-Exchangers for Whey Demineralization, *Materials Today: Proceedings*, 2(6), pp. 3864–3873.
 19. Mokrousova E.R., Dzyazko Yu.S., Volkovich Yu.M., Nikolskaya N.F., Hierarchical Structure of the Derma Affected by Chemical Treatment and Filling with Bentonite: Diagnostics with a Method of Standard Contact Porosimetr. In *Nanophysics, Nanophotonics, Surface Studies, and Applications* (O. Fesenko, L. Yathenko, eds.): *Springer Proceedings Phys., Switzerland*, 2016, V. 183. – p. 277–290.
 20. Mulder M. (2000) *Basic principles of membrane technology*, Kluwer, Dordrecht.
 21. Dzyazko Yu.S., Rudenko A.S., Yukhin Yu.M., Palchik A.V., Belyakov V.N. (2014), Modification of ceramic membranes with inorganic sorbents. Application to electro-dialytic recovery of Cr(VI) anions from multicomponent solution, *Desalination*, 342, pp. 43–51.
 22. Dzyazko Yu.S., Volkovich Yu.M., Sosenkin V. E., Nikolskaya N.F., Gomza Yu.P. (2014), Composite inorganic membranes containing nanoparticles of hydrated zirconium dioxide for electro-dialytic separation, *Nanoscale Research Letters*, 9(1), pp. 271–282.
 23. Ho C.C., Zydney A.L. (2000), A Combined Pore Blockage and Cake Filtration Model for Protein Fouling during Microfiltration, *Journal of Colloid and Interface Science*, 232, pp. 389–399.

Co-combustion of solid biomass in pulverized anthracite-coal firing boilers

Nataliia Dunaievskia, Mykola Chernyavskiy, Taras Shchudlo

Coal Energy Technology Institute, Kyiv, Ukraine

Abstract

Keywords:

Co-combustion
Biomass
Coal
Anthracite

Article history:

Received 12.09.2016
Received in revised
form 24.11.2016
Accepted 27.12.2016

Corresponding author:

Taras Shchudlo
E-mail:
tarry@ukr.net

DOI: 10.24263/2304-974X-2016-5-4-14

Introduction. Combustion of solid biomass as a mix with domestic coal in existing industrial and utility boilers can not only reduce harmful emissions but also diversifies the generations' fuel base. It also allows effective utilization of solid food processing wastes which otherwise would be dumped and thus cause a strong unfavorable environmental impact.

Materials and method. The pulverized pine-sawdust and anthracite co-combustion has been carried out in down fired experimental unit at 30 kg/h fuel rate. The kinetics of the pine sawdust cokes' thermal degradation has been studied in fluidized bed unit. The thermal decomposition kinetics of pine wood and straw pellets of wheat, rape, corn and soy were studied by thermogravimetric (TG) method.

Result and discussion. The co-combustion of pulverized domestic anthracite and wood in the unit VGP-100V has proven its technical realizability and a noticeable potential to significantly improve the quality of low-reactive anthracite combustion. As a result the optimum share of solid biomass of approximately 10% has been determined. This share allows the stabilization of flame without natural gas addition along with the highest level of fuel carbon conversion.

The internal kinetic mode of pine cokes' samples' combustion was determined for particles size 0,1–1,6 mm in temperatures' range of 390–560 °C at the fluidized bed unit RSK-1D.

Some stages of organic biomass thermal decomposition (namely demoiurization, devolatilization and coke burn out) and their kinetics have been detected by means of TG methods. Comparison of pine sawdust and wheat straw pellets' devolatilization kinetics with those available in literature sources indicates that the existing minor deviations may be explained by the difference in sample heating rate, size of sample particles, variation in organic and mineral composition of samples, methods of reaction constants calculation and interpretation. At the same time, the kinetic constants of the devolatilization stage for pellets of different crops straw examined in the present work turned out to be close enough.

Conclusion. Presented results can be used in calculations of the some stages co-combustion processes which take place in TPP's.

Introduction

The technology of the biomass as supplementary fuel together coal combustion (BCC technology) has widely spread in the last decades. At present, in Europe o more than 200 boiler units are operated following such technology. A variety of solid biomass is being used. For example, straw as a supplementary fuel is utilized in pulverized coal (PC) boilers (TPP Studstrup, Denmark), wood wastes (TPP Kimiyarvi, Finland), sorted municipal solid wastes (so-called RDF – TPP Lakhti, Finland), crushed bones of olives and other horticultural crops (TPP Puertolano, Spain), pellets of different agricultural wastes (TPP Drax, Great Britain, TPP Kozenice, Poland) and many other foreign TPP's and CHP's [1, 2]. The main advantages of the solid biomass and coal co-combustion technology (BCCC) over individual biomass combustion in special dedicated boilers are as follows:

- Minimal capital investments, since biomass combustion takes place in already existing boilers and needs the construction of only plants of biomass reception, on site transportation and pre-combustion preparation;
- Reduction of pollutant emissions since biomass is considered as CO₂-neutral fuel, has much lower (in comparison with domestic coal) content of sulphur nitrogen compounds;
- Prospective to reduce thermal and electric generation due to fossil fuel;
- Significant potential to recycle wastes of different production types and thereby reduce the environmental pollution;
- Growing feasibility of biomass using in coal boiler units under appropriate legislation (the “green tariff”, the fee for biomass dumping in landfills, etc.).

The said technology has so far been implemented in a variety of arrangements, as follows [1]:

- in PC boiler units;
- in CFB boilers;
- the biomass gasification in separate gasifiers with subsequent burning in coal boilers.

As per environmental performances of the co-combustion process, the above-mentioned sulphur oxide reduction can be noted due to lower content of such substance in the biomass, its CO₂- neutrality in combustion processes, experimental data on nitrogen oxide reduction are in many foreign editions [3, 4, 5].

The NO_x reduction can be explained by technological factors, also: a high devolatilization rate of biomass can be explained the creation of enriched fuel zone at the beginning of the torch at the exit of the burner. A high moisture content of some biomasses could also effect on nitrogen oxide reduction in boiler furnace.

It should be noted that just a few domestic works addressed the problems of the dynamics of biomass dehydration and devolatilization. In works [6,7] the set of equations for the calculating kinetic constants has been proposed. Particularly, the equation [6] allow to calculate the time span of the dehydration and devolatilization stages of complex process of certain types of biomass combustion. At the same time it is clear that the data available in literature are insufficient and lacking fist of all the kinetic characteristics of biomass mixtures combustion and biomass cokes burned out.

The BCC technology combustion of such heterogeneous fuel as anthracite and plant solid biomass is of particular interest. A small part only of volume of the total world BCC technology studies is devoted to these fuels, mostly the studies of scientists are from those regions where anthracite is mined (in general - 5% of the world's deposits explored). These

are the countries, such as: Korea, Vietnam, South Africa, Spain and Pennsylvania State in the USA.

Currently, the irregular supply of the anthracite from the occupied territories of the Donetsk coal basin is typical for Ukraine. For instance, in 2015 compared to 2013 the supply of the anthracite (rank A and T) at TPP's reduced from 18 to 8 million tons taking into account the supplies from Russia and Republic of South Africa. At the same time, the market of biomass as fuel is rapidly growing (the pellet plants that were built for the money of foreign grants and investors). The displacement at least of the anthracite part for the biomass is a partial solution of the critical situation that led to boiler units' shutdown of Zmiyevska and Trypilska TPP's this winter.

The CETI almost for 10 years has been working on the biomass and anthracite co-combustion technology development, the beginning of which founded a joint project with Pittsburgh Energy Technology Center (PETC) of the Ministry of Energy of the USA under the NATO Program "Science for Peace" since 2007. In the course of works, the optimum regime characteristics, the synergetic effects of the mutual influence of two different solid fuels, the kinetic characteristics of the pine sawdust for combustion process calculation, defined [8, 9]. The purposes of the studies were the following:

- to identify the optimum biomass/anthracite ratio for the most complete burnout of both fuels at residence time in the anthracite PC boiler furnace;
- to determine the optimal performance characteristics of such combustion;
- to determine the characteristics of a wide range of the domestic biomass (pine sawdust, pulp, pellet of wheat straw, rape, etc.) for the BCCC calculation;
- to investigate the effect of the biomass impurities on coal burnout efficiency;
- to study the effect of the biomass impurities on environmental performances of the mixture burnout;
- based on experimental and theoretical studies, to develop the burners' and primary furnaces' constructions for combustion as separately biomass as its mixtures with coal.

Materials and methods

The BCC experiments were conducted at the pilot unit VGP-100V which simulate the processes that take place in the lower radiation part of boiler furnace. The aim of pilot co-combustion was to confirm the possibility of natural gas, injected for torch "lighting", substitution by volatiles of biomass. Here the biomass with a high volatile content is supposed to offset the deficiency of volatiles in coal, better torch ignition, provides its stability when firing high-ash low-reactive anthracite,

The principal schematics of the pilot unit VGP-100V (thermal output up to 100 kW in the mode of coal combustion in raw air) is shown on Figure 1. It includes the vertical downstream reactor 1, the burner 2, the slag bath 3, the turning area with cyclone 4, the cooling and afterburn chamber 5. The total length of the reactor is 4,8 m, the reactor area to the turn into a cyclone is 3,2 m; the length of the diagnostic area from the original section of the burner is 2,4 m.

The diagnostic area consists of 4 sections length of 0,6 m, the internal diameter is 0,28 m (the diameter of the rest channel to turn is 0,2 m). The water-cooling walls of the reactor are covered with the three-layer lining from the inside: the fire layer – zirconium dioxide, the heat-insulation layer – chamotte, the strain isolation layer – asbestos fabric.

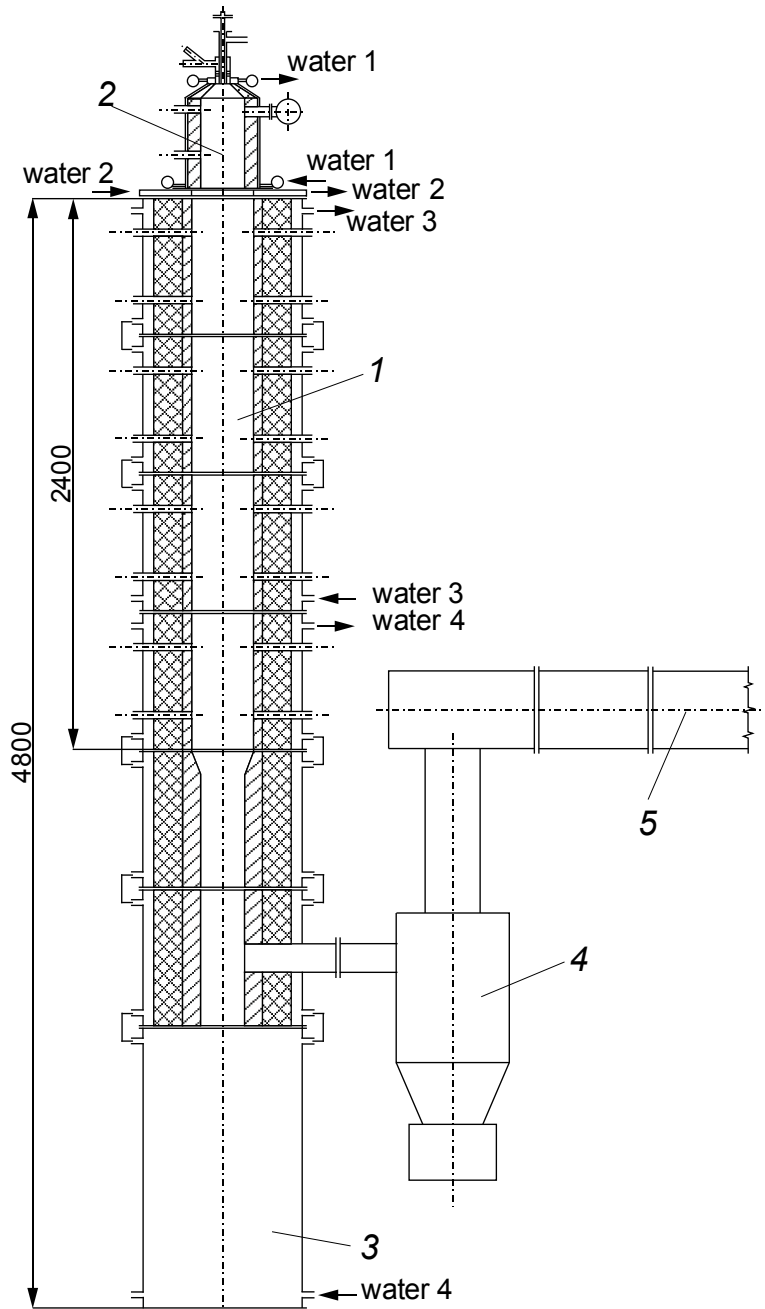


Figure 1. Experimental unit VGP-100V

The burner is vertical water-cooling lined cylinder with internal diameter of 0,2 m, length of 0,5 m, installed through water-cooling transition flange on the upper section of the reactor, equipped with two burners and operational and diagnostic windows.

From its end the primary gas burner is installed and designed for combustion of the natural gas, sawdust or its mixture. The natural gas duct is coaxially located to main gas burner which ends short section with perforation for gas release. The air or air/sawdust mixture supply duct is coaxially located to gas duct which ends vane swirler to intensify air blowing with gas and sawdust – with combustible products.

The auxiliary gas burner with electroignition that is differed by air walls' air-cooling with heated air supply to the burner, is installed on the side wall of the burner.

The supply of the following reagents is foreseen, such as:

- the natural gas – in the main and auxiliary burners;
- the air – in the main and auxiliary burners, transporting air with coal and sawdust, secondary air;
- the coal – in the upper part of the burner through the side wall;
- the biomass – in the primary burner.

The unit is equipped with two independent measuring devices: the coal measuring device - the productive efficiency from 5 to 40 kg per hour and the sawdust measuring device – the productive efficiency from 3 to 15 kg per hour.

The experiments are controlled:

- the natural gas and air consumption behind each of the input channels – by the rotameters;
- the sawdust consumption – following the calibration chart of voltage on windings of the motor and following the pressure in front of the ejector;
- the coal dust consumption – following the calibration chart of voltage on windings of the motor;
- the lining temperature on the reactor length – by two-spectral pyrometer “DPR-1” (the fire layer, at times) and K-type thermocouples immersed in the lining layer over 5-10 mm from fire surface (always);
- the gas flow temperature – by the S-type thermocouples embedded to axis of the channel;
- the rarefaction in the reaction zone – by the U-shaped sensor;
- the composition of combustible products at reactor output – by gas analyzers: by mass-spectrometer MX-1215 and portative gas analyzer MRU Vario Plus.

The indications of the K-type thermocouples and mass-spectrometer are processed from analog to digital signals, displayed on monitor screen for operational control (updating each 0,5 s) and registered (each 20 s) by automated control system on the basis of PC. The gas phase analysis is constantly taken off at the reactor outlet by water cooling sampling probe, the probe transporting time (constant time delay) to gas analyzer no more than 15 s. At $T_{\text{reactor}} = 1200\text{--}1250\text{ }^{\circ}\text{C}$, the residence time τ was at the level of 0,75–0,8 s which is close to residence time of particles in the lower radiation part of the pulverized boilers' furnace.

The kinetic studies of dehydration, devolatilization and cokes' burning of different biomass types

The above-mentioned studies of the BCC processes examined with use of wood that is considered one of the most environmental types of the solid biomass available in Ukraine.

However, due to high demand on the wood and its wastes in wood processing and other industries, the shortage for this type of biomass as fuel could take place in some regions of Ukraine. At the same time, there is a large number of available straw of different crops in the country that is also used in the world in the BCCC technology but not so prevalent because of high chlorine content in it, which has a negative impact as on the state of the boiler heating surface as on environmental friendliness of its operation. In the event of chlorine problem solution in the future, the biomass number for a large-scale BCCC technology implementation is significantly expanded. Therefore, to determine the possibility of straw using of the different crops available in Ukraine for co-combustion technology, in cooperation with the Ural Federal University (the Yekaterinburg city, Russia) and the Institute of Macromolecular Chemistry of NAS of Ukraine (the Kyiv city) were held the thermogravimetric studies of the wheat straw, canola, corn and soybeans' pellets' samples, and for comparison, samples of wood (sawdust), which used in previous studies on panels of the CETI of NAS. The pellet samples' studies conducted on derivatograph of the Paulik-Paulik-Erdey Q-1000 system in air atmosphere with heating rate of 20 °C / min. in temperature range of $T_{ambient} - 1000$ °C. The mass of test samples was 100 mg. The wood samples studied at integrated complex of simultaneous thermal analysis STA 449 Jupiter by NETZSCH company in air atmosphere with heating rate of 5 °C/min. in temperature range of $T_{ambient} - 700$ °C.

The kinetic studies of the wood cokes' burning at unit RSK-1D

To calculate the next biomass combustion in the upper part of the boiler furnace it is necessary to determine the kinetic characteristics of the biomass coke burning. Despite the fact that during the wood combustion, the volatile yield is 80-85 %, the burnout time of just biomass coke residue determines the total time required for combustion of fuel mixture. Therefore, to clarify the characteristics of the wood coke burnout, the kinetic studies at unit RSK-1D of the Coal Energy Technology Institute (CETI) were held, that is a vertical pulse gradientless fluidized bed reactor.

The unit RSK-1D (Figure 2) is designed to study the kinetics interaction with gases-reagents at temperature up to 1250 °C. It is a differential pulse reactor that operates in modes near to ideal elimination in gas phase and ideal mixing in solid phase, as well as allows to support small temperature gradients (less than 10 K) in the reaction zone along the height mounting under performance of the experiments.

The intensive fuel particles' blending provides the mode of ideal mixing in solid phase and also almost the uniform concentration of the gas-reagent in the sample layer. The gas flow in the reactor promotes the ideal elimination mode in gas-reagent pulse.

The base of the unit (Figure 2) is vertical tube furnace with one-through cylindrical reactor located inside and manufactured of heat-resistant steel (height 1,1 m, internal diameter 3,3 cm). At the bottom of the reactor is inert magnesium oxide filling intended for gas-reagent heating that is supplied from the bottom, on the top of which the fluidized air distribution grate is located. The grate is made of fine-mesh ceramics and has a resistance of 1000 Pa due to which an equal distribution of the gas-reagent flow rates in cross section of the reactor is achieved. The temperature in the reaction zone is controlled by K-type thermocouples located in the centre of the fluidized volume of the coke sample examined, in furnace and outside of the reactor (all at one level). The temperature measurement is

provided by multichannel analogue/digital converter (ADC UKT-38). The gases' supply is made by means of gas conditioning – air and helium bottle batteries (argon, nitrogen).

During the kinetic experiment carrying out the gas flow passing through reactor, is measured. The gas components' concentrations are measured by gas analyzer Siemens Ultramat 23.

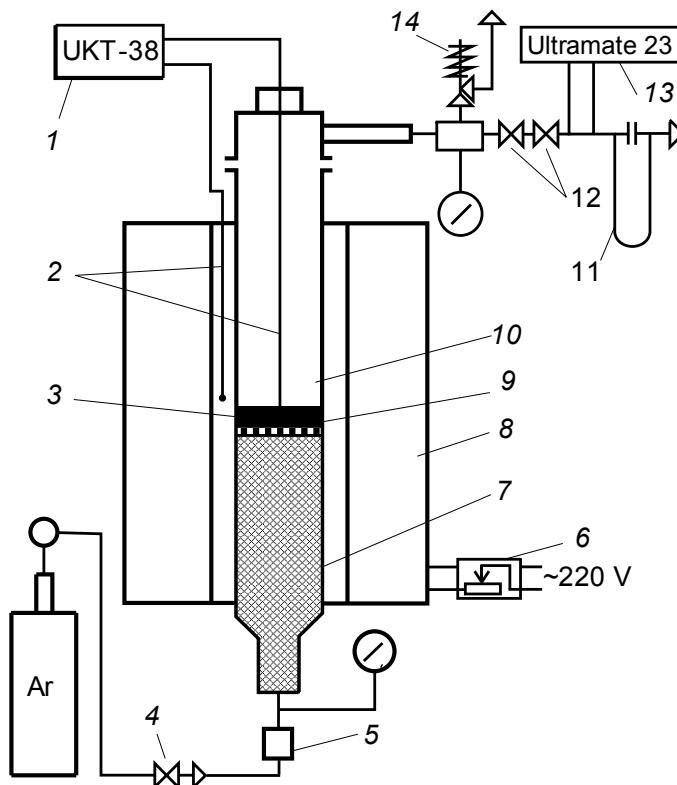


Figure 2. Unit RSK-1D:

- 1 – ADC; 2 – thermocouples; 3 – **timber weight**; 4 – needle valves; 5 – dosing device; 6 – voltage regulator; 7 – magnesium oxide filling; 8 – tube furnace; 9 – perforated grate; 10 – reactor; 11 – flowmeter; 12 – needle valve; 13 – gas analyzer; 14 – explosive valve.

At the beginning of the experiment, the dependence $R_m = f(T)$ is read step by step (in 10°C). The pulse input is made no more than two times at each temperature level.

Upon receipt of the rate dependencies from the temperature, the gas-reagent pulse value chosen so as to the reduction of the carbon mass D_m in timber weight was much less its initial value m_0 , and based on the marginal sensitivity of the gas analyzer used and compliance with isothermality conditions in the reaction zone. During the kinetic studies, the gas-reagent pulse value that is given by loop volume, was chosen experimentally.

The technical analysis of fuels examined at unit VGP-100V, derivatograph Q-1000 and unit RSK-1D are shown on Table 1.

Table 1

Sample	W ^r ,%	A ^d ,%	V ^d ,%	V ^{dar} ,%
unit VGP-100V				
Anthracite №1	1,1	24,8	5,5	7,3
Anthracite №2	0,6	27,9	5,3	7,3
Pine sawdust	10,0	1,8	83,5	85,0
derivatograph Q-1000				
Pine sawdust 1	8,3	2,9	82,93	85,41
Pine sawdust 2	10	0,9	83,06	83,81
Wheat straw pellets	9,2	8,9	74,52	81,80
Rape pellets	9,6	11,2	73,08	82,30
Corn pellets	10,6	15,0	70,55	83,00
Soy beans pellets	11,4	11,8	73,82	83,70
unit RSK-1D				
Pine sawdust	-	1,75	80,85	82,3

Results and discussion

The primary experimental data from derivatograph Q-1000 obtained in the form of electronic tables and in graphic form, also. The data include curves of mass and temperature changes, rate of mass change, rate of temperature change during the experiment. Conventionally, it can be separated on stage of dehydration, formation and release of volatiles and coke-ash residue burning. To determine the temperature limits of the each stage of the fuel samples thermal decomposition, the initial temperature T_0 where the sample weight is 0,975 from the original and the maximal temperature of the stage T_{max} which the second derivative from the mass change is zero and the final temperature of the stage where the first derivative from the mass change has a minimal value and the second is zero, are defined.

The following kinetic equation of each stage of thermal decomposition is considered [10]:

$$-\frac{d\alpha}{d\tau} = k \cdot f(\alpha) \quad (1)$$

where α – the degree of the experimental sample conversion shows which part of the experimental sample reacted to the timepoint τ ; k – the reaction rate constant; $f(\alpha)$ – the function that characterizes the reaction mode. The conversion degree at the timepoint τ is

$$\alpha = \frac{m_0 - m_\tau}{m_0 - m_\infty}$$

where m_0 – the initial sample weight; m_∞ – the thermal decomposition final mass; m_τ – the current sample mass. To represent the reaction rate constant, the Arrhenius formula is used:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where k_0 – pre-exponential factor; E – energy of activation, J/mol; R – universal gas constant, 8,314 J/mol·K; T – temperature, K.

Combining the equations (1) i (2), we obtain the following form of equation (1):

$$\frac{d\alpha}{d\tau} = k_0 \cdot \exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \quad (3)$$

To simplify the calculations, the assumption common in thermogravimetric studies was accepted that existing reactions of the thermal decomposition are of the first order. Then, the function $f(\alpha) = (1 - \alpha)$ and, as a result, (3), we obtain known differential kinetic equation:

$$\text{Ln}\left(\frac{1}{1-\alpha} \frac{d\alpha}{d\tau}\right) = -\frac{E}{RT} + \text{Ln}(k_0) \quad (4)$$

The equation (4) is a linear dependence of the expression $\text{Ln}\left(\frac{1}{1-\alpha} \frac{d\alpha}{d\tau}\right)$ from reciprocal temperature $\frac{1}{T}$ in form of $y=k \cdot x+b$, where $k = \left(-\frac{E}{R}\right)$, a $b = \text{Ln}(k_0)$.

During the experimental data processing on kinetics of the wood coke burning at unit RSK-1D, the calculations of the specific burning rate and degree of conversion carried out on the basis of the mass flow measurement CO and CO₂ by gross reaction of C + O₂: $R_m = (\Delta m/\Delta t)/m$;

$$R_{m0} = (\Delta m/\Delta t)/m_0;$$

$(\Delta m/\Delta t) = M_C G_{\text{gas}}([CO] + [CO_2])/22.4$, where m, m_0 – the current and initial mass of carbon; R_m, R_{m0} – the specific carbon burning rate, kg/(kg·s); Δm – the carbon mass reduction, kg; Δt – the pulse time, s; $(\Delta m/\Delta t)$ – the overall rate of the carbon burn-out in sample, kg/s; $M_C = 12$ – the molar carbon mass, kg/kmol; G_{gas} – the total consumption of combustible products at the reactor outlet, m³/s (under normal conditions); $[CO], [CO_2]$ – the average during pulse time concentrations CO и CO₂, the percentage (by volume).

The degree of the carbon conversion in pulse i is the expression $X_i = R_{m0}\Delta t$.

The experimental data are accumulated in electronic spreadsheet, the rated elements among others were (for pulse i): $(\Delta m/\Delta t)_i, \Delta m_i = \Delta t(\Delta m/\Delta t)_i$, where $m_i = m_0 - (\Delta m_1 + \Delta m_2 + \dots + \Delta m_{N-1})$ – the current carbon mass that is not reacted in weight for pulse starting (where N – the pulse number, $m_1=m_0$); the sample conversion degree $X_i = 1 - (m_i/m_0)$; the carbon burning specific rates $(R_m)_i = (\Delta m/\Delta t)_i/m_i$ and $(R_{m0})_i = (\Delta m/\Delta t)_i/m_0$. The initial mass m_0 of the carbon in weight is determined on the basis of the coke technical analysis. The obtained data were processed in the form of the reaction rate dependence from conversion degree at a given temperature T [$R_m = f(X)$ at $T = \text{const}$] and reaction rate dependence from temperature [$R_m = f(T)$].

Following the above-mentioned method, the primary data of derivatograms were processed. The temperature ranges of thermal decomposition individual stages of the biomass samples under examination, as well as distribution of fuel samples' initial mass following thermal conversion stages, are shown in Table 2.

Analyzing the temperature-zero coefficients and its extremes in certain stages of thermal decomposition, the attention is drawn to the proximity of these values for all biomass types explored. However, among others it could be possible to mark pine sawdust

which due to large release of volatiles has almost 20 % more thermal mass fraction of appropriate thermal stage and less mass of the coke residue. Moreover, the temperature ranges of the sawdust sample dehydration stage are shorter for 34–78 °C compared to other samples.

The pre-exponential factor calculation results (k_0) and activation energy (E) for dehydration and devolatilization stages of the fuel samples studied, as well as similar research data from sources of literature, are shown in Table 3.

Table 2
Temperature ranges and mass distribution of thermal decomposition individual stages of biomass samples

Fuel sample	Fuel thermal decomposition stage								
	dehydration			devolatilization			Coke residue burn-out		
	Range, °C	Maximum, °C	Mass fraction, %	Range, °C	Maximum, °C	Mass fraction, %	Range, °C	Maximum, °C	Mass fraction, %
Pine sawdust 1	27-120	65	7,20	120-416	301	79,80	416-697	n/s	13,00
Pine sawdust	32-136	56	6,80	136-404	307	77,20	404-610	n/s	16,00
Wheat straw pellets	24-187	100	6,18	187-440	290	62,60	440-920	n/s	31,19
Rape pellets	23-194	103	9,54	194-418	303	57,98	418-872	n/s	32,32
Corn pellets	24-186	99	9,44	186-416	281	58,02	416-940	n/s	32,51
Soy beans pellets	23-161	98	9,23	161-404	294	56,79	404-898	n/s	33,89

n/s – not specified

The graphical dependence of the devolatilization rate from reciprocal temperature in acc. to equation (4) for solid biomass samples studied is shown on Figure 3.

From the Figure, we can see a significant difference in devolatilization rate from the wood compared to other straw pellet samples studied, which can be explained by differences in nature of the above-mentioned crops growth, somewhat different heating rate during the study, as well as different step of its previous processing. Compared the pine sawdust samples and wheat straw pellets' results received during the study with results obtained in foreign studies [6, 11–14] (Table 3), mainly we see the difference in devolatilization rate that is explained by discrepancy in heating rate of samples during the experiment, different grinding degree of samples studied, difference in organic and mineral composition of samples due to different growth and storage conditions, difference in approaches to calculate reaction constants. Instead, the devolatilization rate values' proximity of the straw pellets' samples of the different crops in the given study that were obtained under the same conditions and at the same facilities, is observed.

Table 3

The pre-exponential factor (k_0) and activation energy (E) calculation results for stages of dehydration and devolatilization of fuel samples studied and its literature analogues

Fuel sample	Heating rate, °C/min.	Fuel thermal decomposition stage			
		dehydration		devolatilization	
		k_0 , 1/s	E, kJ/mol	k_0 , 1/s	E, kJ/mol
Pine sawdust 1	5	4373,85	39,19	80,02	54,76
Pine sawdust 2	5	1018,31	35,02	2627,79	71,34
Wheat straw pellets	20	1,51	16,35	177,03	52,15
Rape pellets	20	8,90	22,82	472,72	55,58
Corn pellets	20	13,18	23,32	2145,44	63,11
Soy beans pellets	20	443,86	33,78	740,19	56,57
Тирса сосни [11]	15	-	-	$6,60 \cdot 10^8$	102,30
Pine [12]	10	-	-	$7,32 \cdot 10^7$	122,56
Pine sawdust [6]	20	13,60	24,52	164400	87,37
Wheat straw [13]	30	-	-	$2,61 \cdot 10^8$	115,59
Wheat straw [6]	20	13,70	25,85	92470	82,00
Soy beans [14]	5-20	-	-	-	182,00

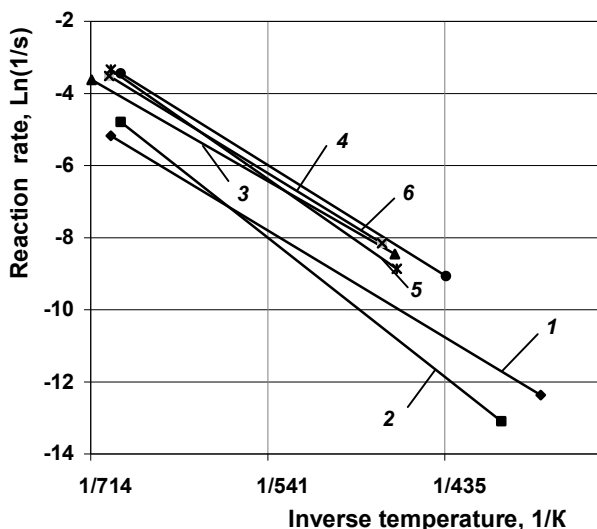


Figure 3. Comparison of the volatile yield rate dependencies from pine sawdust and pellets' sample reciprocal temperature studied, where 1 and 2 – pine sawdust as per 1 and 2, 3 – wheat straw pellets, 4 – rape straw pellets, 5 – corn straw pellets, 6 – soy straw pellets

The studies' results at the unit RSK-1D to determine the carbon burn-out specific rate dependence of wood coke (fraction size 0,1–1,6 mm) from inverse temperature (the temperature range of 390–560 °C in the study), which were obtained following the above-mentioned approach, are shown on Figure 4 in semilog coordinates. As can be seen from the graph, in temperature range studied, the wood coke particle size, as well as gas-reagent rate change in the reactor does not affect the ambient oxygen interaction rate which indicate the presence of intra-kinetic burning regime of the samples studied in the temperature range of 390–560°C.

Analyzing the linear dependence obtained for wood cokes following the above-mentioned approach, we get the rate constant of the reaction $K_{o1} = 4,9 \cdot 10^4 [1/s]/[kg/m^3]$ and activation energy $E = 199,3 \text{ kJ/mol}$. As the study of the specific surface area of the wood coke particles has not been conducted, the K_{oII} constant value was not measured.

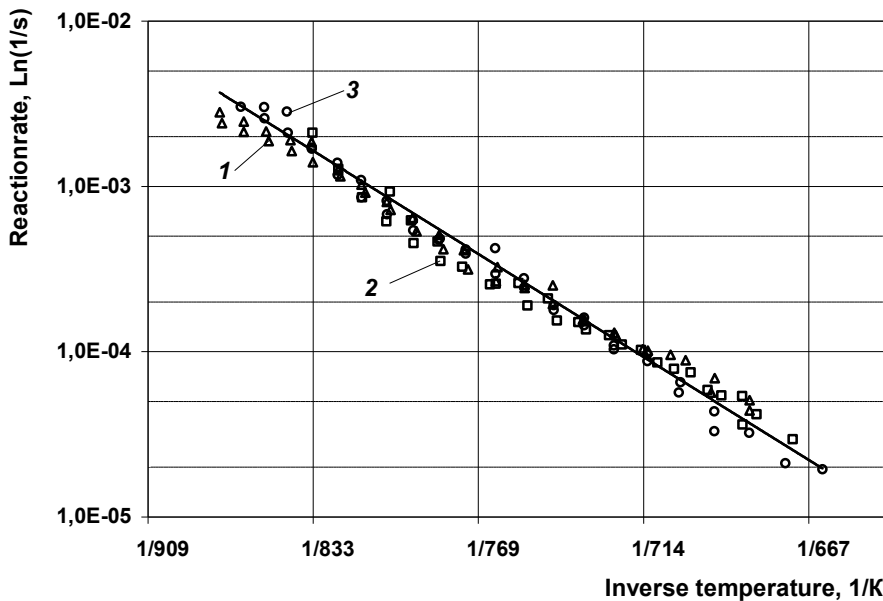


Figure 4. The dependence of the wood coke carbon burn-out rate from inverse temperature ($T=390-560 \text{ }^\circ\text{C}$): 1 – coke 0,1-0,2 mm; 2 – coke 0,4-0,5 mm; 3 – coke 1,25-1,6 mm;

The BCCC experiments at unit VGP-100V conducted using natural gas both to simulate the thermal input of the hot air the temperature of which at TPPs of Ukraine reaches 400 °C (for anthracite burning), as to compare the effect of gas (under “lighting”) and biomass (under co-combustion) for the coal burnout process.

The Table 4 shows the summary experiments' results at unit VGP-100V. The coal carbon conversion degree during the coal/natural gas co-combustion depends on coal ash content and gas share for “lighting”. The degree of common influence of such factors could be changed depending on specific combination of the process parameters. Thus, under gas consumption that provided steady burning, the further increase of its consumption under other identical process parameters reduces the carbon conversion degree that confirmed by regimes 1 and 4. For coal of even ash content in conditions of the gas consumption increase

(by heat rate) from 6,9 to 20,8 %, the conversion degree is reduced from 63,4 to 52,3 % that is explained by intense oxygen absorption under combustion of more reactive gas with lower temperature ignition.

The experiments conducted of the biomass and anthracite (of different ash content) co-combustion are shown in Table 4 (regimes 6–8). In the experiments, the biomass portion (that is burnt) is varied in appropriate range of heat portion introduced within 2,9–13,9 % taking into account heat expended for air heating. The anthracite carbon conversion degree under its co-combustion with biomass, is determined based on consideration of reference value of the biomass conversion degree when it is burning with gas, which was obtained during the separate regime of combustion. Based on the values of the anthracite carbon conversion degree found in this way, it is possible to determine the optimal sawdust share which provides the torch stability along with maximal carbon conversion degree.

Table 4

The experimental regime characteristics

Regime	Coal ash content, %		Conversion degree, %		Excess air	Total power, kW	Residence time, s	Gas temperature in sections, °C				Fuel share under heat, %			
	sawdust	coal	sawdust	coal				1	2	3	4	gas	gas/sawdust*	coal	sawdust
Natural gas and coal combustion															
1	24,8	0	63,4	0,74	146,6	0,9	1340	1340	1330	1200	11,3	6,9	88,7	0	
2	27,9	0	60,8	0,76	141,4	0,9	1300	1350	1355	1250	11,7	7,2	88,3	0	
3	24,8	0	59,2	0,8	147,8	0,9	1002	1275	1320	1202	12,0	6,5	88	0	
4	27,9	0	52,3	0,82	146	0,8	940	1260	1380	1320	25,7	20,8	74,3	0	
5	27,9	0	73,3	0,86	148,1	0,9	940	1090	1100	1010	26,8	20,2	73,2	0	
Biomass and coal co-combustion															
6	24,8	80	56,5	0,47	172,9	0,8	1380	1445	1405	1290	0	2,9	92,9	7,1	
7	27,9	80	70,4	0,78	154,4	0,7	1445	1445	1415	1305	0	13,9	80,9	19,1	
8	27,9	80	75,9	0,85	145,7	0,7	1445	1445	1405	1330	0	8,4	85,7	14,3	

Notes:

* – the natural gas/sawdust heat share taking into account its consumption for air heating up to 320°C at TPP that is operated.

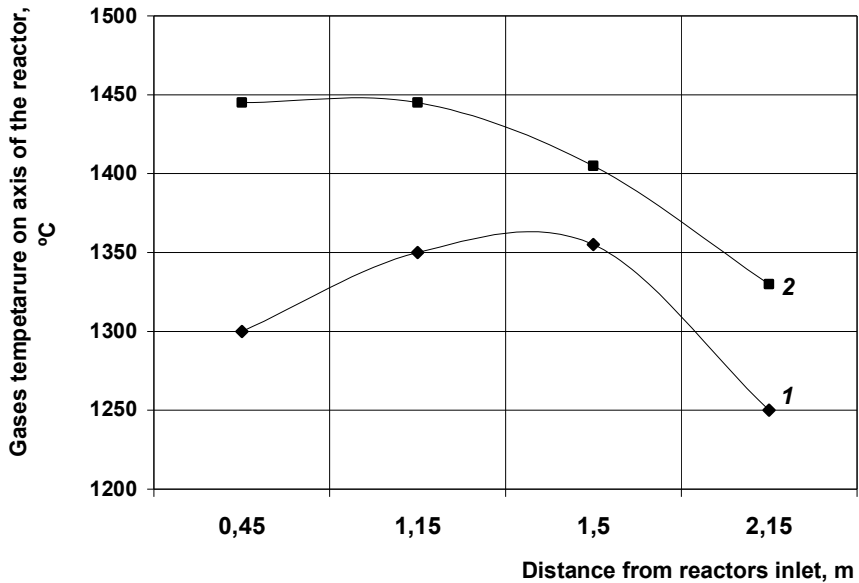


Figure 5. Temperature distribution in reactor and coal conversion degree comparison under its lighting by natural gas and sawdust: 1 – mode anthracite/gas (93,8%/6,2%), $X_{\text{coal}}=60,8\%$; 2 – mode anthracite/sawdust (97,1%/2,9%), $X_{\text{coal}}=56,5\%$.

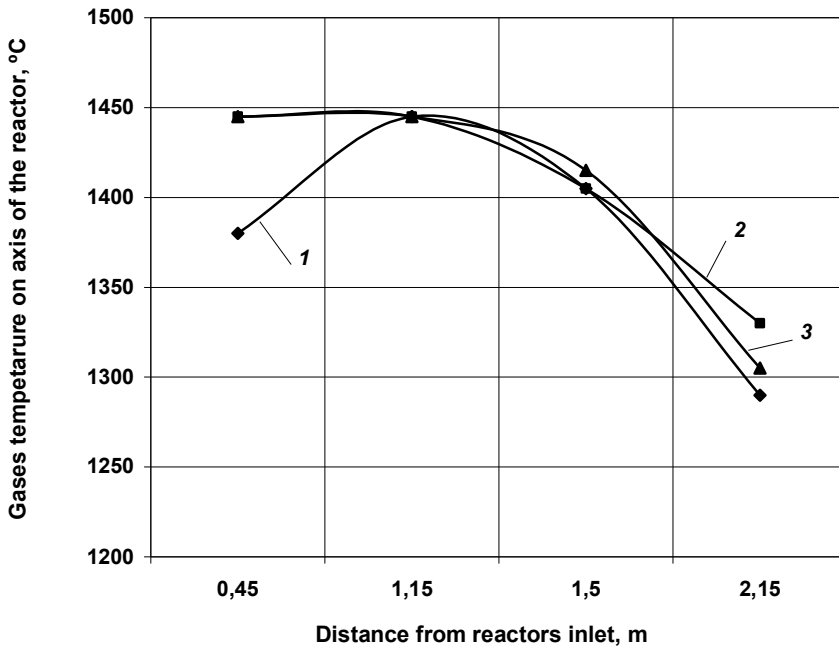
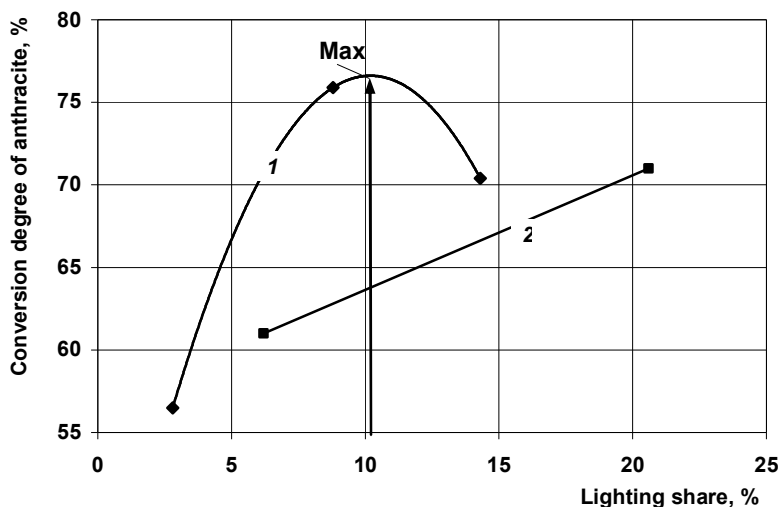


Figure 6. Dependence comparison of the sawdust conversion degree under- co-combustion with anthracite: 1 – sawdust share 2,9%; $X_{\text{coal}}=56,5\%$; 2 – sawdust share 8,4% $X_{\text{coal}}=75,9\%$; 3 – sawdust share 14,3% $X_{\text{coal}}=70,4\%$.

As per temperature measurement results in the reactor and coal carbon conversion degree under its lighting by the natural gas and co-combustion with sawdust, then the obtained results show that even under biomass supply at a rate of 2,9 % by heat value it completely succeeded to refuse from the torch lighting by natural gas although coal conversion degree slightly decreased compared to gas lighting regime (see Figure 5). Herewith, the core torch temperature significantly increased. By increasing the supply of the biomass up to 8,4% by the heat value, the significant increase of the coal conversion degree is observed, as well as palpable extension of torch (Figure. 6) due to increase in time of the coke residue burn-out time of the biomass particles that can exceed the anthracite coke burn-out time. The further increase in biomass supply while maintaining the torch stability and high heat density of reactor volume leads to the carbon conversion degree reduction. This fact is connected with that highreactive fuel that is this case is sawdust rapidly consumes air oxygen in high temperature core zone thereby worsening the conditions of coal burn-out.

Based on the above-mentioned, on the basis of the co-combustion regimes' comparison under heat share variation that is brought by the biomass (Figure 6), the optimal thermal share of the biomass was determined that is about 10% (Figure 7). The supply of such biomass share in high-ash anthracite and biomass co-combustion regimes provides torch stabilization without gas lighting and highest degree of the coal carbon conversion.

The conducted studies confirmed the feasibility of efficient substitution of lighted natural gas by wood processing wastes in pulverized boiler units' furnaces which burn anthracite. The full natural gas substitution by biomass is accompanied by steady burning in the experiments. Upon this, the gas temperature increase in reactor is observed. The volatiles' shortage compensation in the anthracite due to sawdust is proven efficient measure to support the low-reactive coal burning, even in case of high-ash coal combustion.



**Figure 7. The dependence of the coal conversion degree from the natural gas and sawdust lighting:
1 – sawdust; 2 – natural gas; Max – the optimal thermal share of the biomass.**

Conclusions

The co-combustion of pulverized domestic anthracite and wood in the unit VGP-100V has proven its technical realizability and a noticeable potential to significantly improve the quality of low-reactive anthracite combustion. In the event of unsatisfactory state of boiler units or supplies of high-ash coal at TPP's, wood is more efficient alternative to use natural gas to maintain anthracite burning stability.

The study of the carbon reaction rate dependence of wood coke with air oxygen from the temperature at unit RSK-1D indicates the presence of intra-kinetic burning regime in the temperature range of 390-560 °C.

The analysis of thermogravimetric study results shows possible significant differences in characteristics of solid biomass as separate types, as different samples of the same type. Therefore, unlike with coal in each case of the BCCC technology implementation, it is necessary to study biomass that is planned to burn.

Presented results can be used in calculations of the some stages co-combustion processes which take place in TPP's.

References

1. Dunaievska N., Zasiadko Ya., Shupik I., Shchudlo T. (2007), Ohliad tekhnolohii spilnoho spaliovannia biomasy i vuhillia v pylovuhilnykh topkakh, *Enerhotekhnolohyy y resursoberezhnye*, 3, pp. 3–8.
2. (2016), Database of Biomass Cofiring initiatives, available at: <http://www.ieabcc.nl>
3. (2002), National Renewable Energy Laboratory (NREL), May 2002, NREL/TP-510-32260, available at: <http://www.nrel.gov/docs/fy02osti/32260.pdf>
4. (2010), Lesley Sloss. Emissions from cofiring coal, biomass and sewage sludge (IEA Clean Coal Centre), available at: https://www.usea.org/sites/default/files/102010_Emissions%20from%20cofiring%20coal%2C%20biomass%20and%20sewage%20sludge_ccc175.pdf
5. Fernando R. (2005), Fuel for biomass cofiring, *IEA Clean Coal Centre*, pp.37
6. Zasiadko Ya.I., Myroshnyk M.M., Zasiadko P.Ya. (2012), Termohravimetrychni doslidzhennia buriakovoho zhomu, *Tsukor Ukrainy*, 2(74), pp. 29–32.
7. Matveichuk A. (2012), O tekhnologii sovместnogo szhiganiia burogo uglia i solomy v topochnykh kamerakh s nepodvizhnym sloem, *Vidnovliuvana energetika*, 3(30), pp.79–83.
8. Maistrenko O., Dunaevska N., Zasiadko Ya., Bondzyk D., Shchudlo T., Vyfatniuk V. (2012), Tekhnolohiia ta palnyk dlia spaliovannia biomasy yak dopomizhnoho palyva v fakelnykh kotloahrehatakh, *Nauka ta innovatsii*, 4, pp. 83–88.
9. Dunaevskaya N., Zasyad'ko Ya., Shchudlo T., Bestsennyi I., Bondzik D. (2009), Eksperimental'noe issledovanie protsessa sovместnogo fakel'nogo szhiganiya antratsita s drevesnoy biomassoy, *Energotekhnologii i resursoberezhenie*, 3, pp. 10–17.
10. Guo J., Lua A. (2001), Kinetic Study on Pyrolytic Process of Oil-Palm Solid Waste Using Two-Step Consecutive Reaction Model, *J. Biomass and Bioenergy*, 20, pp. 223–233
11. Gil M., Casal D., Pevida C., Pis J., Rubiera F. (2010), Thermal behaviour and kinetics of coal/biomass blends during co-combustion, *Bioresource Technology*, 101(14), pp. 5601–5608

12. Sema Yurdakul Yorulmaz, Aysel T. Atimtay (2009), Investigation of combustion kinetics of treated and untreated waste wood samples with thermogravimetric analysis, *Fuel Processing Technology*, 90, pp. 939–946
13. Yu Zhaosheng, Ma Xiaoqian, Liu Ao (2008), Kinetic studies on catalytic combustion of rice and wheat straw under air- and oxygen-enriched atmospheres, by using thermogravimetric analysis, *J. Biomass and bioenergy*, 32, pp.1046–1055
14. (2013), Maria Inez G. de Miranda, Clara I. D. Bica*, Sonia M. B. Nachtigall, N. Rehman, Simone M. L. Rosa, Thermal decomposition of soybean hull cellulose: a kinetic study, 12^o Congresso Brasileiro de Polimeros (12^oCBPol), September 22–26: Proceedings, available at:
<https://www.lume.ufrgs.br/bitstream/handle/10183/81824/000901361.pdf?sequence=1>

Thermocouple errors in temperature measurements and validation of CFX and FLUENT models of natural gas combustion

Pavlo Zasiadko, Mykola Priadko

National University of food Technologies, Kyiv, Ukraine

Abstract

Keywords:

Combustion
Thermocouple
Bead
Heat flux
Simulation

Article history:

Received 06.09.2016
Received in revised form
16.10.2016
Accepted 27.12.2016

Corresponding author:

Pavlo Zasiadko
E-mail:
iaroslav@nuft.edu.ua

DOI: 10.24263/2304-974X-2016-5-4-15

Introduction. Technological processes associated with combustion pose serious environmental problems due to the emission of harmful substances predominantly in gaseous state. According to the generally accepted view, the nitrogen oxides mostly originate in combustion plants in the regions of high temperatures.

Materials and methods. Therefore the problems associated with the thermocouple errors at temperature measurements in the flames carried out during experimental combustion of natural gas in the experimental unit VGP-100B are being dealt with.

Results and discussion. A model has been derived aimed at the evaluation of correction factors that are to be applied, when processing data from the direct thermocouples' readings. The model takes into account the convective heat transfer, irradiation on a part of the thermocouple bead, which falls from the combustion products. It also takes into consideration that a part of the thermocouple bead irradiates in the direction of the cooled surrounding. As a result, a transcendent fourth order equation has been obtained and solved numerically by MathCad. A set of correction coefficient was obtained which, when added to the direct readings of thermocouples, have shown a close conformity to the results obtained from the 3-d modeling of the natural gas combustion in the cylindrical down flow reactor.

Conclusion. The developed correction methodology may be recommended to be used in practice, when experimental temperature measurements may be performed by means of bare thermocouples, when sheathed thermocouple or suction pyrometer cannot be used.

Introduction

Literature sources [1–8, 10, 11] deal with the flame temperature measurements with bare thermocouples. They mainly discuss the measurement of temperature in combustion processes within the flame or near in the vicinity of cooled walls or with temperature measurements of relatively cold gas flows in the presence of high-temperature enclosures that are in direct exposure to the thermocouple.

If a thermocouple measures the temperature of gas flow outside of the radiating flame, it most likely gives too high temperature readings, since the thermocouple bead receives not only the convective heat from the flow itself, but radiative flux from the flame as well. Because the radiant flux is proportional to the 4th temperature degree, it is clear that thermocouple measurements in high temperature processes, particularly combustion the input of radiant flux will be much more significant than that from convection.

On the contrary, when measurements take place in a close vicinity of flame with the enclosure kept at a lower temperature and with optically semitransparent medium, the thermocouple readings will be lower than the actual flame temperature. This is due to the effect that the thermocouple bead, being a participant of complex heat transfer, will receive heat as a result of convection from the gas flow and radiation from the flame, will also irradiate towards the cooled enclosure. Shannon and Butler [1] suggested a mathematical model that takes into account the heat balance of the thermocouple bead:

$$[\varepsilon_{fl} \sigma T_{fl}^4 - \varepsilon_{bead} \sigma T_{bead}^4] F_{form-bead} - [\varepsilon_{bead} \sigma T_{bead}^4 - \varepsilon_{\infty} \sigma T_{\infty}^4] (1 - F_{form-bead-\infty}) = h A_{bead} (T_{fl} - T_{bead}) \quad (1)$$

where F – a function that takes into account the relative exposure, flame-bead or bead surrounding, respectively.

In [2] an extremely simplified model was accepted, according to which the thermocouple radiates all the heat, obtained by the convection from the flow:

$$(T_{fl} - T_{bead}) = \frac{\sigma \varepsilon}{h} (T_{bead}^4 - T_{\infty}^4), \quad (2)$$

where h – heat transfer coefficient from the gas flow calculated by:

$$Nu \left[\frac{1}{2} \frac{(T_{fl} - T_{bead})}{T_{bead}} \right]^{-0.17} = 0.24 + 0.56 \left(\frac{wd}{\nu} \right)^{0.45}, \quad (3)$$

Combining (2) and (3) one can approximately determine the thermocouple error from the re-radiation:

$$(T_{fl} - T_{bead}) \approx \frac{d^{0.55}}{w^{0.45}} (T_{bead}^4 - T_{\infty}^4). \quad (4)$$

Where w – gas flow speed, may be termed as a portion of heat delivered by convection. Some conclusions are readily available from this correlation: the reduction of the error can be achieved by reducing the diameter of the thermocouple bead or by decreasing the proportion of radiant heat transfer between the gas flow and the bead.

Walker-Stokes [3] proposed the method of measuring the temperature with thermocouple set, whose diameter is decreased progressively. This method has allowed to reduce inertia of thermocouple readings and to determine the effect of radiation basing upon the expression (4). This method allows also to increase the accuracy of measurements, but its implementation is too complex, because it requires simultaneous temperature measurement with the range of thermocouples of different sizes. The method becomes absolutely unrealizable due the temperature instability of flows and necessity to install the thermocouple in the same place of a flow.

Most often, the protective screens are used to shield thermocouple beads [1–4]. Since the protective screen has an intermediate temperature between the actual temperature of bead and the ambient temperature, it significantly reduces the re-radiation flux. Protective screens can be accompanied with the suction of flow through a cylindrical screen, which leads to an increase of flow speed around the thermocouple bead and, as a result, increasing convective heat transfer coefficient thus bringing closer bead actual temperature to that of flow. In practice, the speed of sucked flow is limited by the experimental considerations (prevention of significant disturbance in the flow). Comparative results of the temperature measurement in industrial furnaces by means of unprotected thermocouples of different diameters, two types of shielded thermocouples, that differed by the place of suction, were given in [1, 2, 8]. The authors have shown that the greatest error occurs at measuring the temperature of medium with the thermocouple irradiation.

From the data given in [1-8] follows that the error of "cold" flow measurement by bare thermocouple within the radiating environment reaches 250%. Errors of temperature measurements by bare thermocouples in "hot" flows surrounded by cooled walls reach 25%. Installing of a dual screen can reduce the error to 25% and 7%.

Materials and methods

Experiments have been conducted in the experimental rig designed and erected at the Coal Energy Technology Institute of the National Academy of Science of Ukraine. The scope of experimentation covered the following:

- Obtaining experimental data of the direct temperature and components' concentration distribution within the reactor when burning natural gas, which then will be used for the 3-D CFX and FLUENT models validation by the comparison of the measured and modeled data;
- Co-combustion of coal and solid biomass aimed at the determination of the optimal process conditions;
- Combustion of solid biomass at different regime parameters aimed at the determination of the effect of the various types of biomass burning kinetics, its conditions and properties aimed at the determination of the optimal process conditions.

Since the experimental rig closely models the conditions which exist in the lower radiation section of industrial boiler furnaces in the vicinity of burners, the experimental results obtained thus may be applicable for the designing optimal combustors.

The schematic (layout) of the stand is shown in Figure 1.

Thermal capacity of the unit when burning coal with air as an oxidant reaches 100 KW.

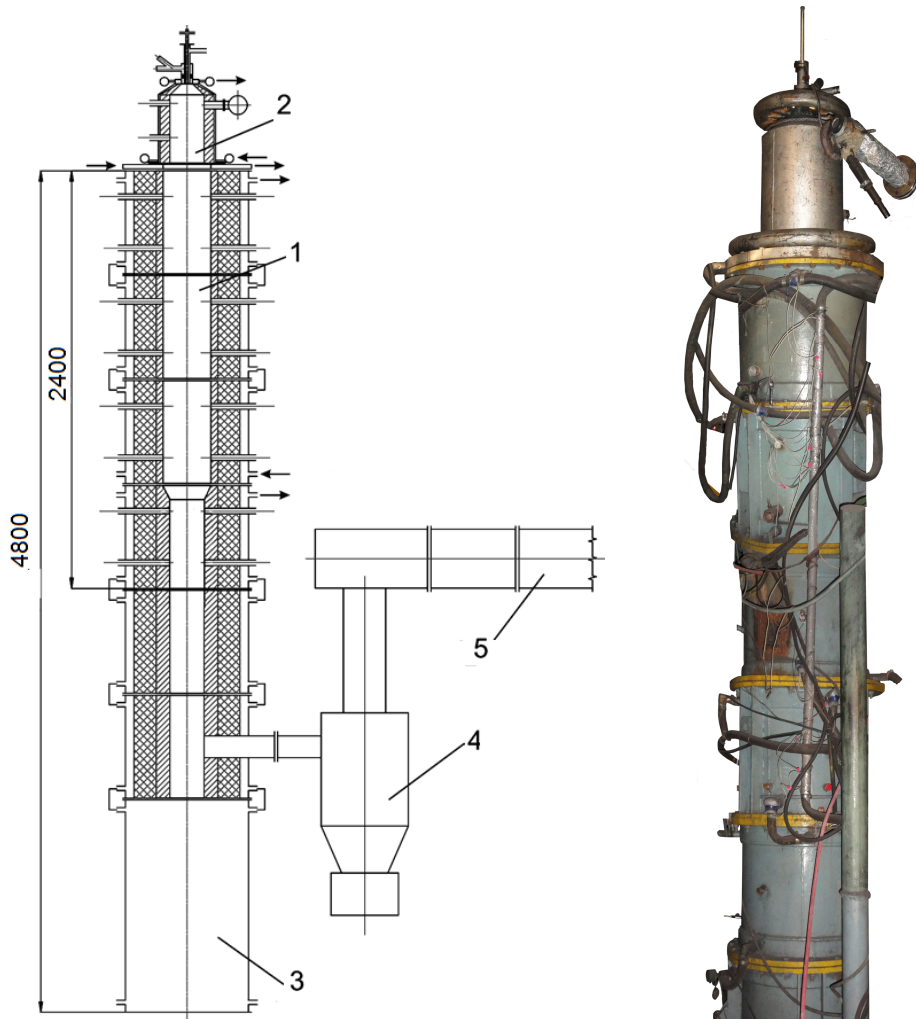


Figure 1. Experimental down flow reactor VGP-100 B:
1 - experimental sections, water cooled jackets for calorimetry;
2-Burner head with multiple air inlets;
3-ash collector;
4-cyclon for fly ash removal;
5-flue gases duct.

The main part of the unit is a down flow test channel with four diagnostic sections in which combustion takes place. Each of three initial sections is 0.6 m long with the internal diameter 0.28m. The last one has the same length and 0.2 m internal diameter. The internal walls of all test sections have a tree layer protective covering consisting of consecutive

layers of zircon dioxide, fire clay and asbestos. Each section has a water cooled jacket with the individual supply and water flow measurement, which in turn allows the calorimetry of each section. The burner head is equipped with two natural gas burners. The main burner has an additional channel for the injection of pulverized (ground) solid biomass or coal together with NG and initial air. The secondary burner is designed to inject natural gas and air only. There are also additional inlets allowing to inject any of the combustion components with the respective measurements of the component's flow rate. Each section also equipped with the inlets allowing inserting probes and thermocouples allowing direct measurements of local temperature and flue gases composition.

The experiments of natural gas combustion were carried out in the down flow cylindrical reactor VGP-100, Figure 1. The temperature of test sections' walls was measured by chromel-alumel (type K) thermocouples that were built in the fire proof lining 10 mm deep from the fire layer. Periodical measurements of fire layer of lining were performed with the pyrometer "DPR-1" through the diagnostic openings. The temperature of the gas flow on the axis of the reactor was measured by Platinum-Platinum-Rhodium thermocouples (Type R) with 0,2 mm diameter wires in corundum protective cover with 0,5 mm diameter channels positioned in probes at a midsection of each test section. Hot thermocouple junctions were covered with a layer of corundum making the bead diameter-5 mm.

Thus obtained data related to the combustion of natural gas of a known composition were used for the validation of the developed 3-D CFX model of the process along with the direct temperature measurements which were used as benchmark data for developed model of measured temperatures correction.

In order to carry out the validation, a complex 3-d meshes of the reactor has been developed. The mesh represents the experimental stand VGP in general and in minor details. The main problem of the mesh development consisted in finding an optimum compromise between the number of mesh cells (which eventually determines accuracy and calculations convergence time and, thus, the required computer capacity) on the one hand, and the necessity to represent minor stand details which affect the actual process and are to be represented in the mesh – on the other.

Combustion of methane in down flow cylindrical reactor VGP-100B of the Coal Energy Institute of the National Academy of Sciences of Ukraine (ICE NASU) has been studied. The temperature inside the reactor was measured as follows –temperature of walls was measured by chromel-alumel (type K) thermocouples that were built in the fire proof lining 5-10 mm deep from the fire layer with continuous registration of temperature. Periodical measurements of fire layer of lining were performed with the pyrometer "DPR-1" through the diagnostic openings. The temperature of the gas flow on the axis of the reactor was measured by thermocouples, Platinum-Platinum-Rhodium (Type R) with 0,2 mm diameter wires embedded in corundum protective cover with 0,5 mm diameter channels and put through the diagnostic openings. Hot thermocouple junctions were covered with a layer of corundum making the bead diameter-5 mm. Lack of thermal stabilization of cold junctions was accounted for by correction factor for a local air temperature. The process has been modeled in a 3-d arrangement with the CFX-15 and FLUENT (Lic.No1023420) commercial codes.

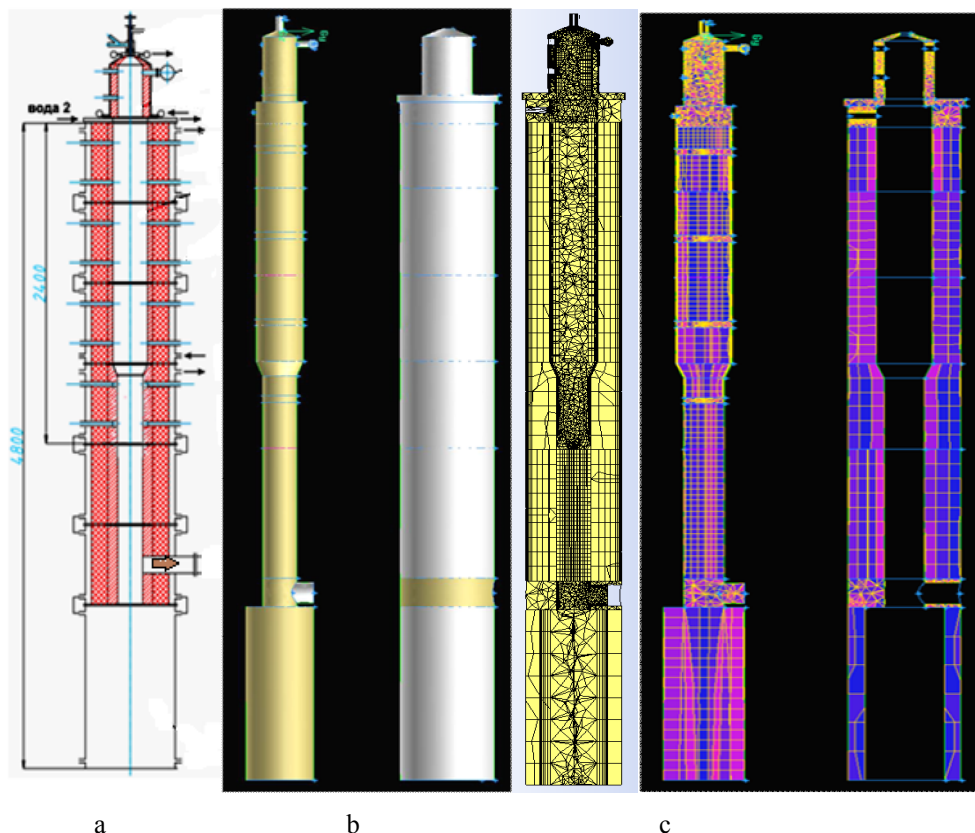


Figure 2. Reactor VGP:
a – VGP Reactor, b – geometry model with and without insulation,
c – 3-D mesh of the reactor core and insulation

Results and discussion

The results of simulation with CFX and FLUENT software, particularly the temperature distribution along the reactor axis, heat fluxes from the diagnostic sections were compared to those observed experimentally.

It was found that the gas temperature measured in 4 points in the middle of each diagnostic section on the axis were 120-150 °C lower than respective CFX-FLUENT simulated values. The difference in the obtained data can be explained by re-radiation of thermocouple beads towards the cooled walls. Thermal balance of thermocouple bead, that considers both convective and radiant flows, can determine the value of error of flow temperature measurement on the axis of the reactor.

It should be noted that the model under consideration becomes significantly complex as a result of taking into account radiant heat transfer between the thermocouple and gas flow, since gases are characterized by selective spectral energy absorption and emission. The absorption and emission of energy by monatomic and diatomic gases, including nitrogen,

oxygen, and hydrogen are insignificant and may be neglected. Polyatomic gases, including carbon dioxide CO₂, water vapour H₂O, sulphur dioxide SO₂, ammonia NH₃, and others, have a large capacity for absorption and emission of radiant energy. Carbon monoxide CO also has a significant level of emission and absorption, but this gas occurs only as traces in the products of methane combustion at a proper air-fuel ratio.

The model of radiant heat exchange of bead with the environment has been derived under the assumption that the gas has a constant temperature T_{fl} , and the wall has a constant temperature T_{wall} .

Flue gas and the walls are considered gray bodies. Radiation of the wall is characterized by a continuous spectrum and the medium (combustion gases) has selectively radiation in a form of separate bands $e_1, g_1; e_2, g_2$. In the general case the number of such bands varies.

Radiation heat transfer from the gas to the wall can be expressed as:

$$Q_{fl-wall} = (E_{ef,fl-wall} - E_{ef,wall-fl}) A_{wall}, \quad (5)$$

where A_{wall} – surface area of the wall;

$E_{ef,fl-wall}, F_{ef,wall-fl}$ – effective radiation heat flux from gas medium and the effective radiation of the wall, respectively.

The effective radiation heat flux of the gas medium and the walls was calculated based upon the balance method. The values can be represented by the expressions that are valid within certain radiation spectral bands [9,13]:

$$\begin{aligned} E_{ef,fl} &= (E_{0,fl})_{\Delta\lambda} + q_{fl-wall} \left(1 - \frac{1}{\varepsilon_{fl,\Delta\lambda}} \right), \\ E_{ef,wall} &= (E_{0,wall})_{\Delta\lambda} + q_{wall-fl} \left(1 - \frac{1}{\varepsilon_{wall,\Delta\lambda}} \right). \end{aligned} \quad (6)$$

The fractions of black body emission of the gas and wall at the limiting values of their emissivity factors can be expressed by the following expressions:

$$\begin{aligned} (E_{0,fl})_{\Delta\lambda} &= C_0 \left(\frac{T_{fl}}{100} \right)^4 \cdot \varepsilon_{fl}^{\infty}, \\ (E_{0,wall})_{\Delta\lambda} &= C_0 \left(\frac{T_{wall}}{100} \right)^4 \cdot \varepsilon_{wall}^{\infty}, \end{aligned} \quad (7)$$

where $\varepsilon_{fl}^{\infty}$ and $\varepsilon_{wall}^{\infty}$ – are limit values of emissivity factors for gas and walls, respectively, which in case of the wall radiation assumes the black body radiation at the wall temperature, whereas in case of gas radiation it is assumed that the optical length of the gas layer approaches infinity, i.e. gas radiates at its spectral bands as a black body.

The values are determined from the charts [12] at temperatures of gas and wall, respectively. Gas emissivity $\varepsilon_{fl,\Delta\lambda}$ is determined by the following:

$$\varepsilon_{fl,\Delta\lambda} = \frac{k_1 l_1 e_1 g_1 + k_2 l_2 e_2 g_2}{a_1 b_1 e_1 g_1 + a_2 b_2 e_2 g_2} = \frac{E_{fl,\Delta\lambda}}{(E_{0,fl})_{\Delta\lambda}} = \frac{\varepsilon_{fl} E_{0,fl}}{\varepsilon_{fl}^{\infty} E_{0,fl}} = \frac{\varepsilon_{fl}}{\varepsilon_{fl}^{\infty}} \quad (8)$$

Equation (8) can be interpreted by means of Figure 3. As it can be seen, J_{bb}, J_{gr} are lines that depict spectral radiation intensity of black and “grey” body, respectively at a certain temperature.

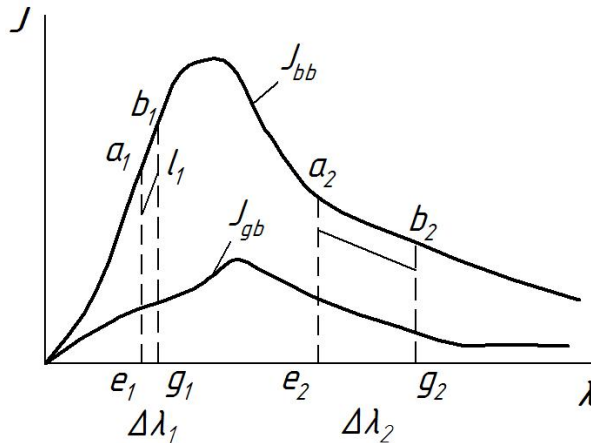


Figure 3. Spectral radiation intensity of black, grey bodies and selective radiation of gas

If one suggests that a certain gas radiates within two bands $\Delta\lambda_1, \Delta\lambda_2$ and energy emitted within these bands somewhat lower than that of the black body, namely those equal graphically to the area within the bands $e_1 k_1 l_1 g_1$ and $e_2 k_2 l_2 g_2$.

At the same time, within the same bands the black body radiates energy that can be depicted by area $e_1 a_1 b_1 g_1$ and $e_2 a_2 b_2 g_2$, see Figure 3. Therefore, the gas emissivity (absorptivity) within the bands $\Delta\lambda_1, \Delta\lambda_2$ can be calculated by (8), where $\varepsilon_{fl}^{\infty}$ can be interpreted as the emissivity (absorptivity) of a gas layer with infinite thickness within a whole range of wave length λ . When taken within all spectral bands the gas radiates, this value will be equal to the fraction of black body radiation.

The degree of wall emissivity within certain bands $\Delta\lambda$ can be considered as equal to integral emissivity factor $\varepsilon_{wall,\Delta\lambda} = \varepsilon_{wall}$. For the stationary conditions regime holds the following $q_{fl-wall} = q_{wall-fl}$.

Substituting (7, 8) into (6), we obtain the following expression for the radiant flux $Q_{c,c}$, that is transmitting from the gas medium to the thermocouple bead:

$$Q_{fl-wall} = \frac{C_0 A_b \left[\varepsilon_{fl}^{\infty} \left(\frac{T_{fl}}{100} \right)^4 - \varepsilon_{fl,wall}^{\infty} \left(\frac{T_{wall}}{100} \right)^4 \right]}{\frac{\varepsilon_{fl}^{\infty}}{\varepsilon_{fl}} + \frac{1}{\varepsilon_{wall}} - 1} \quad (9)$$

Integral values of emissivity factor (absorption coefficient) for a gas mixture, as it was shown above, in general case is not equal to the sum of the values of the individual components of the mixture. Thus, for a mixture of CO₂ and H₂O the emissivity factor and the absorption coefficient are less than the sum of their values for CO₂ and H₂O separately, due to its partial overlapping of emission spectral bands:

$$\varepsilon_{fl} = \varepsilon_{H_2O} + \varepsilon_{CO_2} - \Delta\varepsilon_{fl} \quad (10)$$

The individual values of steam and carbon dioxide emissivity were taken from [12,13] at gas temperature and corresponding component's partial pressure in the gas mixture, and beam path length, pl . Average path length of the beam was determined from the following expression:

$$l = m \frac{4V}{A},$$

where V is a volume of a gas body;

$m=0,9$ – correction factor.

The results of direct temperature measurements with bare thermocouples during the experimental combustion of natural gas in a vertical reactor VGP-100B (100 KW th) of the Coal Energy Technology Institute were taken as benchmark values for the validation of the model. The objective of the proposed model is to derive a comparatively simple equation which will allow to calculate the temperature of a hot bead of a thermocouple (T_{th}) placed into the flow of hot combustion gases at a given (T_g) and being exposed to the relatively cold walls at given T_w . Thus, the correction temperature can be determined which is to be used when direct readings of unsheathed thermocouples which are used for temperature measurements in media with convective-radiative heat transfer.

The equation was derived under the condition of equality of heat supplied to a thermocouple bead and the amount of heat, that thermocouple gave off to the walls as a result of re-radiation. Heat input is realized by means of convective heat transfer, radiation of hot flue gas and by radiation of heated head burner lining.

For the approximate estimation of the re-radiation effect it was decided to apply the simplified model of radiant heat transfer between the bead surface and the heated lining surface under the following conditions: a) bead surface and radiating lining surface are plane-parallel; b) the area of bead surface, that receives radiation, is equal to a half of the total area of thermocouple bead; c) absorbing capacity is $\varepsilon_{ef}=0.9$; d) the temperature of the heated lining is taken equal to the temperature of the gas core T_{fl} . Then, the components of a heat balance of the bead will be:

Absorbed heat

$$Q_{bead,abs} = h(T_{fl} - T_b)A_b + \frac{\varepsilon_{ef}A_b \left[\left(\frac{T_{fl}}{100} \right)^4 - \left(\frac{T_b}{100} \right)^4 \right]}{2} + \frac{C_0 A_b \left[\varepsilon_{fl}^{\infty} \left(\frac{T_{fl}}{100} \right)^4 - \varepsilon_{fl,t wall}^{\infty} \left(\frac{T_b}{100} \right)^4 \right]}{\frac{\varepsilon_{fl}^{\infty}}{\varepsilon_{fl}} + \frac{1}{\varepsilon_{wall}} - 1} \quad (11)$$

Heat, radiated by the thermocouple bead on the wall

$$Q_{bead,rad} = \varepsilon_c A_b \left[\left(\frac{T_b}{100} \right)^4 - \left(\frac{T_{wall}}{100} \right)^4 \right] \quad (12)$$

where T_b , T_{wall} , T_{fl} – temperatures of thermocouple, wall, actual temperature of the gas, respectively, [K];

h – heat transfer coefficient from the thermocouple bead surface to gas environment;

ε_{fl} – emissivity factor of gas;

$\varepsilon_{fl}^{\infty} \varepsilon_{fl,t wall}^{\infty}$ – limiting emissivity factor of gas at $l=\infty$, gas at the temperature of gas, and gas at temperature of the wall, respectively;

ε_c – emissivity factor of corundum,

A_b – surface area of the bead.

The heat transfer coefficient was calculated for the case of an external flow of hot flue gases around a thermocouple. The correlation for determination of Nu number was taken from [9] and thermophysical parameters were calculated by the software EnecCalc3, and checked with data base [9]:

$$\overline{Nu} = 2 + 0.03 Re^{0.54} Pr^{0.33} + 0.35 Re^{0.58} Pr^{0.36} \quad (13)$$

The speed of the flue gases for determining the Reynolds number was calculated on the basis of process modeling CFX 15 Fluent code (Lic.No 1023420) and conventionally accepted as constant $w=4.5$ m/s. The diameter of the thermocouple bead accepted at $d=0.005$ m. The values of heat transfer coefficients were calculated for three different temperatures of incoming flow – flue gases core.

The calculations were performed with variations of temperatures of the gas core within the limits $T_{fl} = 2200 \dots 1600$ K and with the temperature of cooled walls variation so that the temperature difference between the wall-flow changed recursively 200 ... 400 ... 600 K, which corresponds to the actual conditions of the experiment. Thermophysical parameters of combustion products, optical properties of CO_2 and H_2O , both individually and in mixtures were defined as a result of the process modeling). Convective heat transfer coefficients were calculated for each pair of the assumed combustion gas and walls temperatures, accordingly.

Thus derived transcendental equation of 4th degree with nonlinear coefficients was solved in Mathcad software package as the point of intersection of the two functions (11 and 12). The solution was obtained in graphical and numerical forms.

The results of equations solving for different cases of gas stream and wall temperatures are summarized in Table 1 and shown in the graph (Figure 4).

Table 1

Summary table of thermocouple readings at different temperatures of the gas core and walls

T_{fl} , K	T_{wall} , K	T_{beads} , K
2200	2000	2077
	1800	1986
	1600	1910
	1400	1854
2000	1200	1814
	1800	1880
	1600	1792
	1400	1724
1800	1200	1677
	1600	1686
	1400	1606
	1200	1548

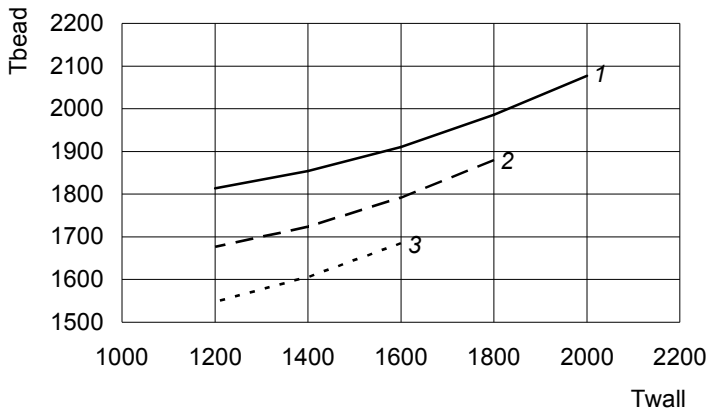


Figure 4. Calculated readings of a thermocouple installed in the flow of flue gases and emitting radiation on the channel wall (T_{wall}) at different temperatures of a flow (T_{fl}):
1 - $T_{fl}=2200$ K, 2- $T_{fl}=2000$ K; 3 $T_{fl}=1800$ K.

According to the obtained data, shown in the Figure 1, at the actual temperature of the flow 2200 K and 2000 K temperature of the wall, thermocouples will show the temperature at 123 K less than the actual gas temperature. At the same gas temperature, the difference between actual temperature and measured thermocouple will increase to 386 K at 1200 K temperature of the wall. At 1800 K of core temperature and 1600 K of wall temperature specified difference will be 114 K that is slightly smaller than the measurement of a core temperature.

Analyzing the obtained data, one can conclude that re-radiation plays a significant role in the measurement of temperature at the considered conditions. The graphical interpretation of Mathcad solution of the developed model at a flow temperature of 1400 K and variations of wall temperature is presented in Figure 5.

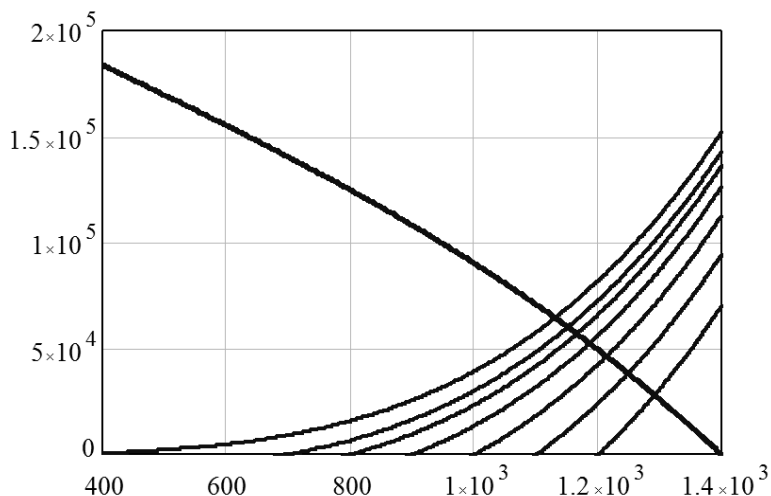


Figure 5. Calculation by the model for conditions [2,8]

Each abscissa value of the lines' intersection gives the value of thermocouple bead temperature at the flue gas temperature 1400 K and respective wall temperature. The bigger the wall temperature, the closer to the 1400 K value moves the intersection point, and respectively closer to 1400 K moves the reading of the thermocouple.

To define a degree of reliability of the developed model, the data obtained from the above calculation were displayed in coordinates given in [2,8] namely, T_{error} - difference between the gas temperature and thermocouple bead temperature as a function of wall temperature T_{wall} . The result are given in of Figure 6.

Apparently, the data obtained from the proposed model are slightly lower than those given in [2, 8] at wall temperatures below 850 C. This can be explained by the fact that in our model it is assumed that the bead emits energy by the half of its surface that is directed down towards the ash collector, as the upper part of the bead is directed to head with burners, which emit the energy to the bead. In addition, the proposed model takes into account emission and absorption of triatomic gases in the combustion products, whereas the models treat the gas flow as a transparent medium.

It seems possible to use the obtained data to adjust the results of a direct temperature measurement of the thermocouples located at stand VGP-100D, and to compare them with the calculated data of the CFD modeling process by means of FLUENT and CFX packages. The comparison of direct measurement readings and with those determined by the 3-d model and proposed correction are shown in Figure 7. Data in Figure 7 show that the readings of a direct temperature measurement by thermocouples located along the axis of the channel of the reactor VGP 100B and respective temperatures determined on the basis of simulation are significantly differ. This happen because the measurements by thermocouples are taken under the condition of reradiation from the thermocouples to the cooled walls toward downstream direction. Correction of thermocouple readings was based on the model described above. Thus, the calculation of correction factors was based on the stream temperatures according to the model.

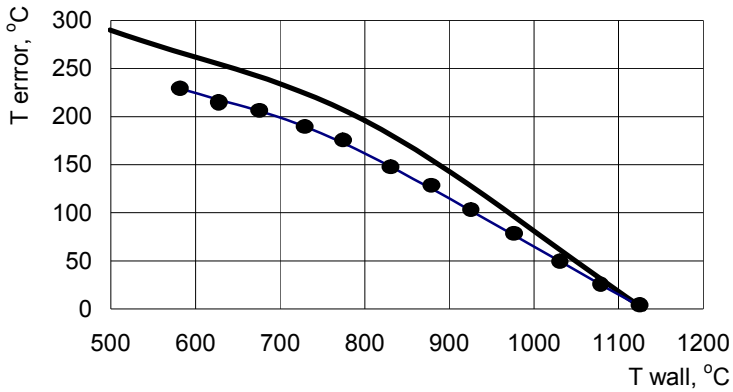


Figure 6. Comparison of the calculations based upon the developed model and data [2,8]. The solid line are data [2, 8]. The points – calculation by the model.

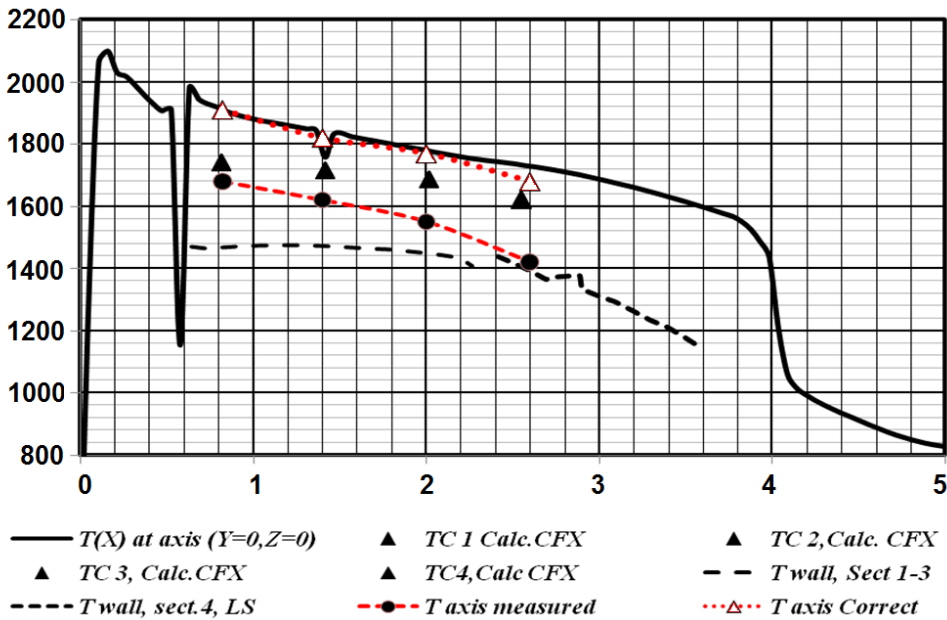


Figure 7. Comparison of the results of calculation by means of CFX package with the results of measurements with a consistent refinement that based on the model of reradiation accounting

The temperature of the wall was taken according to the measurements that were considered reliable because the wall thermocouples, being embedded in the lining, do not participate in radiation heat transfer, and their readings are deemed as reliable. Thus, obtained corrections were added to the thermocouple readings because they reflect the bead

temperature and not the temperature of the flow of combustion products that flows around the thermocouple bead. Instead, corrections to the thermocouple readings reflect the temperature of stream that flow around beads, see equation (11.12).

As it can be seen from Figure 4, based on the readings of thermocouples and proposed model of measuring the temperature of the flow on VGP channel axis matched with the modeling results close enough (within 5%), which indicates adequacy of the proposed model and accuracy of data obtained by measurements by the thermocouples. In general, the comparison of the results of CFX simulation of the process of natural gas burning in VGP stand by expendable and operational parameters that correspond to the results of the experiment, indicates their resemblance, which, in turn, is an evidence of a model validation (confirmation of adequacy).

Validation of the models was based on a comparison of heat loss from the parts of VGP stand, that were subjected to calorimetric measurement and losses, that were deducted on the CFX model basis.

Table 2

Comparison of heat losses on the calorimetric stand sections

Section of the experimental unit	Heat loss measured on the stand, W	Heat loss of a model, W	Δ , %
Burner	8600	9113	5.9
Flange of a burner	2500	2320	7.2
Diagnostic section	4300	4641	7.3
Total	15400	15738	2.2

Apparently, there is a close correspondence of the results within 7.5% on sections and 2.2% on stand.

Examples of modeling the processes of natural gas combustion using FLUENT package in VGP stand are shown in Figure s 5–7.

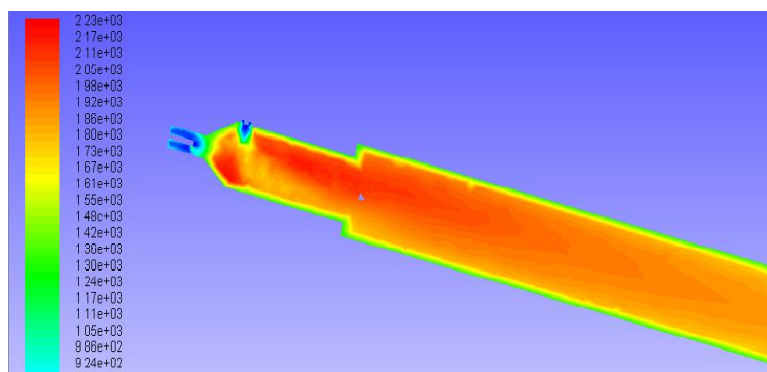


Figure 5. Temperature field in the axial section of VGP with the supply of 125 m³ of air to the burner head

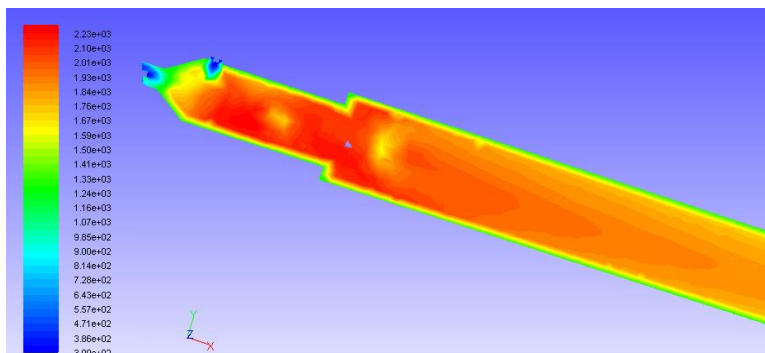


Figure 6. Temperature field in the axial section VGP, mode B 41, supply of 77 m³ of air to the burner head and 48 m³ to the diagnostic section

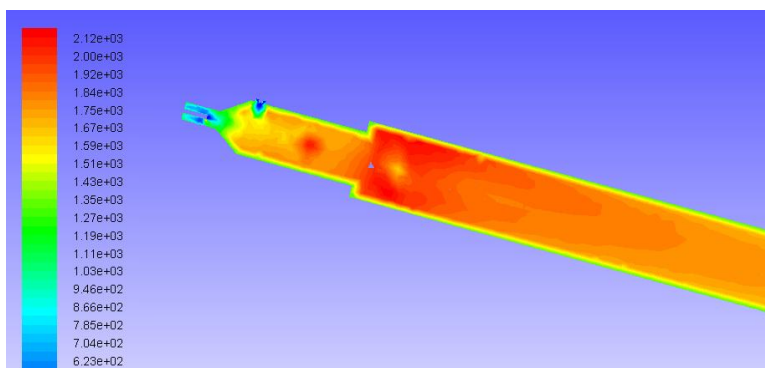


Figure 7. Temperature field in the axial section VGP, supply of 25 m³ of air to the burner head and 100 m³ to the diagnostic section

Conclusions

1. CFD modeling gives a very powerful tool for the study of combustion processes of different fuels, allowing any variation of operational parameters and process components flow rates.
2. The model which accounts for the thermocouple bead heat balance has been developed.
3. As a result of model validation a method of adjustment thermocouple readings when measuring the temperatures in the presence of strong radial flows has been presented.
4. A set of 3-d models of the experimental natural gas combustion in the down flow reactor VGP-100 B was developed. The models may be used for simulation of the process with a wide range of regime parameters and flow rates variation.

References

1. Shannon K.S., Butler B.W. (2003), A review of error associated with thermocouple temperature measurement in fire environments, *2-nd International Wildland Fire Ecology and Fire Management Congress*, November 16-20, 2003, Orlando.
2. Pitts W.M., Braun E. (2002), *Temperature uncertainties for bare and aspirated thermocouple measurements in fire environments. Thermal measurements: the foundation of fire standards*, Dallas.
3. Walker D., Stocks D. (1968), Thermocouple errors in forest fire research, *Fire technology*, pp. 58-64.
4. Martin R., Cushwa C. (1969), Fire as a physical factor in wildland management, *Proceedings of tall timbers fire ecology conference*.
5. Sung Chan Kim, Anthony Hamins (2008), On the Temperature Measurement Bias and Time Response of an Aspirated Thermocouple in Fire Environment, *Journal of Fire Sciences*, 26, pp. 509-529.
6. Peter Struk, Daniel Dietrich, Russell Valentine, Ioan Feier (2003), Comparisons of Gas-Phase Temperature Measurements in a Flame Using Thin-Filament, *Pyrometry and Thermocouples NASA/TM*, 2003-212096.
7. Z'Graggen A., Friess H., Steinfeld A. (2007), Gas temperature measurement in thermal radiating environments using a suction thermocouple apparatus, *Meas. Sci. Technol.*, 18, pp. 3329–3334.
8. Linda G. Blevins, William M. (1999), Pitts Modeling of bare and aspirated thermocouples in compartment fires, *Fire safety Journal*, 33, pp. 239-359 .
9. Grigorev V.A., Zorin V.M. (1998), *Teoreticheskie osnovy teplotekhniki*, Moscow.
10. Smith E.J., Natan G.I., Omar N.H., Dally B.B. (2005), Comparison of thermocouple temperature measurements of simple and processing jet propane flames, *5-th Asia-Pacific Conference on Combustion, The University of Adelaide, Australia, 17-20 July 2005*, pp. 89-92.
11. Roberts I.L., Coney J.E.R., Gibbs B.M. (2011), Estimation of Radiation Losses from Sheathed Thermocouples, *Applied Thermal Engineering*, 2011, p. 14
12. Available at: <http://web.iitd.ac.in/~prabal/gas-radiation.pdf>
13. Isachenko V.P., Osipova V.A., Sukomel A.S. (1975), *Teplotperedacha*, Moscow.

Modelling of pulsating mode of fluidization when obtaining organic-mineral fertilizers

Yaroslav Korniyenko, Serhii Haidai,
Andrii Liubek, Serhii Turko, Oleksandr Martynyuk

National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine

Abstract

Keywords:

Hydrodynamics
Pulsation
Fluidization
Fertilizers
Ash

Article history:

Received 30.10.2016
Received in revised form
29.11.2016
Accepted 27.12.2016

Corresponding author:

Serhii Haidai
E-mail:
GaidaiSS@i.ua

DOI: 10.24263/2304-
974X-2016-5-4-16

Introduction. The objective of this work is mathematical modeling of inhomogeneous hydrodynamic regime of fluidization, which will improve the efficiency of heat and mass transfer in processes of obtaining organic-mineral fertilizers, which include sunflower ash, stimulating and nutritional components.

Materials and methods. The process of inhomogeneous fluidization, which causes an active volumetric mixing of granular material with the intensive circulation in bed, was held in camera of granulator, equipped with a special gas distribution device in the bottom and the directing insertion in the upper part. Measurements of pressure drop in the bed and video-fixation of hydrodynamics have been done by using the special equipment.

Results and discussion. An inhomogeneous regime of fluidization is implemented with applying the original gas-distributing device (with a factor of cross-section $\varphi=4.9\%$) and the improved chamber of granulator. An intensive macro-mixing of a granular material (with an equivalent diameter $D_e=3.97$ mm and density $\rho_p=1450$ kg/m³) is provided with ratio of nominal pressure drop to height of layer – $\Delta P_b/H_0 \geq 8500$ Pa/m and frequency of pulsations $f=1.67$ Hz. The absence of stagnant zones provides the coefficient of granule formation $\psi \geq 90\%$, and the average specific load of bed's surface by moisture $a_f = 0.8 \div 0.9$ kg_{wet}/(m²·h). A chosen mathematical model was modified what allowed to define the conditions of the process considering inhomogeneity in which 25% of the layer mass is in active phase above the bed with a frequency $f=1.67$ Hz. It confirms the results of research with accuracy of 94.8%.

Conclusions. Hydrodynamics without formation of stagnant zones in chamber of granulator was implemented. Modified mathematical model allowed to determine the intensity of an active volumetric circulating mixing that will significantly improve the stability of a granule formation process in dewatering of liquid heterogenous systems.

Introduction

Rapid population growth causes an increase in the demand of agricultural products, quality and amount of which depends on agricultural land [1]. However, over 30% of the world arable lands have been lost as a result of erosion and pollution by chemical fertilizers for the past 40 years [2]. The deterioration of state of the environment compels the humanity to seek ways to reduce the negative impact on the soil [3].

In modern terms to increase yields is advisable to create a complex granulated organic-mineral fertilizers that contain mineral nutrients NPK, deoxidizing additives and humic substances, contributing the simultaneous soil formation.

As phosphorus-potassium substances a sunflower ash which is obtained by burning of husk can be used in the production of fertilizers. The husk is a by-product of sunflower oil production, percentage of which in market is constantly increasing, and reached to 6.6% among 17 oilseeds. This is evidenced by the constant increase of acreage for planting of sunflower in the world and at the year 2016 amounted to 25,640,000 Ha [4].

Content of the main valuable components that are a part of sunflower ash is 93.67% of the total weight, Table 1, and the rest 6.33% – Zn, C, Co, Mn, Fe, Mo [5].

Table 1

The chemical composition of sunflower ash

Chemical compounds	K₂O	CaO	MgO	SO₃	P₂O₅
wt. %	31.40	19.07	18.58	13.68	10.94

Dehydration and granulation of a sunflower ash water solution is proposed with an implementation of rotary drum granulators [6–8], but due to the lack of nitrogen-containing components and humic substances the effectiveness of their use reduces. The authors [9–11] propose to eliminate the aforementioned drawbacks by pressing the mixture composed of ammonium sulfate and humic substances in addition to sunflower ash, but in this case the component distribution is at macro level and finished product have a low strength and great capacity for caking.

To obtain a granular product with desired properties the most effective is technique of fluidization which allows to combine multiple technological stages in one device with the coefficient of heat using more than 50%. An important factor for implementation of this method is hydrodynamics [12].

Effectiveness of the process kinetics depends on the hydrodynamic regime in chamber of granulator, which provides the necessary intensity of renewal the contact surface of phases by moving a considerable mass of granular material.

Therefore, research of hydrodynamic regime of fluidization that provides an active volumetric mixing of granular material with an intensive circulation in bed with absence of stagnant zones in chamber of granulator and on the surface gas-distributing device and significantly to intensify the process by the use of heat carrier with a temperature that is significantly higher than the melting point of nitrogenous components is topical.

The aim of experimental research is to determine the conditions under which the jet-pulsating mode of fluidization provides an active volumetric mixing of granular material with an intensive circulation in bed.

Analysis of scientific works

Researches of the transfer process in a bubbling mode of fluidization were held in works of D. Gidaspow, J. Davidson [13, 14] and other. In the main they considered the jet injection of gas flow with the further movement of gas bubbles formed in layers of granular material with height $H_0 > 1\text{m}$.

In particular, the authors [15] propose to improve a layer mixing due to formation of large bubbles $D_{\text{apparatus}}/D_{\text{bubbles}} < 1.5$, that in a layer partially moves its part while lifting. Material that is above a layer is sliding due to a presence of stern in a lower part of the bubble. With this is proposed reduction of a step between the gas jets in the gas distribution device. In this can be achieved a merger of bubbles with the formation of a large one, occupying nearly the whole volume of chamber, thus providing a local piston mode of fluidization. However, movement of a granular material into the bottom of an apparatus chamber is significantly slowing and respectively its circulation to.

Regularities of inhomogeneous fluidization were profoundly investigated in the works of scientists [14, 16–18] but most fully the interaction of gas with solid particles in dispersion medium was investigated in the [13].

The author [13] propose a determination of the total pressure drop as the sum of three basic components: pressure drop due to momentum of gas and solid particles, pressure drop due to friction of gas and particle and pressure drop due to the weight of solids, that can be written in differential form as [13]:

$$\left(\frac{dP}{dz}\right)_{\text{total}} = \left(\frac{dP}{dz}\right)_{\text{momentum}} + \left(\frac{dP}{dz}\right)_{\text{friction}} + \left(\frac{dP}{dz}\right)_{\text{elevation}}, \quad (1)$$

$$\Delta P_{\text{total}} = \Delta P_{\text{momentum}} + (\Delta P_{\text{friction due to gas}} + \Delta P_{\text{friction due to solids}}) + \Delta P_{\text{elevation}}. \quad (2)$$

Pressure drop in the bed due to momentum of gas and solid particles in integral form [13]:

$$\Delta P_{\text{momentum}} = (\varepsilon_p \rho_p v_p^2 + \varepsilon_g \rho_g v_g^2) H_0, \quad (3)$$

where ε_p , ε_g – void fraction of solid particles and gas; ρ_p , ρ_g – density of solid particles and gas, kg/m^3 ; v_p , v_g – velocity of solid particles and gas, m/s ; H_0 – height of the motionless bed, m .

Pressure drop due to friction of gas and of solid particles [13]:

$$\Delta P_{\text{friction due to gas}} = \frac{2f_g \varepsilon_g \rho_g v_g^2 H_0}{D_t}, \quad (4)$$

$$\Delta P_{\text{friction due to gas}} = 5.7 \cdot 10^{-2} \frac{1}{D_t} \varepsilon_g v_g \rho_g \theta H_0 \sqrt{g D_t}, \quad (5)$$

where f_g – coefficient of gas friction; D_t – diameter of the apparatus, m ; $\theta = (\varepsilon_p \rho_p v_p) / (\varepsilon_g \rho_g v_g)$ – the loading ratio of solid and gas phases.

Pressure drop due to the weight of solid particles [13]:

$$\Delta P_{\text{elevation}} = g(\rho_g \varepsilon_g + \rho_p \varepsilon_p) H_0. \quad (6)$$

Thus, the equation (2) in expanded form:

$$\begin{aligned} \Delta P_{\text{total}} = & (\varepsilon_p \rho_p v_p^2 + \varepsilon_g \rho_g v_g^2) H_0 + \frac{2f_g \varepsilon_g \rho_g v_g^2 H_0}{D_t} + \\ & + 5.7 \cdot 10^{-2} \frac{1}{D_t} \varepsilon_g v_g \rho_g \theta H_0 \sqrt{g D_t} + g(\rho_g \varepsilon_g + \rho_p \varepsilon_p) H_0 \end{aligned} \quad (7)$$

Materials and methods

Experimental installation

In order to achieve the specified requirements for the granular product was used a specifically developed method of the experiment [19].

Investigation of the hydrodynamic mode of fluidization carried out at the experimental installation of granulator with the chamber sizes $A \times B \times H = 0.3 \times 0.11 \times 0.8$ m. To create a jet-pulsating mode of fluidization, the chamber of granulator in a bottom part is equipped with the gas distribution device (GDD) of a slit type [Patent of Ukraine № 109509 IPC B01J 8/44. Gas distribution device of a fluidized bed apparatus], and the with the guiding insertion at the top [Patent of Ukraine № 95431 IPC B01J 8/44. Section of fluidized bed apparatus]. The cross-section coefficient of GDD is $\varphi = 4.9\%$, and a step between the slits, relatively to a chamber's width – $t = 0.4A$ [20].

Materials

As a granular material was applied a polydisperse granular product on the basis of sunflower ash and ammonium sulfate with additives of humins containing components.

It was obtained by the application of dehydration of composite liquid systems in the apparatus of a fluidized bed [Patent of Ukraine № 4465. IPC C05 G 1/00. The method of granulated organic-mineral fertilizers production]. Equivalent diameter of particles $D_e = 3.97$ mm and density – $\rho_p = 1450$ kg/m³. Mass of loaded into the apparatus bed of granules was $M_{\text{bed}} = 8.2$ kg. From this mass the bed height was determined as $H_0 = 0.32$ m and the nominal hydrostatic pressure $\Delta P_{\text{nom.}} = 2780$ Pa at porosity $\varepsilon_0 = 0.4$.

Measuring complex

Pressure drop in the bed was continuously measured by the computerized system with using of low pressure sensors MPXV7007DP with an accuracy ± 0.1 Pa and the frequency of 63 measurements per second (63 Hz) connected to the computer via the controller Arduino Pro Mini. The scheme of placement devices and sensors for fixing data is shown in Figure 1.

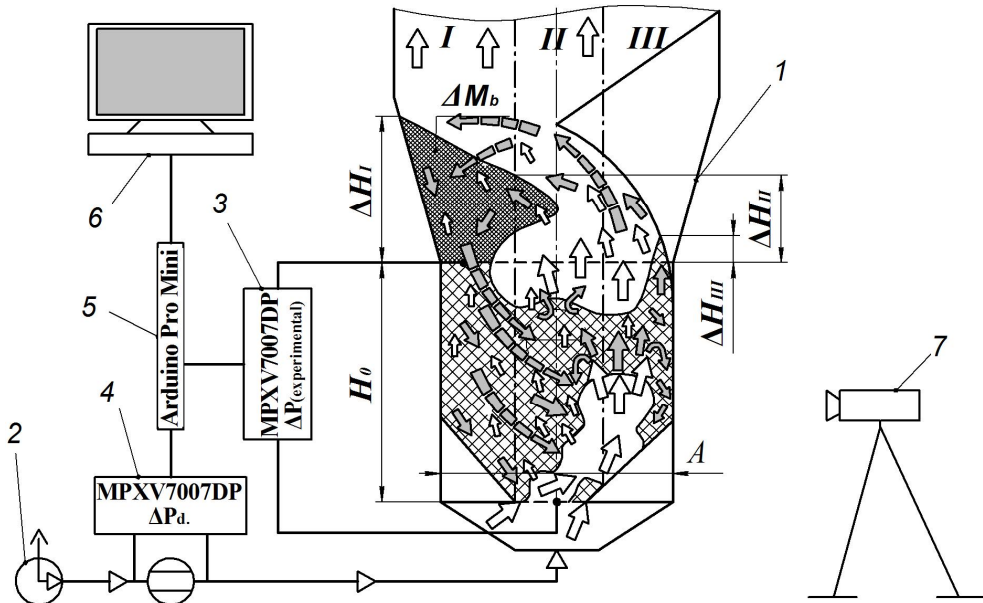


Figure 1. The scheme of computerized system for measuring the pressure drop in the experimental installation

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

The porosity of bed was determined with the use of photo-analysis of the bed state in time with step $\Delta\tau = 0.04$ s. The calculation of velocities that are included in equation (7) was carried out by the known dependencies of Reynolds number from Archimedes number ($Re=f(Ar)$) [13,14].

Results and discussion

Physical modeling of inhomogeneous fluidization

Apparatus is roughly divided into three zones *I-III* (Figure 2, a) with almost the same width $A/3$. Inside the zone *II* at height $H_{irrigation\ zone}$, which is $0.68H_0$, is a dispersant for filing the liquid phase.

The basic technical idea is to organize such interaction of gas phase with solid particles, which would ensure an active granular material passing through the irrigation zone (*II*), relaxation (*I*), intensive heat transfer (*D*), located directly at the surface of GDD, and upward flow through the zone (*III*) – airlift (Figure 2).

The gas jet through the slits of GDD is filing into a chamber of granulator by two streams: horizontal – point *p* and at the angle α – point *k*, (Figure 2, b).

Long range of a gas jet in horizontal direction (p. *p*) $x_{hor.}=f(V)$ and in active mode is almost equal to the width of fluidization zone *II* ($A/3$). Vertical part of the jet (from p. *p*) is connecting to the stream (from p. *k*) at the height $\Delta+y_f$. As a result of this method of filing the fluidizing agent at the height of the torch y_f , that comes out of p. *k* there is horizontal coalescence of gas phase in

zone III. This further causes an intense inertial ejection of the granular material into space above the bed. Velocity of these particles must be sufficient for moving to the surface of zone I (line segment *bc*) when contacting with the insert 3 (Figure 2).

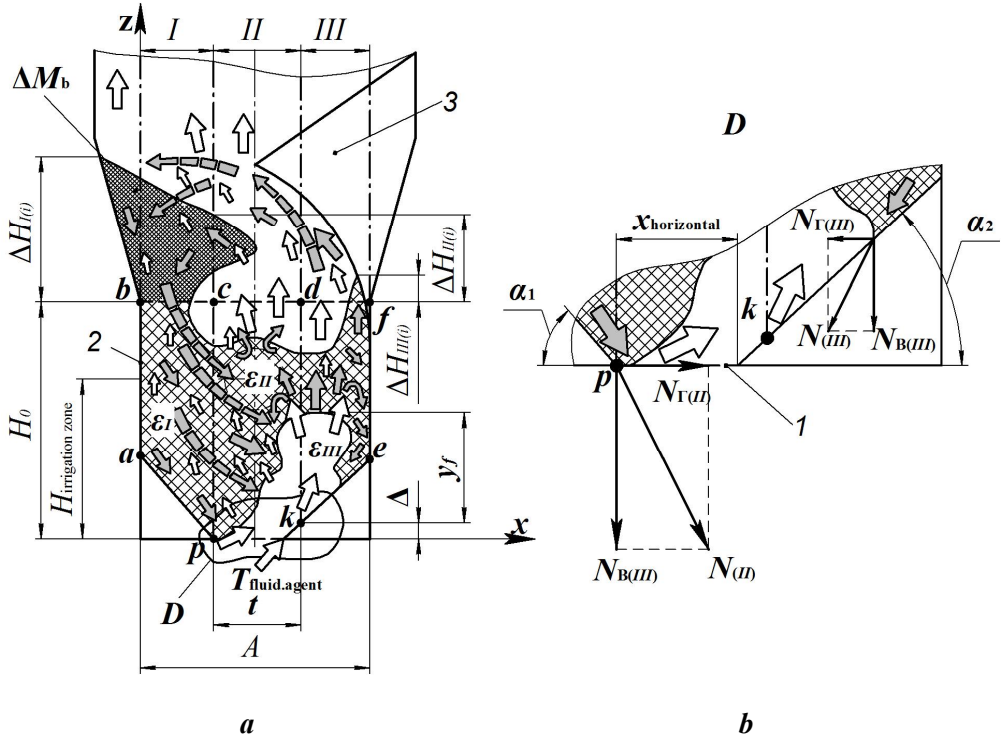


Figure 2. Physical model of the jet-pulsating mode of fluidization
a – the flows scheme in chamber of the apparatus; *b* – scheme of forces acting on the gas jet in working area GDD; 1 – gas distribution device (GDD);
 2 – chamber of granulator; 3 – guiding insertion;
 I – zone of downward movement (*a, b, c, p*); II – transition zone (*p, c, d, k*);
 III – zone of an upward flow (the ascending zone) (*k, d, f, e*); D – zone of an intense heat exchange

As a result, there is a significant pulsational increase of a bed height in zone I to magnitude $\Delta H = (0.4 \div 0.8)H_0$ (Figure 2) and as a result the hydrostatic pressure in zone of the downward movement I (*p. p*) is significantly increasing. This leads to shifting of large mass of granular material into transition zone II, through the line *cp* as the pressure *N* acting on the *p. p* increases due to its vertical and horizontal components ($N_{hor.} = K \cdot N_{vertical}$), (Figure 2, b). For this reason, further is happening the displacement of a gas torch trajectory (that comes out of *p. p*) and its union with stream from *p. k*. Thus, gas heat carrier that is injected into the zone III creates a local piston-mode of fluidization ($V_{bubbles} = 0.33 \cdot V_{apparatus}$) the zone of an upward flow III by increasing of pressure of material in zone I and II.

This physical model of inhomogeneous fluidization (Figure 2), is possible at velocity of particle moving out of the bed $W_{moving} > 2$ m/s, and is calculated from the equation, m/s, [21]:

$$W_{moving} = (2 \cdot g \cdot H_0)^{1/2}. \quad (8)$$

Justification of the mathematical model

With taking into account the developed physical model in the momentum equation (3) and in the pressure loss equation (6) for H_0 is necessary to enter a variable additional of material bed height $H_{variable} = f(\tau)$ that is transferred into the zone I. This depends on the intensity of the hydrodynamic mode. Accepted that for each moment of time $\varepsilon_p + \varepsilon_g = 1$.

taking into account of these assumptions, an equation (7) takes the form:

$$\begin{aligned} \Delta P_{total} = & (\varepsilon_p \rho_p v_p^2 + \varepsilon_g \rho_g v_g^2) (H_0 + H_{variable}) + \frac{2 f_g \varepsilon_g \rho_g v_g^2 H_0}{D_t} + \\ & + 5.7 \cdot 10^{-2} \frac{1}{D_t} \varepsilon_g v_g \rho_g \theta H_0 \sqrt{g D_t} + g (\rho_g \varepsilon_g + \rho_p \varepsilon_p) (H_0 + H_{variable}) \end{aligned} \quad (9)$$

Experimental studies of hydrodynamic mode

The dynamics of pressure drop fluctuations in bed with volumetric flow of fluidizing agent $V = 0.039$ m³/s and number of fluidization $K_w = 1.02$ as a graphical dependency and photographs of layer state in local extremums ΔP are presented on Figure 3, 4.

Maximum values of pressure drop in the bed at a $K_w = 1.02$ are lower then $\Delta P_{nom.}$. This indicates the absence of inertial mass transfer of bed.

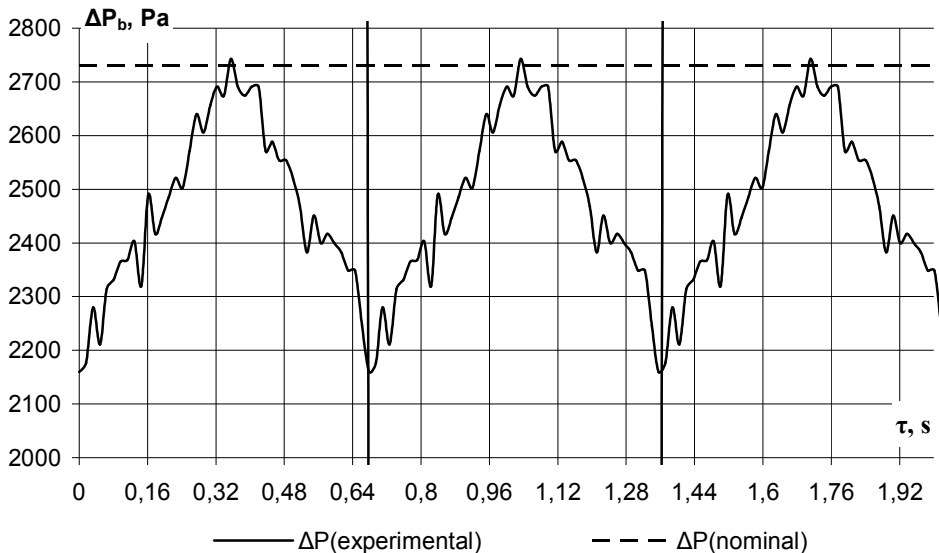


Figure 3. Experimentally determined dynamics of pressure drop changes in bed for $H_0 = 0.32$ m, $K_w = 1.02$ and frequency of pulsations $f = 1.47$ Hz

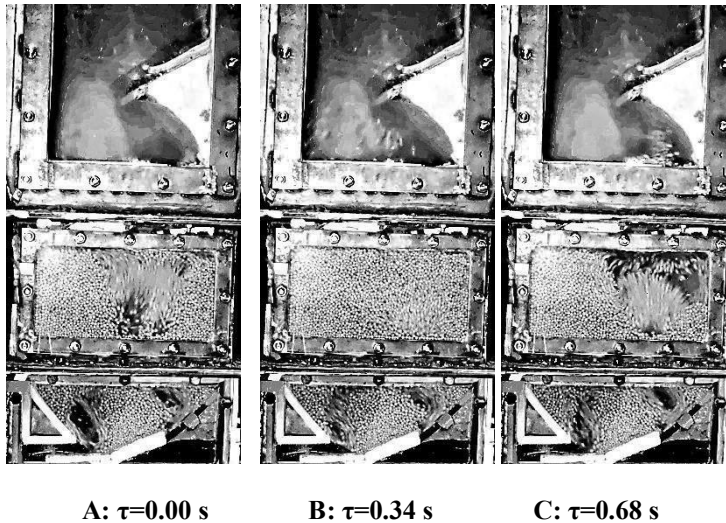


Figure 4. Experimentally determined photofixation of bed at minimum and maximum values of pressure drop for $H_0=0.32$ m, $K_w=1.02$ and frequency of pulsations $f=1.47$ Hz

The minimum values of ΔP_b (Figure 4 A, C) $\Delta P_b < \Delta P_{nom}$, comply with the conditions in which vertical jets, emerging from two slits are combined into one at height $y_j=80 \div 100$ mm [12] and locally pass through a bed of granular material, causing a small inertial particle removal (point B), that is characterized by a slight increase of $\Delta P_{max} - \Delta P_{nom} \leq 100$ Pa. Thus the kinetic energy of particles that are moving from the bed is insufficient to interaction with the directing insert 3, Figure 1. Therefore, moving of granular material from the zones II and III into a zone I do not occur. That means that there is no motion of material into space above the bed.

When increasing the energy of the gas flow injected through the slits of GDD to the bed of granular material, for values of $V=0.0528$ m³/s and $K_w=1.37$, Figure 5, pulsation frequency increases from $f=1.47$ Hz to $f=1.67$ Hz, that is confirmed by the photographs of bed condition in local extremes, Figure 6.

For these conditions the amplitude of exceeding the nominal pressure $\Delta P_{nom}=2780$ Pa is $\Delta P_{ampl}=670$ Pa, that indicates moving of the particle mass into space above the bed. This mass is equivalent $\Delta M_b=(\Delta P_{ampl} \cdot A \cdot B)/g$ and in this case is 2.01 kg.

Value of ΔP_b is considered as parameter that determines mass of the bed. So in this case the ratio of $\Delta P_{max}/\Delta P_{nom} \geq 0.25$ indicates that the number of cycles required to exchange of all the mass of bed $n_c=4$ implemented by $\tau=2.4$ s. It means, that the system works in auto-oscillatory mode [15]. In this case, energy that enters with the fluidizing agent is enough for implementation of the jet-pulsating mode of fluidization with intensive moving of particulates out of bed and efficient transport of it into the zone I (Figure 5, 6). This It confirms position of the physical model.

The minimum values of ΔP_b (Figure 5, 6) are $0.8P_{nom}$ and appear as a result of moving the material out of the bed (Figure 6) – points A and C. The height of bed in zone I significantly increases with a simultaneous movement of granular material into the middle of zone II and to the lower part of zone I (Figure 2).

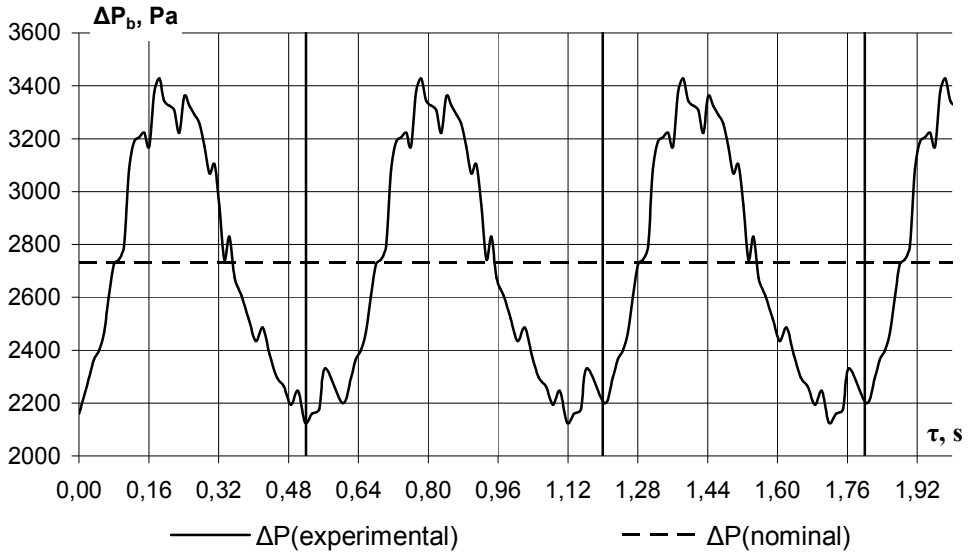


Figure 5. Experimentally determined dynamics of pressure drop changes in bed for $H_0=0.32$ m, $K_w=1.37$ and frequency of pulsations $f=1.47$ Hz

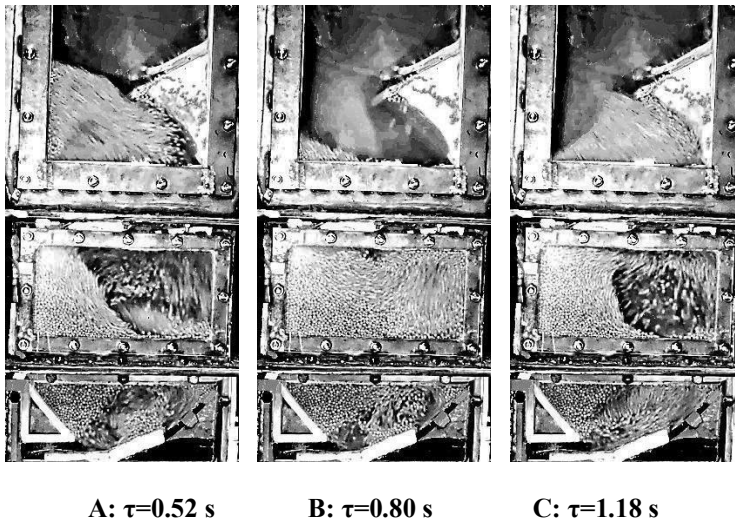


Figure 6. Experimentally determined photofixation of bed at minimum and maximum values of pressure drop for $H_0=0.32$ m, $K_w=1.37$ and frequency of pulsations $f=1.47$ Hz

The peak of pressure drop is observed when energy of the injected gas phase is expended on formation of gas bubbles i.e.:

$$\Delta P_{max} - \Delta P_{nom} = (1 - \varepsilon_0)gD_{bubbles} \quad (10)$$

where $D_{bubbles}$ – vertical size of voids formed in the bed, m.

The effect of oscillatory jet-pulsing mode is reinforced by presence of pulsations expenditure of gas-blower (Figure 7) that occur in opposite phase against the bed pulsations.

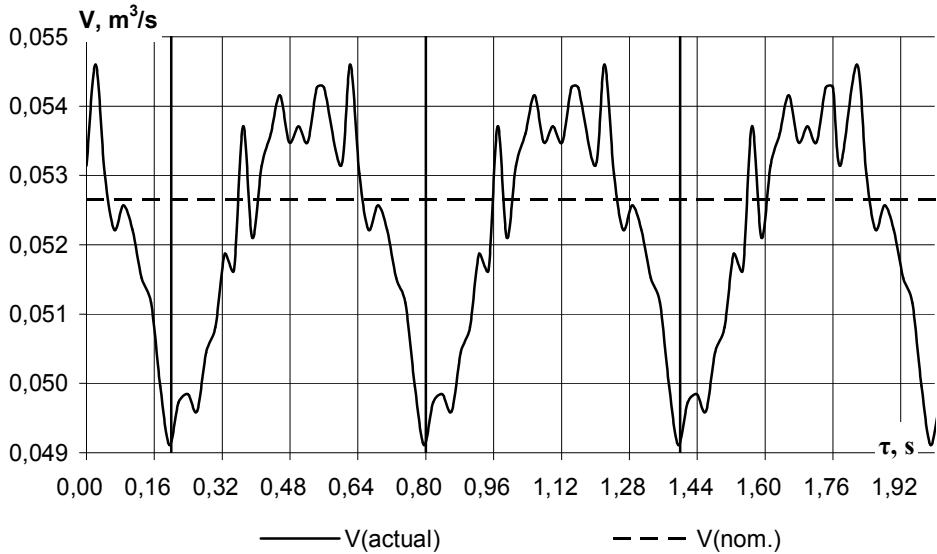


Figure 7. Experimental obtained values of volumetric flow changes when filing fluidizing agent for $K_w=1.37$ and frequency of pulsations $f=1.67$ Hz

At the same time, the volumetric flow value of fluidizing agent is changing within the limits $0.049 \text{ m}^3/\text{s} \leq V \leq 0.0545 \text{ m}^3/\text{s}$ with a frequency $f = 1.67$ Hz.

Analysis of the dynamic changes of the void fraction

For calculating the dynamics of changes of the total pressure drop according to equation (9) a bed void fraction was defined. Dynamics of the void fraction change in selected zones and the average values are shown on Figure 8.

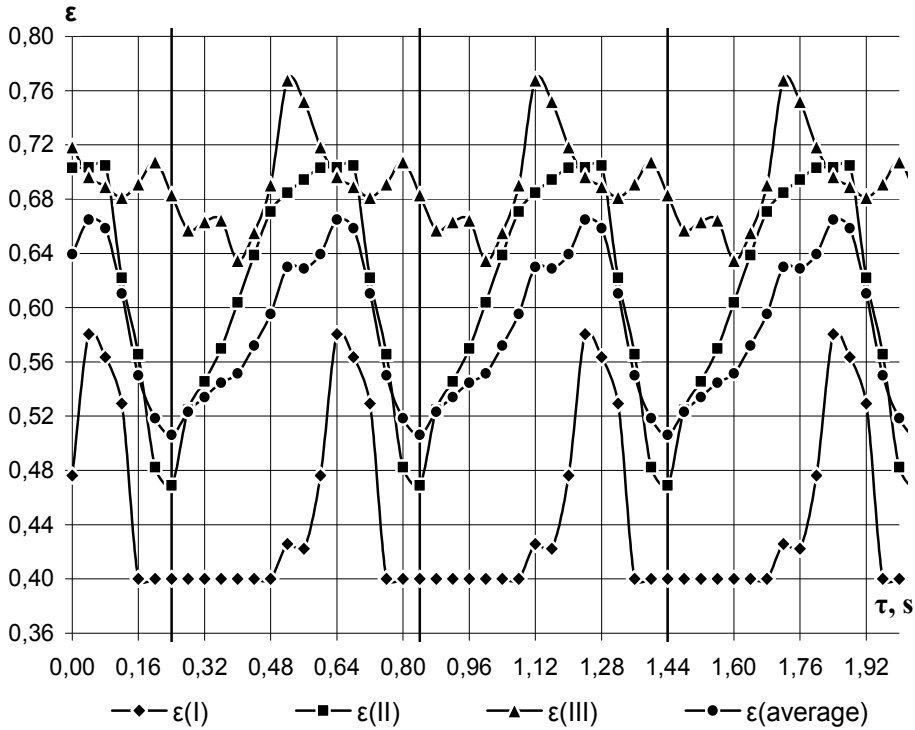


Figure 8. Dynamics of the void fraction change in selected zones (I, II and III) and the average values in chamber of an apparatus for $H_0=0.32$ m, $K_w=1.37$ and frequency of pulsations $f=1.47$ Hz

The selected time interval $0.24s \leq \tau \leq 0.84s$ is a typical cycle that is repeated in further. So in the ascending zone III void fraction is changed with pulsations. So in the ascending zone III the void fraction is changed pulsatingly within the limits of $0.63 \leq \varepsilon_{III} \leq 0.77$ with the pronounced local extremes. The change of voids in zone II $0.46 \leq \varepsilon_{II} \leq 0.70$ is also in pulsating mode with coincidences of the maximum values at the time interval of depending $\varepsilon_2=f(\tau)$ for zone III. In zone I a practically constancy values of void fraction at the level $\varepsilon_I=0.4$ is observed, except certain cases ($\varepsilon_I=0.58$), when the void fraction reaches the maximum values in adjacent areas. The calculated average values of the void fraction in the bed varies within the limits $0.5 \leq \varepsilon_{average} \leq 0.65$. It is logical that the frequency of changes void fraction is equal to the frequency of pulsations $f=1.67$ Hz.

Analysis of the dynamic changes in the height of bed

The experimentally determined height of bed in three zones taking into account a local growth of bed due to changes of void fraction is shown in Figure 9.

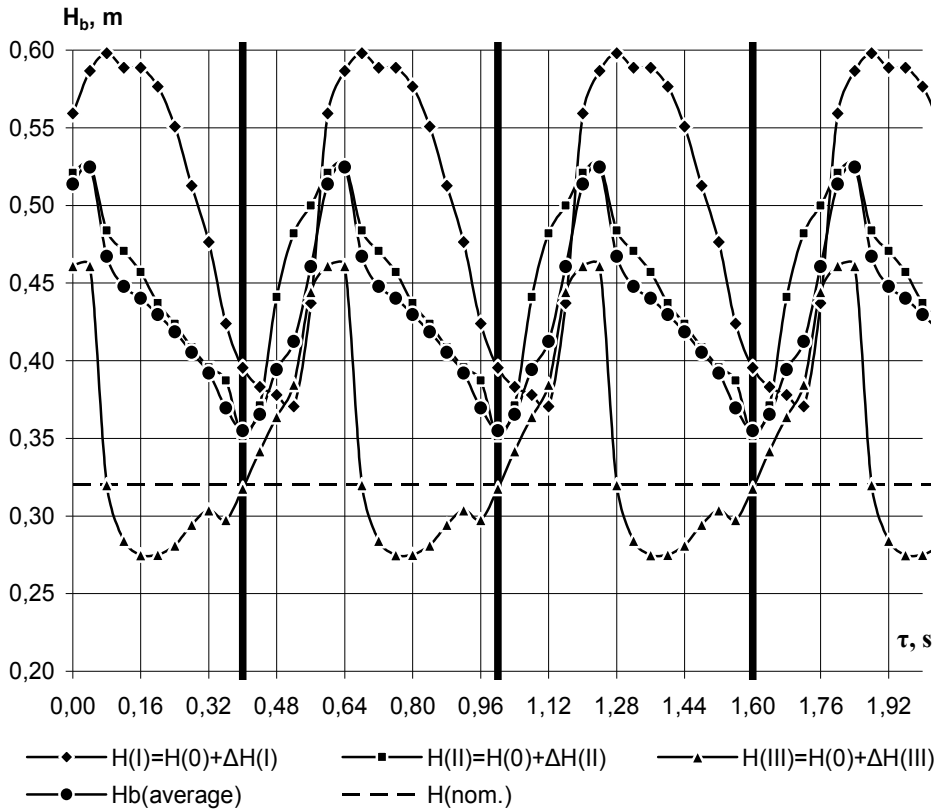


Figure 9. Dynamics of the bed height change in selected zones (I, II and III) and the average values in chamber of an apparatus for $H_0=0.32$ m, $K_w=1.37$ and frequency of pulsations $f=1.47$ Hz

Dynamics of the bed height change confirms the pulsating movement of the material mass in bed from zones II and III into zone I. Thereby increasing the height of bed in zone of downward movement (I) to magnitude $I \Delta H_{(I)\max}=280$ mm with frequency $f=1.67$ Hz causes an increase in weight of bed in a zone I and an appropriate increase of vertical and horizontal components of material's pressure on the gas torch in $p.p$ and $p.c$ lines, Figure 2. This provides an increase of the horizontal jet range, x_{hor} , and therefore reduces the probability of formation of stagnant zones on the work surface of GDD.

Verification of mathematical model

Based on the results of experimental studies by defined values of void fraction of the bed of granular material, Figure 8, and its height, Figure 9, by equation (9) the values of the total pressure drop of bed are calculated ΔP_{total} . Comparison of the results of solving mathematical model with experimental data ($\Delta P_{\text{experimental}}$) and with nominal value ΔP_{nom} is shown on Figure 10. The comparison shows the satisfactory convergence with the correlation coefficient $\sigma=5.2\%$.

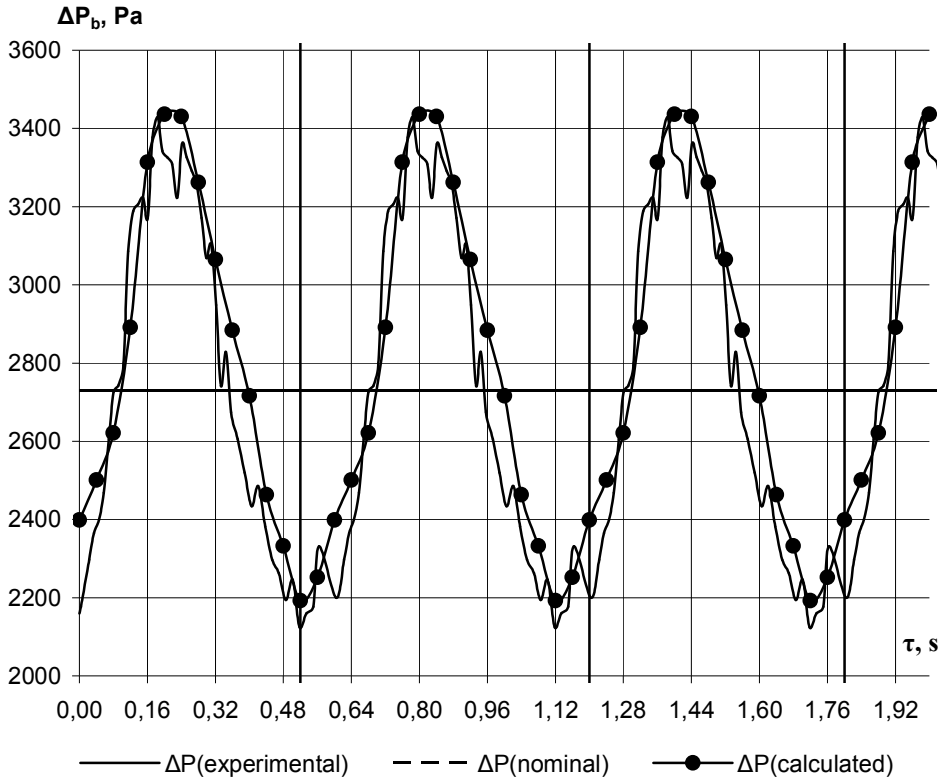


Figure 10. Comparison of the results of solving mathematical model with experimental data of the total pressure drop of bed for $H_0=0.32$ m, $K_w=1.37$ and frequency of pulsations $f=1.47$ Hz

Result of the work is that theoretically substantiated and experimentally proved that applying of the jet-pulsating mode of fluidization allowed to provide an intense circulation of granular material in the apparatus at values $\Delta P_b/H_0 \geq 8500$ for an equivalent diameter $D_e=3.97$ mm with the minimum value of fluidization number $K_w=1.37$.

Conclusion

Mathematical model of hydrodynamic regime of fluidization allows to calculate the intensity of the circulating mixing in bed what is necessary to provide a stable kinetics of the process of obtaining complex granular organic-mineral fertilizers.

References

1. Ban Ki-moon (2016), In safety and dignity: addressing large movements of refugees and migrants, *United nations*, available at: <https://documents-dds-ny.un.org/doc/UNDOC/GEN/N16/112/62/PDF/N1611262.pdf?OpenElement>

2. FAO (2015), Crop production and natural resource use, available at: <http://www.fao.org/docrep/005/y4252e/y4252e06.htm>
3. J. Foley, R. DeFries, G. Asner, C. Barford, G. Bonan, S. Carp (2005), Global Consequences of Land Use, *Science*, 309 (5734), pp. 570–574.
4. A. Sayduta, S. Erdoganb, A. Beycar Kafadarb, C. Kayab, F. Aydinb (2016), Candan Hamamecib Process optimization for production of biodiesel from hazelnut oil, sunflower oil and their hybrid feedstock, *Fuel*, 183(1), pp. 512–517.
5. Paleckiene R., Sviklas A., Slinksiene R., Streimikis V. (2010), Complex Fertilizers Produced from the Sunflower Husk Ash, *Polish J. of Environ. Stud.*, 19(5), pp. 973–979.
6. Pozin M. (1974), *The technology of mineral salts*, Chemistry, Leningrad.
7. Obraniak A., Gluba T. (2012), Model of energy consumption in the range of nucleation and granule growth in drum granulation of bentonite, *Physicochemical Problems of Mineral Processing*, 48(1), pp. 121–128.
8. Degreve J., Baeyens J., Van de Velden M., De Layet S. (2006), Spray-agglomeration of NPL fertilizer in a rotating drum granulator, *Powder Technology*, 163, pp. 188–195.
9. Gavin M. Walker (2007), Drum granulation processes, *Handbook of Powder Technology*, 11, pp. 219–254.
10. Paleckiene R., Sviklas A. M., Slinksiene R., Streimikis V. (2010), Complex Fertilizers Produced from the Sunflower Husk Ash, *Polish Journal of Environmental Studies*, 19 (5), pp. 973–979.
11. Xue B.C., Hao Q., Liu T., Liu E.B. (2013), Effect of process parameters and agglomeration mechanisms on NPK compound fertiliser, *Powder Technology*, 247, pp. 8–13.
12. Kornienko Y., Gaidai S., Martyniuk A. (2014), Improved process to obtain granular humic fertilizers, available at: <http://ela.kpi.ua/handle/123456789/11943>
13. Dimitry Gidaspow (1994), *Multiphase flow and fluidization: continuum and kinetic theory descriptions with applications*, United Kingdom Edition, London.
14. Davidson J., Harrison D. (1974), *Fluidization*, Chemistry, Moscow.
15. Tuponogov V., Ryzhkov A., Baskakov A., Obozhyn O. (2008), Relaxation oscillations in a fluidized bed, *UPI. hermophysics and Aeromechanics*, 15(4), pp. 643–657.
16. Stroh A., Alobaid F., Hasenzahl M.T., Hilz J., Ströhle J., Epple B. (2015), Comparison of three different CFD methods for dense fluidized beds and validation by a cold flow experiment, *Particuology*, 862, pp. 245–259.
17. Tianyu Wang, Tianqi Tang, Yurong He, Hongliang Yi (2016), Analysis of particle behaviors using a region-dependent method in a jetting fluidized bed, *Chemical Engineering Journal*, 283, pp. 127–140.
18. Oevermann M., Gerber S., Behrendt F. (2009), Euler–Lagrange DEM simulation of wood gasification in a bubbling fluidized bed reactor, *Particuology*, 7, pp. 307–317.
19. Korniyenko Y., Hayday S., Semenenko D., Martynyuk O. (2013), Hranul'ovani azotno-kal'tsiyevu-huminovi tverdi kompozyty, modyfikovani bentonitom. Protse oderzhannya, *Khimichna promyslovist' Ukrayiny*, 5, pp. 46–51.
20. Buevich J., Minaev G. (1984), *Jet fluidization*, Chemistry, Moscow.
21. Sasic S., Leener B., Johnsson F. (2005), Fluctuation and waves in fluidized bed systems: the influence of the air-supply system, *Powder Technology*, 153, pp.176–195.

Анотації

Харчові технології

Дослідження процесу утворення аромату з ліпідів плодової сировини

Валерій Сукманов¹, Андрій Маринін², Галина Дубова¹,
Анатолій Безусов³, Валентина Воскобойник¹

1 – Полтавський університет економіки і торгівлі, Полтава, Україна

2 – Національний університет харчових технологій, Київ, Україна

3 – Одеська національна академія харчових технологій, Одеса, Україна

Вступ. Досліджено процес утворення аромату плодів за участю попередників і ферментів. Такий спосіб має переваги порівняно з іншими способами отримання ароматичних компонентів.

Матеріали і методи. Ліпідні емульсії плодів (огірків, гарбуза, кавуна) отримували в апараті Сокслета за класичною методикою з використанням розчинника хлороформ-етанол. Інтенсивність окисних процесів оцінювали за розробленою методикою, заснованою на реакції карбонільних сполук (КС) у паровій фазі з 2,4-динітрофенілгідразином. Розподіл часток за розмірами (PSD), ζ -потенціал колоїдної фракції був зроблений на аналізатор Malvern Zetasizer Nano ZS з кутом виявлення 173°C. Відновлення свіжого смаку й аромату, втраченого при тепловій обробці, оцінювали на хромато-мас-спектрометричній системі Agilent 6890N/5973.

Результати і обговорення. Дослідження базується на тому, що молекули сполуки-посередника можуть витримувати режими переробки, тоді як ферменти й ароматичні сполуки часто руйнуються. Велика частина ароматичних компонентів – проміжні сполуки реакції між субстратом (гідроперекисними похідними ліпідів, НРО) і відповідними ферментами (гідропероксид ліази, НРЛ). Новими аспектами в утворенні свіжих ароматів можуть служити умови попередньої обробки плодів і умови перебігу ферментативних реакцій.

Зміни ароматичних компонентів рослин у процесі теплової або комбінованої обробки пов'язані з перетвореннями ліпідних компонентів. Доступність цих компонентів для здійснення ферментативних реакцій залежить від розподілу ліпідних частинок за розміром, їх потенційної рухливості. В свіжих плодах зі збільшенням гідродинамічного розміру часток і зменшенням ζ -потенціалу пов'язані ферментативні процеси призводять до утворення свіжого запаху (GLVs). У плодах, що пройшли комбіновану обробку, збільшується концентрація гідроперекисних з'єднань (субстрату) і знижується доступність мембранозв'язаних ферментів гідропероксидліази НРЛ.

Під час нагрівання у вакуумі (розрідження 6 ± 1 кПа, температура $32 \pm 2^\circ\text{C}$) суспендованих рослинних гомогенатів субстрат-ферментні взаємодії найбільш інтенсивні через умови межфазної активації, коли відбувається зміна гідрофобної взаємодії, ковалентних зв'язків, Ван-дер-Ваальсових сил. Такі ефекти забезпечують полімолекулярну адсорбцію і біосинтез зеленого запаху GLVs в плодах після теплової обробки.

Висновки. У подальшому необхідне проведення експериментів для відновлення свіжого аромату за допомогою ферментів, отриманих з рослинних матеріалів. Посилення профілю аромату буде відобразитися на зниженні кількості солі або

цукру, що використовуються в приготуванні багатьох продуктів і, особливо, у виробництві знежиреної групи.

Ключові слова: *аромат, гомогенат, попередник, ферменти, субстрат, ζ-потенціал.*

Вплив обробки окисними вибілювальними речовинами на колірні параметри шкаралупи волоського горіха (*Juglans Regia* L.)

Євгенія Боагі

Технічний університет Молдови, Кишинев, Республіка Молдова

Вступ. Волоські горіхи раніше продавалися в невибіленому стані, але попит на торгівлю призвів до загальної практики вибілювання. Завдання цього дослідження – визначити вплив різних вибілюючих речовин на ядра волоського горіха (*Juglans Regia* L.).

Матеріали і методи. Для кількісного визначення кольору застосовувалася найпопулярніша система кольорового зображення сільськогосподарських продуктів Міжнародної комісії з освітлення (CIE), в якій використовуються індекси L^* , a^* і b^* . Також була розрахована загальна різниця в кольорі (E), середнє арифметичне значення, яке враховує відмінності між L^* , a^* і b^* зразка і стандарту.

Результати і обговорення. У результаті аналізу отриманих значень для кольорових параметрів для кожного з використаних вибілювальних агентів було встановлено, що вони варіюються залежно від вибілювального агента, концентрації, рН середовища, температури і часу утримування волоських горіхів у розчині. Концентрація має велике значення, і її збільшення скорочує час, необхідний для досягнення очікуваного результату. Значення рН середовища відіграє важливу роль у каталітичному окисненні. Вибілювання і яскравість шкаралупи волоського горіха (L) збільшуються зі збільшенням рН від 3 до 10. Досліджені агенти утворюють такий ряд вибілювальної активності: $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4 > \text{Окорон 12} > \text{H}_2\text{O}_2 > \text{Ca}(\text{ClO})_2$. Встановлено, що оптимальними умовами вибілювання за допомогою $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4$ є: $C=5\%$, $\text{pH}=10$; $t=60$ °C.

Висновок. Усі вибілювальні речовини виявилися придатними для освітлення шкаралупи волоського горіха. Порівняно із широко використовуваним H_2O_2 процес старіння розвивався одночасно, але спостерігалися відмінності в загальній зміні освітлення. Зразки, оброблені перборатом натрію, залишалися світлішими.

Ключові слова: *волоський горіх, колір, вибілювання, пероксид водню, перборат натрію, Окорон 12, гіпохлорит кальцію.*

Компонентний склад ефірної олії коренеплоду редьки

Галина Селютіна, Оксана Гапонцева

Харківський державний університет харчування та торгівлі, Харків, Україна

Вступ. Коренеплоди редьки містять у своєму складі ефірні олії, які знаходяться у формі глюкозидів і зумовлюють її специфічний запах та смак. Вміст летких речовин є важливим показником для визначення споживчих характеристик коренеплоду.

Матеріали і методи. Досліджено коренеплоди редьки сортів Чорна зимова Сквирська, Біла зимова Сквирська, Марушка, Лебідка, Трояндова, Серце дракона, Маргеланська та дайкон Біле ікло. Ідентифікацію та кількісний компонентний склад ефірних олій редьки визначали методом хромато-мас-спектрометрії.

Результати і обговорення. Складні леткі композиції, виділені з коренеплодів редьки різних господарсько-ботанічних сортів, головним чином представлені такими сполуками: вуглеводні, сірковмісні речовини, органічні кислоти, альдегіди, ефіри, кетони, терпени, спирти та ацени, загальна масова частка яких знаходиться в діапазоні від 23,69 мг/кг (Лебідка) до 1605,94 мг/кг (Біла зимова Сквирська). Виявлено від 26 до 40 хімічних сполук, більшість яких є специфічними для кожного досліджуваного сорту, але 14 речовин спільні для всіх сортів редьки: нонаналь, пентадеканаль, діоктилфталат, диізобутилфталат, сквален, лінолева кислота, ліноленова кислота, олеїнова кислота, стеаринова кислота, трикозан, тетракозан, пентакозан, гексакозан і гептакозан.

Різноманітний компонентний склад летких речовин редьки обумовлює специфічність та інтенсивність її аромату, має суттєвий вплив на смакові властивості, а також зумовлює антибактеріальну активність щодо грамположитивних і грамнегативних мікроорганізмів.

Висновки. Вперше проведено комплексне дослідження якісного та кількісного складу летких речовин коренеплоду редьки в сортовому розрізі.

Ключові слова: редька, ефірні олії, леткі речовини, аромат.

Очищення соку з цукрових буряків електрокоагуляцією

Хабібех Азізі¹, Вахід Хакімзаде¹, Хоссеїн Алізаде² Голестані²

1 - Кафедра харчової науки і технології, Кучанська філія Ісламського азадського університету, Кучан, Іран

2 - Кафедра хімічної інженерії, Кучанська філія Ісламського азадського університету, Кучан, Іран

Вступ. Проведено дослідження з метою вивчення процесу електрокоагуляції як нового методу для видалення домішок і сполук не цукрів з цукру-сирцю бурякового соку.

Матеріали і методи. Дослідження виконано в періодичному хімічному реакторі, обладнаному баком на 5 л, що містить 3 алюмінієвих анодних і 3 залізних катодних електроди, з'єднані паралельно. Досліджено вплив напруги 5, 10 і 15 вольт, час обробки з 15, 30 і 45-хвилинними інтервалами і значеннями рН 6, 7 і 8 на чистоту, каламутність і колір цукрового бурякового соку з використанням методу поверхні відгуку Бокс-Бенкена і статистичного проектування на основі програмного пакета Minitab 17.

Результати і обговорення. В ході процесу електрокоагуляції каламутність зменшується з підвищенням напруги. З підвищенням напруги розчинність анодних електродів також збільшується, що призводить до видалення більшої кількості забруднювальних речовин. Таким чином, зниження каламутності і збільшення напруги може бути пов'язано зі збільшенням виробництва стружки, в той час як зміни в значенні рН не мають істотного впливу на каламутність. Хоча збільшення напруги істотно не впливає на посилення кольору, проте воно може бути пов'язане зі збільшенням бульбашок і подальшим підвищенням ферментативної активності в

процесі флотації. Збільшення ферментативної активності підсилює колір меланіну протягом певного часу через відкритість реактора під час флотації й аерації. Однак збільшення значення рН незначно посилює колір. Результати показали, що підвищення напруги призводить до збільшення ступеня чистоти. Розчинність анодних електродів збільшується з підвищенням напруги, згодом більш велика кількість домішок видаляється шляхом виробництва гідроксиду алюмінію. Підвищення напруги також призводить до отримання більшої кількості бульбашок, які посилюють контакт між гідроксидом алюмінію із забруднювачами і домішками, що сприяє флотації більшої кількості отриманого осаду і, таким чином, видаленню більшої кількості домішок. Збільшення тривалості процесу також призводить до підвищення ступеня чистоти, оскільки збільшення тривалості реакції призводить до більшої флотації осаду на поверхні рідини. Збільшення значення рН істотно не впливає на рівень чистоти.

Висновок. У цілому процес електрокоагуляції позитивно позначається на зниженні каламутності і підвищенні чистоти цукру-сирцю бурякового соку в процесі очищення, хоча на інтенсивність кольору вплив незначний.

Ключові слова: цукровий буряк, електрокоагуляція, колір, чистота, каламутність.

Аналіз вибору сортів винограду для технології крижаних вин

Вікторія Остапенко

Одеська національна академія харчових технологій, Одеса, Україна

Вступ. Вибір відповідних сортів винограду для виробництва крижаного вина суттєво впливає на ринковому пропозицію, розширюючи преміум-сегмент сільськогосподарського сектору.

Матеріали і методи. Бази даних і міжнародні закони у виноробстві були використані для аналізу характеристик винограду, призначеного для виробництва крижаного вина у різних країнах світу.

Результати і обговорення. Даний аналіз ілюструє повний асортимент сортів винограду, що використовується виноробами, які вирішили залишити лозу при низькій температурі у різних країнах-виробниках: у Німеччині, Чеській Республіці, Австрії, Словенії та Канаді. Виробники у цих країнах використовують різні виноградні класи для виробництва вин. У Європі існують різні сорти винограду для заморожування природним шляхом, але загальний випуск крижаних вин нижчий порівняно з країнами Північної Америки, включаючи Канаду і Сполучені Штати.

Більшість країн вибирають клас *V. Vinifera*, що має товсту шкірочку, яка захищає від зимового пошкодження, проте сорти цього класу більш чутливі до погодних умов, ніж гібриди або автохтонні сорти. Найбільш часто для виробництва крижаного вина використовується виноград сорту Ріслінг, який характеризується високою стійкістю виноградної лози упродовж зимового періоду.

Кліматичні умови є основною умовою отримання врожаїв для крижаного вина, оскільки можуть значно зменшити очікувані обсяги врожаю, тому заходи щодо захисту винограду передбачаються до початку низьких температур.

Висновки. Результат, отриманий за підсумками аналізу використання різних сортів винограду, демонструє розвиток і розширення виробництва крижаних вин у світових масштабах.

Ключові слова: крижане вино, виноград, сорт пізнього дозрівання, клімат.

Хімічний склад ефірної олії шавлії (*Salvia officinalis* L.) з Болгарії

Станка Дамянова¹, Сільвія Моллова², Албена Стоянова³, Олексій Губеня⁴

1 – Русенський університет, філія в м. Разград, Болгарія

2 – Інститут троянди, Казанлик, Болгарія

3 – Університет харчових технологій, Пловдив, Болгарія

4 – Національний університет харчових технологій, Київ, Україна

Вступ. Проведені дослідження з метою визначення хімічного складу ефірної олії шавлії лікарської (*Salvia officinalis* L.), вирощеної в Болгарії.

Матеріали і методи. В дослідженнях використано трав'яну сировину із шавлії, придбану в місцевій торговельній мережі. Ефірну олію отримували шляхом гідродистиляції протягом 3 год в скляному лабораторному апараті. Хімічний склад олії визначали хроматографічним шляхом.

Результат і обговорення. Вологість сировини становила 12,16%, а вихід ефірної олії – 0,93%.

В ефірній олії було визначено 28 компонентів. Основні з'єднання ефірної олії такі: α -туйон (26,68%), (E)- β -каріофілен (7,47%), 1,8-цинеол (7,19%), α -гумулен (6,11%), β -пінен (5,44%), β -туйон (5,35%), камфора (4,84%), алло-аромадендрен (4,55%), борнеол (3,69%), і α -пінен (3,58%). Три групи з'єднань було знайдено в гідродистильованій олії із шавлії. Сумарні кисневмісні монотерпени становили найвищий відсоток компонентів ефірної олії – 59,15%, сесквітерпенові вуглеводні – 24,37% і монотерпенові вуглеводні – 14,66%. Найбільш поширеною в олії кисневмісна монотерпенова фракція, яка особливо багата на кетони (70,96% від цієї фракції)

Висновок. Можна констатувати, що в ефірній олії із шавлії лікарської було виявлено ряд кисневмісних монотерпенів, сесквітерпенових вуглеводнів і монотерпенових вуглеводнів.

Ключові слова: шавлія, ефірна олія, склад, Болгарія.

Вплив параметрів переробки на склад і сенсорні характеристики хлібного дерева елубо

Тіяні Акім Олуміде¹, Бакаре Хенрі Адегоке²,
Оке Еммануел Кехінде³, Оєдеї Аїбола Баміколе⁴

1 – Національне агентство з біотехнології розвитку, Оводе Єва, Нігерія

2 – Департамент готельного бізнесу і туризму, Федеральний університет сільського господарства, Абеокута, Нігерія

3 – Департамент харчової науки і техніки, Федеральний університет сільського господарства, Абеокута, Нігерія

4 – Відділ біотехнології і харчових технологій, Дурбанський технологічний університет, Дурбан, Південно-Африканська республіка

Вступ. Хлібне дерево не відноситься до харчових продуктів і його застосування в харчових технологіях засноване на технологічній обробці з подальшим внесенням до рецептури хлібопекарського продукту елубо (elubo), технологія якого широко застосовується в даний час.

Матеріали і методи. Хлібне дерево промивалося чистою водою для видалення каучуконосів. Кора знімається ручну і розрізається на шматочки. Шматочки витримувалися у воді за температури 30, 50 і 60 °С протягом 90, 120 і 150 хв. Далі хлібне дерево витримувалося у воді 6, 12 і 18 годин. Після видалення надлишку вологи зразки висушуються в сушильній камері за температури 60 °С протягом 2 днів і подрібнюються на борошно (елубо). Зразки тіста хлібного дерева (Амала) були піддані органолептичному аналізу.

Результати і обговорення. Вміст вологи в хлібному дереві елубо варіюється між 9,07 і 12,20%. Вміст вологи у зразках відповідає вмісту твердої матерії. Значна кількість золи у зразках хлібного дерева елубо (ХЕ) є індикатором мінералів у борошні. Величини озолення варіюються в межах 2,00–2,90%. Вміст харчових волокон у хлібному дереві елубо складає 2,86 – 3,60%. Температура і час витримування у воді істотно ($p > 0,05$) не впливають на вміст волокон у зразках. Вміст білків у зразках хлібного дерева елубо складає 3,80 – 5,42%. Вміст білків у зразках змінюється незалежно від параметрів температури й тривалості витримування. Вміст вуглеводів у зразках становить 73,67–78,33%. Висока кількість вуглеводів вказує на високу калорійність готових виробів. На вміст вуглеводів параметри температури і тривалість витримування впливають несуттєво ($p > 0,05$). Органолептичні показники тіста, виготовленого з хлібного дерева елубо, істотно ($p < 0,05$) відрізнялися від тіста, виготовленого з батату елубо (t-показник – 2,523, ступінь свободи – 14, p-величина – 0,01, один зріз).

Висновки. Результати досліджень підтверджують наявність значної кількості харчових волокон і вуглеводів у хлібному дереві елубо, що вказує на можливість його використання як високоенергетичного продукту.

Ключові слова: хлібне дерево, елубо, технологія, обробка, органолептика.

Використання горіхової сировини і насіння чіа для покращення жирнокислотного складу напоїв смузі

Анджела Д'яконова, Вікторія Степанова

Одеська національна академія харчових технологій, Одеса, Україна

Вступ. На сьогодні недостатньо дослідженими є шляхи використання горіхової, насінневої сировини та їх комбінацій як джерела есенціальних жирних кислот харчових продуктів оздоровчого призначення.

Матеріали і методи. Досліджено композицію інгредієнтів універсальної основи для виробництва напоїв. Визначено вміст білків, жирів, вуглеводів, золи та калорійність продукту. Методом газової хроматографії досліджено жирно-кислотний склад рецептурних компонентів та визначено співвідношення ω -3 і ω -6 жирних кислот у готових напоях. Вивчено амінокислотний склад розробленої композиції, її в'язкість і стабільність під час зберігання.

Результати і обговорення. Авторами запропоновано 9 рецептур напоїв смузі з різними органолептичними показниками. 250 мл таких напоїв можуть задовільнити добову потребу здорової людини у ліноленовій і лінолевій кислотах на 30 %, тому що їх вміст у готових напоях складає не менше 0,5 г та 2 г відповідно. Розроблені напої рекомендовано до вживання всім групам населення, зокрема людям, які страждають на захворювання серцево-судинної системи або бажають підтримувати її роботу у нормі.

Використання насіння чіа та ядер волоського горіха значно підвищує вміст біологічно цінних речовин у напоях. Насіння чіа суттєво впливає на реологічні показники смузі, підвищуючи густину та в'язкість напоїв за рахунок слизових речовин на поверхні зерна насіння, а також підтримує стабільність жирової системи при зберіганні. Здатність насіння чіа до слизоутворення пояснюється вмістом водорозчинних полісахаридів – пентозанів, які складають до 8 % від маси зерна. Отримані дані свідчать, що завдяки використанню насіння чіа універсальна основа зберігає 100 % стабільність протягом 24 год, що повністю задовольняє потреби закладів громадського харчування.

Білки розробленої горіхово-насінневої композиції є повноцінними і містять усі незамінні амінокислоти. Лімітуючими амінокислотами є лізін, метіонін + цистеїн, треонін і валін.

Висновки. Вперше вивчено можливість застосування насіння чіа як структуроутворювача напоїв смузі та запропоновано композицію інгредієнтів для виробництва універсальної основи напоїв, яка має збалансований вміст ω -3 і ω -6 жирних кислот.

Ключові слова: горіх, чіа, жирні кислоти, наній, смузі.

Вплив колагенового білка «Білкозин» на біологічну цінність варених ковбас

Анатолій Українець, Василь Пасічний, Максим Полумбрик, Манефа Полумбрик
Національний університет харчових технологій, Київ, Україна

Вступ. Проведені порівняльні дослідження амінокислотного СКОРу білків варених ковбас, виготовлених з додаванням колагенового білка «Білкозин», і швидкості накопичення тирозину в динамічній моделі шлунково-кишкового тракту людини з метою встановлення ступеня засвоєння білків цих ковбас.

Матеріали і методи. Гідроліз проводився в спеціальному пристрої, який складався з внутрішньої і зовнішньої ємності. Внутрішня ємність містить скляну мішалку, призначення якої полягає у постійному перемішуванні ферментаційного середовища і діалізі продуктів реакції. Ферментативне розщеплення тривало 3 год на кожній стадії. Дія пепсину проходила на першій стадії, а трипсину – на другій. Амінокислотний склад ковбасних виробів було визначено за допомогою іонообмінної хроматографії.

Результати і обговорення. Нами були проведені порівняльні дослідження ферментативного гідролізу варених ковбасних виробів, виготовлених з курячого м'яса бройлерів, охолодженого до 0–4 °С. Після додавання трипсину спостерігалось прискорення гідролізу білків варених ковбас, яке досягло максимуму на шостій годині ферментації. Включення білка «Білкозин» до складу рецептур варених ковбас суттєво не впливає на амінокислотний склад готових виробів. У результаті порівняльних досліджень способу введення білкової композиції до складу ковбасних виробів з'ясовано, що ферментативний гідроліз швидше відбувається в ковбасах, виготовлених із сухим білковим стабілізатором, особливо на стадії дії трипсину. Збільшення вмісту білка в рецептурі призводить до зростання біодоступності білків варених ковбас, що свідчить про позитивний вплив колагенового білка «Білкозин» на перетравлюваність цих виробів.

Висновки. Зростання частки гідролізату з 6 до 12 % у ВС підвищує швидкість накопичення тирозину, що утворюється під час послідовного ферментативного

гідролізу в системі пепсин-тирозин, який *in vitro* моделює процеси травлення, що відбуваються в організмі людини. Таким чином, внесення колагенового білка «Білкозин» суттєво підвищує біологічну цінність ковбасних виробів, виготовлених з його додаванням, що проявляється в зростанні перетравлюваності білків варених ковбас при збільшенні в них частки білка «Білкозин».

Ключові слова: *ковбаса, білок «Білкозин», біологічна цінність, гідроліз, пепсин, трипсин.*

Релаксаційна поведінка водних дисперсій крохмалю

Валерій Манк, Оксана Точкова, Оксана Мельник, Олександр Бессараб
Національний університет харчових технологій, Київ, Україна

Вступ. Реологічні властивості водних розчинів полісахаридів показали тиксотропічну поведінку при руйнуванні їх частково впорядкованої структури, що має місце при фізичних або теплових діях.

Матеріали і методи. Готували 3–15% дисперсії нативного картопляного і кукурудзяного крохмалів у дистильованій воді. Зразки термостатували при температурі 20°C протягом 30 хвилин. Дослідження проводили за методикою визначення реологічної поведінки крохмалів при кімнатній температурі через кожні 3 години.

Результати і обговорення. Новий метод релаксації в крохмальних сумішах полягає в тому, що структурна релаксація полімерних ланок полісахаридів у часі проходить повільно і довго.

Згідно з літературними джерелами, лише полісахариди, молекулярна маса яких перевищує 1 млн (на прикладі картопляного крохмалю), характеризуються повільною релаксацією структури. Фізико-хімічна характеристика полісахаридів – релаксація, зумовлюється частково впорядкованою структурою із взаємним розташуванням окремих ланцюгів у просторовій сітці.

Під дією зсувних напруг реотесту зруйнована псевдопластична структура водних дисперсій крохмалю поступово відновлюється до рівноважного при даних умовах стану системи. Час відновлення структури становить 17 годин.

Повільний процес відновлення або структурної релаксації просторових структур водних дисперсій полісахаридів відбувається внаслідок перебудови просторової сітки полімеру, що утворюється завдяки існуванню поперечних хімічних зв'язків. Аналогічна поведінка з меншим часом структурної релаксації характерна і для інших полісахаридів, зокрема ксантану, час релаксації якого становить близько 3 годин.

Висновки. Між ланцюгами існують особливості колоїдної системи, що впливають на її якісні, структурно-механічні й технологічні властивості. Ці особливості необхідно враховувати при виборі раціональних режимів оптимальних умов проведення процесів, а також при проектуванні автоматичних систем керування виробництвом.

Ключові слова: *полісахарид, крохмаль, дисперсія, структура, релаксація.*

Процеси і обладнання харчових виробництв

Забруднення полімерних та органо-неорганічних мембран при розділенні післяспиртової зернової барди

Юрій Змієвський¹, Юлія Дзязько², Валерій Мирончук¹,

Людмила Рождественська², Олександр Віленський³, Людмила Корнієнко¹

1 – Національний університет харчових технологій, Київ, Україна

2 – Інститут загальної та неорганічної хімії ім. В.І. Вернадського НАН України, Київ, Україна

3 – Інститут кристалографії ім. О.В. Шубнікова РАН, Москва, Російська Федерація

Вступ. Процес баромембранного розділення доцільно використовувати для переробки післяспиртової зернової барди. Для того, щоб запобігти забрудненню мембран органічними речовинами, полімерні мембрани модифікують частинками неорганічних іонообмінників. Встановлено та порівняно механізми забруднення для полімерних і композитних мембран, модифікованих частинками неорганічних іонообмінників, під час розділення післяспиртової барди.

Матеріали і методи. Поліетилентерефталатові трекові мікрофільтраційні мембрани були модифіковані агрегатами наночасток гідрофосфату цирконію, матеріал досліджувався за допомогою методу скануючої електронної мікроскопії. Спочатку мембрани опресовувались за допомогою дистильованої води. Післяспиртова зернова барда розділялась при тисках 1–4 бари і температурі 60 °С.

Результати та їх обговорення. Моделі повного та поступового закупорювання пор, а також модель формування осаду були застосовані при фільтруванні води через композитні мембрани. За допомогою моделей повного та поступового закупорювання пор з'ясовано, що при 60 °С відбуваються зміни пористої структури полімеру та фрагментація модифікатора. Встановлено, що при розділенні післяспиртової зернової барди композиційна мембрана демонструє вищу стійкість до забруднення органічними речовинами, ніж немодифікована. Фільтрація через композиційну мембрану підпорядковується закону Дарсі. Максимальна продуктивність досягається при 3 атм. Потік пермеату крізь немодифіковану мембрану знижується з підвищенням тиску, що пов'язано із забрудненням. Для модифікованих мембран характерним є лінійне зростання продуктивності за аналогічних умов, що вказує на менший гідродинамічний опір речовин, які забруднюють мембрану. Механізм повного закупорювання пор характерний для обох досліджуваних мембран. Підвищення тиску призводить до відкладення осаду на стінках пор (немодифікована мембрана) та формування осаду на поверхні (обидві мембрани). Підвищена стійкість композиційної мембрани до забруднень передбачає мінімізацію об'єму хімічних реагентів для регенерації, скорочення часу регенерації та зменшення об'єму води для промивання.

Висновки. Неорганічні іонообмінники дають змогу покращити стійкість мембран до забруднення компонентами післяспиртової барди. Органо-неорганічні мембрани можуть бути застосовані для інших об'єктів харчової промисловості, особливо при кімнатних і нижчих температурах.

Ключові слова: барда, мембрана, наночастка, розділення, модифікування.

Використання твердої біомаси у факельних котлах для спалювання антрациту

Наталія Дунаєвська, Микола Чернявський, Тарас Щудло
Інститут вугільних енерготехнологій НАН України, Київ, Україна

Вступ. Спалювання твердої біомаси у суміші з викопним вугіллям в існуючих котлах може не тільки зменшити шкідливі викиди в атмосферу, а й диверсифікувати паливну базу генерацій. Таке спалювання дає змогу більш ефективно використовувати тверді відходи харчової промисловості, які здійснюють шкідливий вплив на навколишнє середовище.

Матеріали і методи. Спільне факельне спалювання деревини сосни з антрацитом досліджувалось на низхідному експериментальному стенді ВПП-100В з витратою палива 30 кг/год. На установці киплячого шару РСК-1Д досліджувалась кінетика термічної деструкції коксів тирси сосни. Методом термогравіметрії досліджена кінетика термічної деструкції деревної сосни і пелет соломи пшениці, ріпаку, кукурудзи та сої.

Результати і обговорення. Спільне факельне спалювання вітчизняного антрациту з деревиною у факелі на стенді ВПП-100В показало технічну можливість і потенційну здатність до покращення якості горіння низькорекційного антрациту. На підставі аналізу експериментальних режимів з'ясовано, що оптимальна теплова частка біомаси склала близько 10 %. Додавання такої частки біомаси забезпечувало стабілізацію факела без газового підсвічування, а також найвищу ступінь конверсії вуглецю вугілля.

На установці РСК-1Д встановлено внутрішньокінетичний режим горіння зразків коксів сосни розміром 0,1–1,6 мм у діапазоні температур 390–560 °С. На основі методу термогравіметрії були визначені стадії термічного розкладу (зневоднення, вихід летких і горіння коксового залишку) та їх кінетичні характеристики для зразків органічної біомаси.

Порівняння кінетики виходу летких для зразків тирси сосни та пелет соломи пшениці з даними доступних літературних джерел вказує на незначну відмінність у швидкості виходу летких, що пояснюється розбіжністю у швидкості нагрівання зразків під час експерименту, різним ступенем подрібнення досліджуваних зразків, відмінністю органічного та мінерального складу зразків, різницею у підходах для розрахунку констант реакції. Натомість спостерігалась близькість значень швидкості виходу летких зразків пелет соломи різних культур між собою.

Висновки. Представлені результати досліджень можуть бути використані у розрахунках окремих процесів спільного спалювання на ТЕС.

Ключові слова: *спільне спалювання, біомаса, вугілля, антрацит.*

Помилки прямих вимірювань температури термopарамі та валідація CFX і FLUENT моделей спалювання природного газу

Павло Засядько, Микола Прядко
Національний університет харчових технологій, Київ, Україна

Вступ. Технологічні процеси, пов'язані з горінням, створюють серйозні екологічні проблеми, пов'язані з викидом шкідливих речовин переважно в газоподібному стані. Згідно із загальноприйнятою точкою зору, оксиди азоту в основному виникають в установках спалювання в областях високих температур.

Матеріали і методи. Вирішуються завдання, пов'язані з оцінкою помилок термопар при вимірах температури в полум'ях, що проводяться під час експериментального спалювання природного газу в експериментальній установці ВГП-100В.

Результати і обговорення. Виведена модель, що дає змогу отримати поправочні коефіцієнти, які повинні застосовуватися для обробки даних прямих показань термопар. Модель враховує конвективний теплообмін, опромінення на частини кульки термопар, яка падає від продуктів згоряння. Згідно з моделлю, частина королька термопар випромінює в напрямку охолоджувального середовища. В результаті отримано і вирішено математичне рівняння трансцендентного типу четвертого порядку в MathCad. Отримано набір уточнювальних коефіцієнтів, які при додаванні до прямих показань термопар показали близьку відповідність результатам, отриманим у результаті тривимірного моделювання спалювання природного газу в циліндричній низхідному реакторі.

Висновок. Розроблену методологію корекції можна рекомендувати для використання при експериментальних вимірюваннях температури за допомогою незакритих термопар, коли не можна використовувати термопару або всмоктувальний пірометр в оболонці.

Ключевые слова: газ, згорання, термопара, вимірювання, похибка.

Моделювання пульсаційного режиму псевдозрідження під час одержання органомінеральних добрив

Ярослав Корнієнко, Сергій Гайдай,

Андрій Любека, Сергій Турко, Олександр Мартинюк

Національний технічний університет України

"Київський політехнічний інститут імені Ігоря Сікорського", Київ, Україна

Вступ. Метою дослідження є математичне моделювання гідродинамічного режиму неоднорідного псевдозрідження, що забезпечить підвищення ефективності тепло-масообмінних процесів під час одержання органомінеральних добрив, до складу яких входить соняшникова зола, стимулювальні та поживні компоненти.

Матеріали і методи. Процес неоднорідного псевдозрідження, що зумовлює активне об'ємне перемішування з інтенсивною циркуляцією зернистого матеріалу в шарі, проводився у камері гранулятора, спорядженій спеціальним газорозподільним пристроєм у нижній частині та направляючою вставкою – у верхній. Вимірювання перепаду тиску в шарі та відеофіксація процесу здійснювалися за допомогою спеціалізованого обладнання.

Результати і обговорення. Реалізовано неоднорідне псевдозрідження під час застосування 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 $\rho_p=1450$ кг/м³ з відношенням номінального перепаду тиску до висоти шару $\Delta P_b/H_0 \geq 8500$ Па/м із частотою $f=1,67$ Гц. Відсутність застійних зон забезпечує коефіцієнт гранулоутворення $\psi \geq 90\%$ і питоме навантаження поверхні шару за вологою $a_f=0,8 \div 0,9$ кг_{вол.}/(м²·год). Обрано математичну модель, яка з урахуванням неоднорідності надала можливість визначити умови проведення процесу, під час якого до 25% маси шару перебуває в активній фазі поза межами шару з частотою

$f=1,67$ Гц. Математична модель з точністю 94,8% підтверджує результати дослідження.

Висновки. Реалізована гідродинаміка в камері гранулятора без утворення застійних зон. Модифікована математична модель дала змогу визначити інтенсивність активного об'ємного циркуляційного перемішування, що суттєво підвищить стійкість кінетики гранулоутворення при зневодненні композитних рідких систем.

Ключові слова: *гідродинаміка, пульсації, псевдозрідження, добрива, зола.*

Аннотации

Пищевые технологии

Исследование процесса образования аромата из липидов плодового сырья

Валерий Сукманов¹, Андрей Маринин², Галина Дубова¹,
Анатолий Безусов³, Валентина Воскобойник¹

1 – Полтавский университет экономики и торговли, Полтава, Украина

2 – Национальный университет пищевых технологий, Киев, Украина

3 – Одесская национальная академия пищевых технологий, Одесса, Украина

Введение. Исследовано образование аромата плодов с участием предшественников и ферментов. Предложенный способ обладает определенным преимуществом сравнительно с другими способами получения ароматических компонентов.

Материалы и методы. Липидные эмульсии плодов (огурцов, тыквы, арбуза) получали в аппарате Сокслета по классической методике с использованием растворителя хлороформ-этанол. Интенсивность окислительных процессов оценивали по разработанной методике, основанной на реакции карбонильных соединений (КС) в паровой фазе с 2,4-динитрофенилгидразином. Распределение частиц по размерам (PSD), ζ -потенциал коллоидной фракции исследовали на анализаторе Malvern Zetasizer Nano ZS с углом обнаружения 173°C. Восстановление свежего аромата, утраченного при тепловой обработке, оценивали на хромато-масс-спектрометрической системе Agilent 6890N/5973.

Результаты и обсуждения. Исследование базируется на том, что молекулы соединения-предшественника могут выдерживать режимы переработки, тогда как ферменты и ароматические соединения зачастую разрушаются. Большая часть ароматических компонентов – промежуточные соединения реакции, образованные между субстратом (гидроперекисными производными липидов, НРО) и соответствующими ферментами (гидропероксид лиаза, HPL). Новыми аспектами в образовании свежих ароматов могут служить условия предварительной обработки плодов и последующие условия протекания ферментативных реакций.

Изменения ароматических компонентов растений в процессе тепловой или комбинированной обработки связаны с преобразованиями липидных компонентов. Доступность этих компонентов для осуществления ферментативных реакций зависит от распределения липидных частиц по размеру, их потенциальной подвижности. В свежих плодах с увеличением гидродинамического размера частиц и уменьшением ζ -потенциала связаны ферментативные процессы, приводящие к образованию свежего запаха (GLVs). В плодах, прошедших комбинированную обработку, увеличивается концентрация гидроперекисных соединений (субстрата) и снижается доступность мембранносвязанных ферментов гидропероксид лиаза HPL.

Во время нагревания в вакууме (разрежение 6 ± 1 кПа, температура $32 \pm 2^\circ\text{C}$) суспендированных растительных гомогенатов субстрат-ферментные взаимодействия наиболее интенсивны из-за условий межфазной активации, когда происходит изменение гидрофобного взаимодействия, ковалентных связей, Ван-дер-Ваальсовых сил. Такие эффекты обеспечивают полимолекулярную адсорбцию и биосинтез зеленого запаха GLVs в плодах после тепловой обработки.

Выводы. В дальнейшем необходимо проведение экспериментов для восстановления свежего аромата с помощью ферментов, полученных из растительных материалов. Усиление профиля аромата будет отражаться на снижении количества соли или сахара, используемых в приготовлении многих продуктов и особенно в производстве обезжиренной группы.

Ключевые слова: *аромат, гомогенат, предшественник, ферменты, субстрат, ζ-потенциал.*

Влияние обработки окислительными отбеливающими веществами на цветовые параметры скорлупы грецкого ореха (*Juglans Regia* L.)

Евгения Боаги

Технический университет Молдовы, Кишинев, Республика Молдова

Введение. Грецкие орехи раньше продавались в неотбеленном состоянии, но спрос на торговлю привел к общей практике отбеливания. Задача этого исследования состоит в том, чтобы определить влияние различных отбеливающих веществ на ядра грецкого ореха (*Juglans Regia* L.).

Материалы и методы. Для количественного определения цвета выбрана самая популярная цветовая система сельскохозяйственных продуктов Международной комиссии по освещению (CIE), в которой используются индексы L^* , a^* и b^* . Также была рассчитана общая разница в цвете (E), единичное значение, которое учитывает различия между L^* , a^* и b^* образца и стандарта.

Результаты и обсуждение. В процессе анализа полученных значений для цветовых параметров для каждого из использованных отбеливающих агентов было установлено, что они варьируются в зависимости от отбеливающего агента, концентрации, pH среды, температуры и времени удерживания грецких орехов в растворе. Концентрация имеет большое значение, ее увеличение сокращает время, необходимое для достижения ожидаемого результата. Значение pH среды играет важную роль в каталитическом окислении. Отбеливание и яркость скорлупы грецкого ореха (L) увеличиваются с увеличением pH от 3 до 10. Исследованные агенты образуют следующий ряд отбеливающей активности: $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4 > \text{Oxogon 12} > \text{H}_2\text{O}_2 > \text{Ca}(\text{ClO})_2$. Установлено, что оптимальными условиями отбеливания с помощью $\text{Na}_2\text{B}_2\text{O}_4(\text{OH})_4$ являются: C = 5%, pH = 10; t = 60 °C.

Вывод. Все отбеливающие вещества оказались пригодными для осветления скорлупы грецкого ореха. По сравнению с широко используемым H_2O_2 процесс старения развивался одновременно, но наблюдались различия в общем изменении осветления. Образцы, обработанные перборатом натрия, оставались светлее.

Ключевые слова: *грецкий орех, цвет, отбеливание, пероксид водорода, перборат натрия, Оксон 12, гипохлорит кальция.*

Компонентный состав эфирного масла корнеплода редьки

Галина Селютина, Оксана Гапонцева

Харьковский государственный университет питания и торговли, Харьков, Украина

Введение. Корнеплоды редьки содержат в своем составе эфирные масла, которые находятся в форме гликозидов и обуславливают ее специфический запах и вкус. Содержание летучих веществ является важным показателем для определения потребительских характеристик корнеплода

Материалы и методы. Исследованы корнеплоды редьки сортов Черная зимняя Сквирская, Белая зимняя Сквирская, Марушка, Лебидка, Розовая, Сердце дракона, Маргеланская и дайкон Белый клык. Идентификацию и количественный компонентный состав эфирных масел редьки определяли методом хромато-масс-спектрометрии.

Результаты и обсуждение. Сложные летучие композиции, выделенные из корнеплодов редьки различных хозяйственно-ботанических сортов, главным образом представлены следующими соединениями: углеводороды, серосодержащие вещества, органические кислоты, альдегиды, эфиры, кетоны, терпены, спирты и арены, общее содержание которых находится в диапазоне от 23,69 мг/кг (Лебидка) до 1605,94мг/кг (Белая зимняя Сквирская). Выявлено от 26 до 40 химических соединений, которые являются специфическими для каждого исследуемого сорта, но 14 веществ – общие для всех сортов редьки: нонаналь, пентадеканаль, диоктилфталат, диизобутилфталат, сквален, линолевая кислота, линоленовая кислота, олеиновая кислота, стеариновая кислота, трикозан, тетракозан, пентакозан, гексакозан и гептакозан.

Разнообразный компонентный состав летучих веществ редьки обуславливает специфичность и интенсивность ее аромата, оказывает существенное влияние на вкусовые свойства и антибактериальную активность по отношению к грамположительным и грамотрицательным микроорганизмам.

Выводы. Впервые проведен комплекс исследований качественного и количественного состава летучих веществ корнеплода редьки в сортовом разрезе.

Ключевые слова: *редька, эфирные масла, летучие вещества, аромат.*

Очистка сока из сахарной свеклы электрокоагуляцией

Хабибех Азизи¹, Вахид Хакимзаде¹, Хоссеин Ализаде² Голестани²

1 - Кафедра пищевой науки и технологии, Кучанский филиал Исламского азадского университета, Кучан, Иран

2 - Кафедра химической инженерии, Кучанский филиал Исламского азадского университета, Кучан, Иран

Введение. Проведено исследование с целью изучения процесса электрокоагуляции как нового метода для удаления примесей и соединений не сахаров из сахара-сырца свекольного сока.

Материалы и методы. Исследование выполнено в периодическом химическом реакторе, оборудованном баком на 5 л, который содержит 3 алюминиевых анодных и 3 железных катодных электрода, соединенные параллельно. Исследовано влияние напряжения 5, 10 и 15 вольт, время обработки с 15, 30 и 45-минутными интервалами и значениями рН 6, 7 и 8 на чистоту, мутность и цвет сахарного свекольного сока с использованием метода поверхности отклика Бокс-Бенкена и статистического проектирования на основании программного пакета Minitab 17.

Результаты и обсуждение. В ходе процесса электрокоагуляции мутность уменьшается с повышением напряжения. С повышением напряжения растворимость анодных электродов также увеличивается, что приводит к удалению большего

количества загрязняющих веществ. Таким образом, снижение мутности и увеличение напряжения может быть связано с увеличением производства стружки, в то время как изменения в значении рН не имеют существенного влияния на мутность. Хотя увеличение напряжения существенно не влияет на усиление цвета, однако оно может быть связано с увеличением пузырьков и последующим увеличением ферментативной активности в процессе флотации. Увеличение ферментативной активности усиливает цвет меланина в течение определенного времени через открытость реактора при флотации и аэрации. Однако увеличение значения рН незначительно усиливает цвет. Результаты показали, что повышение напряжения приводит к увеличению степени чистоты. Растворимость анодных электродов увеличивается с повышением напряжения, а впоследствии более большое количество примесей удаляется путем производства гидроксида алюминия. Повышение напряжения также приводит к получению большего количества пузырьков, которые увеличивают контакт между гидроксидом алюминия с загрязнителями и примесями, и способствует флотации большего количества полученного осадка, и, таким образом, удалению большего количества примесей. Увеличение продолжительности процесса также приводит к повышению степени чистоты, поскольку увеличение продолжительности реакции приводит к большей флотации осадка на поверхности жидкости. Увеличение значения рН не оказывает существенного влияния на уровень чистоты.

Вывод. В целом процесс электрокоагуляции положительно сказывается на снижении мутности и повышении чистоты сахара-сырца свекольного сока в процессе очистки, хотя на интенсивность цвета он влияет незначительно.

Ключевые слова: сахарная свекла, электрокоагуляция, цвет, чистота, мутность.

Анализ выбора сортов винограда для технологии ледяных вин

Виктория Остапенко

Одесская национальная академия пищевых технологий, Одесса, Украина

Введение. Выбор соответствующих сортов, предназначенных для производства ледяного вина, оказывает все более глубокое влияние на рыночное предложение, расширяя премиум-сегмент сельскохозяйственного сектора.

Материалы и методы. Для анализа характеристик винограда, используемого для ледяного вина в разных странах, использованы базы данных и международные законы в виноделии.

Результаты и обсуждение. Данный анализ иллюстрирует полный ассортимент сортов винограда, используемых виноделами, которые решили оставить лозу при низких температурах в различных странах-производителях: в Германии, Чешской Республики, Австрии, Словении и Канаде. Виноделы из этих стран включают самые разнообразные классы винограда для производства вин. В Европе используются различные сорта винограда для естественного замораживания, но общий выпуск ледяного вина ниже по сравнению со странами, расположенные в Северной Америке, включая Канаду и Соединенные Штаты.

Большинство стран, главным образом, выбирают класс *V. Vinifera*, который обладает толстой кожей, что предполагает лучшую защиту от зимнего

повреждения, однако сорта этого класса более чувствительны к погодным условиям, чем гибриды или автохтонные сорта винограда. Рислинг – наиболее часто используемый сорт для производства ледяного вина, поскольку имеет высокую стойкость виноградной лозы на протяжении зимнего периода.

Климатические условия являются основным источником получения урожая для ледяного вина, однако могут значительно уменьшить ожидаемые объемы урожая, поэтому меры по защите винограда предусматриваются перед низкими температурами.

Выводы. Результат, полученный по итогам анализа использования различных сортов винограда, демонстрирует развитие и расширение производства ледяных вин в рамках мирового винного общества.

Ключевые слова: ледяное вино, виноград, сорт позднего созревания, климат.

Химический состав эфирного масла шалфея (*Salvia officinalis* L.) из Болгарии

Станка Дамянова¹, Силвия Моллова², Албена Стоянова³, Олексій Губеня⁴

1 - Русенский университет, филиал в г. Разград, Болгария

2 - Институт розы, Казанлык, Болгария

3 - Университет пищевых технологий, Пловдив, Болгария

4 - Национальный университет пищевых технологий, Киев, Украина

Введение. Проведены исследования с целью определения химического состава эфирного масла шалфея лекарственного (*Salvia officinalis* L.), выращенного в Болгарии.

Материалы и методы. В исследованиях использовано травяное сырье из шалфея, приобретенное в местной торговой сети. Эфирное масло получали путем гидродистилляции в течение 3 часов в стеклянном лабораторном аппарате. Химический состав масла определяли хроматографическим путем.

Результат и обсуждение. Влажность сырья составила 12,16%, а выход эфирного масла – 0,93%.

В эфирном масле было определено 28 компонентов. Основные соединения эфирного масла следующие: α -туйон (26,68%), (E)- β -кариофиллен (7,47%), 1,8-цинеол (7,19%), α -гумулен (6,11%), β -пинен (5,44%), β -туйон (5,35%), камфора (4,84%), алло-аромадендрен (4,55%), борнеол (3,69%) и α -пинен (3,58%). Три группы соединений были найдены в гидродистиллированном масле из шалфея. Высокий процент компонентов эфирного масла составляли суммарные кислородосодержащие монотерпены – 59,15%, сесквитерпеновые углеводороды – 24,37%, монотерпеновые углеводороды – 14,66%. Самой распространенной в масле была кислородосодержащая монотерпеновая фракция, которая особенно богата на кетоны (70,96% от этой фракции)

Вывод. Можно констатировать, что в эфирном масле шалфея лекарственного был выявлен ряд кислородосодержащих монотерпенов, сесквитерпеновых углеводородов и монотерпеновых углеводородов.

Ключевые слова: шалфей, эфирное масло, состав, Болгария.

Влияние параметров переработки на состав и сенсорные характеристики хлебного дерева элубо

Тяни Аким Олумиде¹, Бакаре Хенри Адегоке²
Оке Эммануэл Кехинде³, Ойедеи Айибола Бамиколе⁴

1 - Национальное агентство по биотехнологии развития, Овод Йева, Нигерия

2 - Департамент гостиничного бизнеса и туризма, Федеральный университет сельского хозяйства, Абеокута, Нигерия

3 - Департамент пищевой науки и техники, Федеральный университет сельского хозяйства, Абеокута, Нигерия

4 - Отдел биотехнологии и пищевых технологий, Дурбанский технологический университет, Дурбан, Южно-Африканская республика

Введение. Хлебное дерево не относится к пищевым продуктам и его применение в пищевых технологиях основано на технологической обработке с последующим внесением в рецептуру хлебопекарского продукта элубо (elubo), технология которого широко применяется в настоящее время.

Материалы и методы. Хлебное дерево промывалось чистой водой для удаления каучуконосов. Кора снимается вручную и разрезается на кусочки. Кусочки выдерживались в воде при температуре 30, 50 и 60 °C на протяжении 90, 120 и 150 мин. Далее хлебное дерево выдерживалось в воде 6, 12 и 18 часов. После удаления избытка влаги образцы были высушены в сушильной камере при температуре 60 °C на протяжении 2 дней и измельчены в муку (элубо). Образцы теста хлебного дерева (Амала) были подвержены органолептическому анализу.

Результаты и обсуждение. Содержание влаги в хлебном дереве элубо варьируется между 9,07 и 12,20%. Содержание влаги в образцах соответствует содержанию твердой материи. Значительное количество золы в образцах хлебного дерева элубо (ХЭ) является индикатором хорошего источника минералов в муке. Величины озоления варьируются в пределах 2,00–2,90%. Содержание пищевых волокон в хлебном дереве элубо составляет 2,86–3,60%. Температура и время выдерживания в воде существенно ($p > 0,05$) не влияют на содержание волокон в образцах. Содержание белков в образцах хлебного дерева элубо варьируется в пределах между 3,80 и 5,42%. Содержание белков в образцах изменяется независимо от параметров температуры и продолжительности выдержки. Содержание углеводов в образцах составляет 73,67–78,33%. Высокое количество углеводов указывает на высокую калорийность готовых изделий. На содержание углеводов параметры температуры и продолжительности выдерживания влияют незначительно ($p > 0,05$). Органолептические показатели теста, изготовленного из хлебного дерева элубо существенно ($p < 0,05$) отличались от теста, изготовленного из батата элубо (t-показатель – 2,523, степень свободы – 14, p-величина – 0,01, один срез).

Выводы. Результаты исследований подтверждают наличие значительного количества пищевых волокон и углеводов в хлебном дереве элубо, что указывает на возможность его использования в качестве высокоэнергетического продукта.

Ключевые слова: *хлебное дерево, элубо, технология, обработка, органолептика.*

Использование орехового сырья и семян чиа для улучшения жирнокислотного состава напитков смузи

Анджела Дьяконова, Виктория Степанова

Одесская национальная академия пищевых технологий, Одесса, Украина

Введение. На сегодняшний день недостаточно исследованными являются пути использования орехового, семенного сырья и их комбинаций в качестве источника эссенциальных жирных кислот пищевых продуктов оздоровительного назначения.

Материалы и методы. В работе исследовано композицию ингредиентов универсальной основы для производства напитков. Определено содержание белков, жиров, углеводов, золы и калорийность продукта. Методом газовой хроматографии исследован жирно-кислотный состав рецептурных компонентов и определено соотношение ω -3 и ω -6 жирных кислот в готовых напитках. Изучено аминокислотный состав разработанной композиции, ее вязкость и стабильность при хранении.

Результаты и обсуждение. Авторами предложено 9 рецептур напитков смузи с различными органолептическими показателями. 250 мл таких напитков могут удовлетворить суточную потребность здорового человека в линоленовой и линолевой кислот на 30 %, так как их содержание в готовых напитках составляет не менее 0,5 г и 2 г, соответственно. Разработанные напитки рекомендуются к употреблению всем группам населения, в частности людям, страдающим заболеваниями сердечно-сосудистой системы или желающим поддерживать ее работу в норме.

Использование семян чиа и ядра грецкого ореха значительно повышают содержание биологически ценных веществ в напитках. Семена чиа существенно влияют на реологические показатели смузи, повышая плотность и вязкость напитков за счет слизистых веществ на поверхности зерна семян, а также поддерживают стабильность жировой системы при хранении. Способность семян чиа к слизееобразованию объясняется содержанием водорастворимых полисахаридов – пентозанов, которые составляют до 8 % от массы зерна семян. Благодаря использованию семян чиа в составе универсальной основы, она имеет 100 % стабильность в течение 24 часов, что полностью удовлетворяет потребности предприятий общественного питания. Белки разработанной орехово-семенной композиции являются полноценными и содержат все незаменимые аминокислоты. Лимитирующими аминокислотами являются лизин, метионин + цистеин, треонин и валин.

Выводы. Впервые изучена возможность применения семян чиа как структурообразователя напитков смузи и предложена композицию ингредиентов для производства универсальной основы для напитков, которая имеет сбалансированное содержание ω -3 и ω -6 жирных кислот.

Ключевые слова: *орех, чиа, жирные кислоты, напиток, смузи.*

Влияние коллагенового белка «Белкозин» на биологическую ценность вареных колбас

Анатолий Украинец, Василий Пасичный, Максим Полумбрик, Манефа Полумбрик
Национальный университет пищевых технологий, Киев, Украина

Введение. Проведены сравнительные исследования амнокислотного СКОРа белков вареных колбасных изделий, изготовленных с коллагеновым белком «Белкозин» и скорости накопления тирозина в динамической модели желудочно-кишечного тракта человека с целью установления степени усвоения белков этих колбас.

Материалы и методы. Гидролиз проводился в специальном устройстве, которое состояло из внутренней и внешней емкости. Внутренняя емкость содержит стеклянную мешалку, назначение которой состоит в постоянном перемешивании

ферментационной среды и диализе продуктов реакции. Ферментативное расщепление длилось три часа на каждой стадии. Действие пепсина проходило на первой стадии, а трипсина – на второй. Аминокислотный состав колбасных изделий был определен с помощью ионообменной хроматографии.

Результаты и обсуждение. Нами были проведены сравнительные исследования ферментативного гидролиза колбас, изготовленных из куриного мяса бройлеров, охлажденного до 0–4 °С. После добавления трипсина наблюдалось ускорение гидролиза белков вареных колбас, которое достигало максимума на шестой час ферментации. Включение коллагенового белка «Белкозин» в состав рецептур вареных колбас существенно не влияет на аминокислотный состав готовых изделий. В результате сравнительных исследований способа введения белковой композиции в состав колбасных изделий определено, что ферментативный гидролиз быстрее происходит в колбасах, изготовленных с сухим белковым стабилизатором, особенно на стадии действия трипсина. Увеличение содержания белка «Белкозин» в рецептуре приводит к росту биодоступности белков колбасных изделий, что свидетельствует о положительном влиянии коллагенового белка «Белкозин» на перевариваемость этих продуктов.

Выводы. Рост доли гидролизата с 6 до 12% в БС повышает скорость накопления тирозина, который образуется при последовательном ферментативном гидролизе в системе пепсин-тирозин, который *in vitro* моделирует процессы пищеварения, происходящие в организме человека. Таким образом, внесение коллагенового белка «Белкозин» существенно повышает биологическую ценность колбасных изделий, изготовленных с его добавлением, что проявляется в росте переваримости белков вареных колбас при увеличении в них доли коллагенового белка «Белкозин».

Ключевые слова: колбаса, белок «Белкозин», биологическая ценность, гидролиз, пепсин, трипсин.

Релаксационное поведение водных дисперсий крахмалов

Валерий Манк, Оксана Точкова, Оксана Мельник, Александр Бессараб
Национальный университет пищевых технологий, Киев, Украина

Введение. Реологические свойства водных растворов полисахаридов показали тиксотропическое поведение при разрушении их частично упорядоченной структуры, что имеет место при физических или тепловых воздействиях.

Материалы и методы. Готовили 3–15% дисперсии нативного картофельного и кукурузного крахмалов в дистиллированной воды. Образцы термостатировали при температуре 20°С в течение 30 минут. Исследования проводили по методике определения реологического поведения при комнатной температуре каждые 3 часа.

Результаты и обсуждение. Новый метод релаксации в крахмальных смесях заключается в том, что структурная релаксация полимерных звеньев полисахаридов во времени проходит медленно и долго.

Согласно литературным источникам, только полисахариды, молекулярная масса которых больше 1 млн (на примере картофельного крахмала), характеризуются медленной релаксацией структуры. Такая физико-химическая характеристика полисахаридов, как релаксация обуславливается частично упорядоченной структурой с взаимным расположением отдельных цепей в пространственной сетке.

Под действием сдвиговых напряжений реотеста разрушенная псевдопластическая структура водных дисперсий крахмала постепенно восстанавливается до равновесного при данных условиях состояния системы. Время восстановления структуры составляет 17 часов.

Медленный процесс восстановления или структурной релаксации пространственных структур водных дисперсий полисахаридов происходит вследствие перестройки пространственной сетки полимера, который образуется благодаря существованию поперечных химических связей.

Аналогичное поведение с меньшим временем структурной релаксации характерно и для других полисахаридов, в частности ксантана, время релаксации которого составляет около 3 часов.

Выводы. Между цепями существуют особенности коллоидной системы, влияющие на ее качественные, структурно-механические и технологические свойства, которые необходимо учитывать при выборе рациональных режимов оптимальных условий проведения процессов при проектировании автоматических систем управления производством.

Ключевые слова: полисахариды, крахмал, дисперсия, структура, релаксация.

Процессы и оборудование пищевых производств

Загрязнение полимерных и органо-неорганических мембран при разделении послеспиртовой зерновой барды

Юрий Змиевский¹, Юлия Дзязько², Валерий Мирончук¹,
Людмила Рождественская², Александр Виленский³, Людмила Корниенко¹
1 – Национальный университет пищевых технологий, Киев, Украина

2 – Институт общей и неорганической химии им. В.И. Вернадского Национальной академии наук Украины, Киев, Украина

3 – Институт кристаллографии им. А.В. Шубникова РАН, Москва, Российская Федерация

Введение. Процесс баромембранного разделения целесообразно использовать для переработки послеспиртовой зерновой барды. Чтобы избежать загрязнения мембраны органическими веществами, полимерные мембраны модифицируют частицами неорганических ионообменников. Установлено и сделано сравнение механизмов загрязнения для полимерных и композитных мембран, модифицированных частицами неорганических ионообменников, во время разделения послеспиртовой барды.

Материалы и методы исследования. Полиэтилентерефталатовые трековые микрофилтрационные мембраны были модифицированы агрегатами наночастиц гидрофосфата циркония. Материал исследован с помощью метода сканирующей электронной микроскопии. Вначале мембраны опресовывались при помощи дистиллированной воды. Послеспиртовая барда разделялась при давлениях 1–4 бар и температуре 60 °С.

Результаты и их обсуждение. Модели полного и постепенного закупоривания пор, а также модель образования осадка были использованы и при фильтровании воды через композиционные мембраны. С помощью моделей полного и постепенного закупоривания пор показано, что при 60 °С происходят изменения пористой структуры полимера и фрагментация модификатора. Установлено, что при

разделении послеспиртовой зерновой барды композиционная мембрана демонстрирует большую устойчивость к загрязнению органическими веществами, чем немодифицированная. Фильтрация через композит подчиняется закону Дарси. Максимальная производительность достигается при 3 атм. Поток пермеата через модифицированную мембрану снижается с повышением давления, что связано с загрязнением. Для модифицированной мембраны характерно линейное возрастание производительности, что указывает на меньшее гидродинамическое сопротивление загрязнителей. Полное закупоривание пор справедливо для обеих мембран. Повышение давления приводит к отложению осадка на стенках пор (немодифицированная мембрана) и формированию осадка на поверхности (обе мембраны). Повышенная устойчивость композиционной мембраны к загрязнению предполагает минимизацию объема химических реагентов для регенерации, сокращение времени регенерации и уменьшение объема воды для промывки.

Выводы. Неорганические ионообменники позволяют улучшить стойкость мембран к загрязнениям компонентами послеспиртовой барды. Органо-неорганические мембраны могут быть использованы для других объектов пищевой промышленности, особенно при комнатных или более низких температурах.

Ключевые слова: барда, мембрана, наночастица, разделение, модифицирование.

Использование твердой биомассы в факельных котлах для сжигания антрацита

Наталья Дунаевская, Николай Чернявский, Тарас Щудло
Институт угольных энерготехнологий Национальной академии наук Украины, Киев, Украина

Введение. Сжигание твердой биомассы в существующих котлах может не только уменьшить вредные выбросы в атмосферу, но и диверсифицировать топливную базу генераций. Сжигание также позволяет внедрить эффективное использование твердых отходов пищевой промышленности, которые осуществляют вредное воздействие на окружающую среду.

Материалы и методы. На нисходящем экспериментальном стенде ВГП-100В с расходом топлива 30 кг/ч исследовалось совместное факельное сжигание древесной сосны с антрацитом. На установке кипящего слоя РСК-1Д исследовалась кинетика термической деструкции коксов опилок сосны. Методом термогравиметрии исследована кинетика термической деструкции образцов сосны и пеллет соломы пшеницы, рапса, кукурузы и сои.

Результаты и обсуждение. Совместное факельное сжигание отечественного антрацита с древесиной в факеле на стенде ВГП-100В показало техническую возможность и потенциальную способность к улучшению качества горения низкорекционного антрацита. На основании анализа экспериментальных режимов определено, что оптимальная тепловая доля биомассы составила около 10%. Такая добавка биомассы обеспечивала стабилизацию факела без газовой подсветки, а также самую высокую степень конверсии углерода угля.

На установке РСК-1Д был установлен внутренний кинетический режим горения образцов кокса сосны размером 0,1–1,6 мм в диапазоне температур 390–560 °С.

С использованием метода термогравиметрии были определены отдельные стадии термического разложения (выход влаги, выход летучих и горение коксового остатка) и их кинетические характеристики для образцов органической биомассы.

Сравнение кинетики выхода летучих для образцов опилок сосны и пеллет соломы пшеницы с данными доступных литературных источников указывает на некоторое различие в скорости выхода летучих, что объясняется расхождением в скорости нагрева образцов в ходе эксперимента, разной степенью измельчения исследуемых образцов, отличием органического и минерального состава образцов, разницей в подходах к расчету констант реакции. Однако наблюдалась близость значений скорости выхода летучих образцов пеллет соломы различных культур между собой.

Выводы. Представленные результаты исследований могут быть использованы в расчетах отдельных процессов совместного сжигания на ТЭС.

Ключевые слова: *совместное сжигание, биомасса, уголь, антрацит.*

Погрешности прямых измерений температуры термометрами и валидация CFX i FLUENT моделей сжигания природного газа

Павел Засядько, Николай Прядко

Национальный университет пищевых технологий, Киев, Украина

Введение. Технологические процессы, связанные с горением, создают серьезные экологические проблемы, связанные с выбросом вредных веществ преимущественно в газообразном состоянии. Согласно общепринятой точке зрения, оксиды азота в основном возникают в установках сжигания в областях высоких температур.

Материалы и методы. Решаются задачи, связанные с оценкой ошибок термометры при измерениях температуры в пламенах, проводимых при экспериментальном сжигании природного газа в экспериментальной установке ВПП-100В.

Результаты и обсуждение. Выведена модель, позволяющая получить поправочные коэффициенты, которые должны применяться при обработке данных прямых показаний термометров. Модель учитывает конвективный теплообмен, облучение на части шарика термометра, которая падает от продуктов сгорания. Модель также учитывает, что часть королька термометра излучает в направлении охлаждаемого окружения. В результате получено и решено математическое уравнение трансцендентного типа четвертого порядка в MathCad. Получен набор поправочных коэффициентов, которые при добавлении к прямым показаниям термометра показали близкое соответствие результатам, полученным при трехмерном моделировании сжигания природного газа в цилиндрическом нисходящем реакторе.

Вывод. Разработанную методологию коррекции можно рекомендовать для использования при экспериментальных измерениях температур, которые могут выполняться с помощью незакрытых термометров, когда нельзя использовать термометру или всасывающий пирометр в оболочке.

Ключевые слова: *газ, сжигание, термометра, измерение, погрешность.*

**Моделирование пульсационного режима псевдооживления при получении
органо-минеральных удобрений**

Ярослав Корниенко, Сергей Гайдай,
Андрей Любэка, Сергей Турко, Александр Мартынюк
*Национальный технический университет Украины "Киевский политехнический
институт имени Игоря Сикорского", Киев, Украина*

Введение. Целью работы является математическое моделирование гидродинамического режима неоднородного псевдооживления, который обеспечит повышение эффективности тепло-массообменных процессов при получении органо-минеральных удобрений, в состав которых входит подсолнечная зола, стимулирующие и питательные компоненты.

Материалы и методы. Процесс неоднородного псевдооживления, что обуславливает активное объемное перемешивание с интенсивной циркуляцией зернистого материала в слое, проводился в камере гранулятора, снаряженной специальным газораспределительным устройством в нижней части и направляющей вставкой в верхней. Измерения перепада давления в слое и видеофиксация процесса осуществлялись с помощью специализированного оборудования.

Результаты и обсуждение. Реализовано неоднородное псевдооживление при применении оригинального газораспределительного устройства с коэффициентом живого сечения $\phi=4,9\%$ и усовершенствованной камеры гранулятора. Обеспечено интенсивное макроперемешивание зернистого материала с эквивалентным диаметром $D_e=3,97$ мм и плотностью $\rho_p=1450$ кг/м³ при отношении номинального перепада давления до высоты слоя $\Delta P_b/H_0 \geq 8500$ Па/м с частотой $f=1,67$ Гц. Отсутствие застойных зон обеспечивает коэффициент гранулообразования $\psi \geq 90\%$ и удельная нагрузка поверхности слоя по влаге $a_f=0,8 \div 0,9$ кг_{вл.}/(м²·ч). Выбрана математическая модель, которая с учетом неоднородности позволила определить условия проведения процесса, при котором до 25% массы слоя находится в активной фазе вне слоя с частотой $f=1,67$ Гц. Математическая модель с точностью 94,8% подтверждает результаты исследования.

Выводы. Реализована гидродинамика в камере гранулятора без образования застойных зон. Модифицированная математическая модель позволила определить интенсивность активного объемного циркуляционного перемешивания, что существенно повысит устойчивость кинетики гранулообразования при обезвоживании композитных жидких систем.

Ключевые слова: гидродинамика, пульсации, псевдооживление, удобрения, зола.

Instructions for authors



Dear colleagues!

The Editorial Board of scientific periodical
«**Ukrainian Food Journal**»
invites you to publication of your scientific research.

Requirements for article:

Language – English, Ukrainian, Russian

Size of the article – 8–15 pages in Microsoft Word 2003 and earlier versions with filename extension *.doc (!)

All article elements should be in Times New Roman, font size 14, 1 line intervals, margins on both sides 2 cm.

The structure of the article:

1. The title of the article
2. Authors (full name and surname)
3. Institution, where the work performed.
4. Abstract (2/3 of page). The structure of the abstract should correspond to the structure of the article (Introduction, Materials and methods, Results and discussion, Conclusion).
5. Key words.

Points from 1 to 5 should be in English, Ukrainian and Russian.

6. The main body of the article should contain the following obligatory parts:

- Introduction
- Materials and methods
- Results and discussing
- Conclusion
- References

If you need you can add another parts and divide them into subparts.

7. The information about the author (Name, surname, scientific degree, place of work, email and contact phone number).

All figures should be made in graphic editor, the font size 14.

The background of the graphs and charts should be only in white color. The color of the figure elements (lines, grid, text) – in black color.

Figures and EXCEL format files with graphs additionally should submit in separate files.

Photos are not appropriate to use.

Website of Ukrainian Food Journal: <http://ufj.ho.ua>

Extended articles should be sent by email to: ufj_nuft@meta.ua

Шановні колеги!

Редакційна колегія наукового періодичного видання «**Ukrainian Food Journal**» запрошує Вас до публікації результатів наукових досліджень.

Вимоги до оформлення статей

Мови статей – англійська, українська, російська
Рекомендований обсяг статті – **8–15 сторінок** формату А4.
Стаття виконується в текстовому редакторі Microsoft Word 2003, в форматі *.doc.
Для всіх елементів статті шрифт – **Times New Roman**, кегль – **14**, інтервал – 1.
Всі поля сторінки – по 2 см.

Структура статті:

1. УДК.
2. **Назва статті.**
3. Автори статті (ім'я та прізвище повністю, приклад: Денис Озеряно).
4. *Установа, в якій виконана робота.*
5. Анотація. Обов'язкова структура анотації:
 - Вступ (2–3 рядки).
 - Матеріали та методи (до 5 рядків)
 - Результати та обговорення (пів сторінки).
 - Висновки (2–3 рядки).
6. Ключові слова (3–5 слів, але не словосполучень).

Пункти 2–6 виконати англійською, українською та російською мовами.

7. Основний текст статті. Має включати такі обов'язкові розділи:
 - Вступ
 - Матеріали та методи
 - Результати та обговорення
 - Висновки
 - Література.

За необхідності можна додавати інші розділи та розбивати їх на підрозділи.

8. Авторська довідка (Прізвище, ім'я та по батькові, вчений ступінь та звання, місце роботи, електронна адреса або телефон).
9. Контактні дані автора, до якого за необхідності буде звертатись редакція журналу.

Рисунки виконуються якісно. Скановані рисунки не приймаються. Розмір тексту на рисунках повинен бути **співрозмірним (!)** тексту статті. **Фотографії бажано не використовувати.**

Фон графіків, діаграм – лише білий. Колір елементів рисунку (лінії, сітка, текст) – чорний (не сірий).

Рисунки та графіки EXCEL з графіками додатково подаються в окремих файлах.

Скорочені назви фізичних величин в тексті та на графіках позначаються латинськими літерами відповідно до системи СІ.

В списку літератури повинні переважати статті та монографії іноземних авторів, які опубліковані після 2000 року.

Правила оформлення списку літератури

В Ukrainian Food 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.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

1. Приклад:

Popovici C., Gitin L., Alexe P. (2013), Characterization of walnut (*Juglans regia* L.) green husk extract obtained by supercritical carbon dioxide fluid extraction, *Journal of Food and Packaging Science, Technique and Technologies*, 2(2), pp. 104–108.

2. Посилання на книгу:

Автори (рік), Назва книги (курсивом), Видавництво, Місто.

Ініціали пишуться після прізвища.

Всі елементи посилання розділяються комами.

Приклад:

2. Wen-Ching Yang (2003), *Handbook of fluidization and fluid-particle systems*, Marcel Dekker, New York.

Посилання на електронний ресурс:

Виконується аналогічно посиланню на книгу або статтю. Після оформлення даних про публікацію пишуться слова **available at:** та вказується електронна адреса.

Приклади:

1. (2013), *Svitovi naukovometrychni bazy*, available at:

http://www1.nas.gov.ua/publications/q_a/Pages/scopus.aspx

2. Cheung T. (2011), *World's 50 most delicious drinks [Text]*, available at:

<http://travel.cnn.com/explorations/drink/worlds-50-most-delicious-drinks-883542>

Список літератури оформлюється лише латиницею. Елементи списку українською та російською мовою потрібно транслітерувати. Для транслітерації з українською мови використовується паспортний стандарт, а з російської – стандарт МВД (в цих стандартах використовуються символи лише англійського алфавіту, без хвостиків, апострофів та ін).

Зручні сайти для транслітерації:

З української мови – <http://translit.kh.ua/#lat/passport>

З російської мови – <http://ru.translit.net/?account=mvd>

Додаткова інформація та приклад оформлення статті – на сайті

<http://ufj.ho.ua>

Стаття надсилається за електронною адресою: ufj_nuft@meta.ua

Ukrainian Food Journal публікує оригінальні наукові статті, короткі повідомлення, оглядові статті, новини та огляди літератури.

Тематика публікацій в Ukrainian Food Journal:

Харчова інженерія	Процеси та обладнання
Харчова хімія	Нанотехнології
Мікробіологія	Економіка та управління
Фізичні властивості харчових продуктів	Автоматизація процесів
Якість та безпека харчових продуктів	Упаковка для харчових продуктів
	Здоров'я

Періодичність виходу журналу 4 номери на рік.

Результати досліджень, представлені в журналі, повинні бути новими, мати чіткий зв'язок з харчовою наукою і представляти інтерес для міжнародного наукового співтовариства.

Ukrainian Food Journal індексується наукометричними базами:

Index Copernicus (2012)
 EBSCO (2013)
 Google Scholar (2013)
 UlrichsWeb (2013)
 Global Impact Factor (2014)
 Online Library of University of Southern Denmark (2014)
 CABI full text (2014)
 Directory of Research Journals Indexing (DRJI) (2014)
 Universal Impact Factor (2014)
 Directory of Open Access scholarly Resources (ROAD) (2014)
 European Reference Index for the Humanities and the Social Sciences (ERIH PLUS) (2014)
 Directory of Open Access Journals (DOAJ) (2015)
 InfoBase Index (2015)

Рецензія рукопису статті. Матеріали, представлені для публікування в «Ukrainian Food Journal», проходять «Подвійне сліпе рецензування» двома вченими, призначеними редакційною колегією: один є членом редколегії і один незалежний учений.

Авторське право. Автори статей гарантують, що робота не є порушенням будь-яких авторських прав, та відшкодовують видавцю порушення даної гарантії. Опубліковані матеріали є правовою власністю видавця «Ukrainian Food Journal», якщо не узгоджено інше.

Політика академічної етики. Редакція «Ukrainian Food Journal» користується правилами академічної етики, викладених в роботі Miguel Roig (2003, 2006) "Avoiding plagiarism, self-plagiarism, and other questionable writing practices. A guide to ethical writing". Редакція пропонує авторам статей і рецензентам прямо слідувати цьому керівництву, щоб уникнути помилок у науковій літературі.

Інструкції для авторів та інша корисна інформація розміщені на сайті

<http://ufj.ho.ua>

Редакційна колегія

Головний редактор:

Валерій Манк, д-р. техн. наук, проф., *Національний університет харчових технологій, Україна*

Члени редакційної колегії:

Александр Мамцев, д-р. техн. наук, проф., *філія Московського державного університету технології та управління в м. Мелеуз, Республіка Башкортостан, Росія*
Анатолій Сайганов, д-р. екон. наук, проф., *Інститут системних досліджень в АПК НАН Беларусі*

Валерій Мирончук, д-р. техн. наук, проф., *Національний університет харчових технологій, Україна*

Віктор Стабніков, канд. техн. наук, доц., *Національний університет харчових технологій, Україна*

Віргінія Юреніс, д-р., проф., *Вільнюський університет, Литва*

Віталій Таран, д-р. техн. наук, проф., *Національний університет харчових технологій, Україна*

Володимир Ковбаса, д-р. техн. наук, проф., *Національний університет харчових технологій, Україна*

Володимир Іванов, д-р., проф., *Державний університет Іови, США*

Владімір Груданов, д-р. техн. наук, проф., *Беларуський державний аграрний технічний університет*

Галина Сімахіна, д-р. техн. наук, проф., *Національний університет харчових технологій, Україна*

Ірина Федулова, д-р. екон. наук, проф., *Національний університет харчових технологій, Україна*

Йорданка Стефанова, д-р, *Пловдивський університет "Паїсій Хілендарскі", Болгарія*

Крістіна Попович, д-р., доц., *Технічний університет Молдови*

Микола Сичевський, д-р. екон. наук, проф., *Інститут продовольчих ресурсів НААН України*

Марк Шамця, канд. техн. наук, доц., *Санкт-Петербурзький державний технологічний інститут, Росія*

Олександр Шевченко, д-р. техн. наук, проф., *Національний університет харчових технологій, Україна*

Олена Грабовська, д-р. техн. наук, проф., *Національний університет харчових технологій, Україна*

Олена Драган, д-р. екон. наук, проф., *Національний університет харчових технологій, Україна*

Ольга Петухова, д-р. екон. наук, доц., *Національний університет харчових технологій, Україна*

Ольга Рибак, канд. техн. наук, доц., *Тернопільський національний технічний університет імені Івана Пулюя, Україна*

Паскаль Дюпю, д-р, *Університет Клод Бернард Ліон 1, Франція*

Стефан Стефанов, д-р., проф., *Університет харчових технологій, Болгарія*
Тетяна Мостенська, д-р. екон. наук, проф., *Національний університет харчових технологій, Україна*
Тетяна Пирог, д-р. біол. наук, проф., *Національний університет харчових технологій, Україна*
Томаш Бернат, д-р., проф., *Щецинський університет, Польща*
Юлія Дзязько, д-р. хім. наук, с.н.с., *Інститут загальної та неорганічної хімії імені В. І. Вернадського НАН України*
Юрій Білан, д-р., *Щецинський університет, Польща*
Олексій Губеня (відповідальний секретар), канд. техн. наук, доц., *Національний університет харчових технологій, Україна.*

Contents of Volume 5 Year 2016

Food Technologies

Issue 1

- Tamara Nosenko, Irina Levchuk, Volodymyr Nosenko, Tamara Koroluk*
Effect of rape seeds microwave pretreatment on the composition and antioxidative properties of press rape oil 7
- Olesia Priss*
Effect of heat treatment with antioxidants on oxygen radical scavenging during storage of bell pepper fruits 16
- Yuriy Posudin*
Laser light scattering by milk particles. 27
- Valerii Sukmanov, Viktoriia Kiiko*
High pressure in the technology of milk and soft cheese 44
- Gjore Nakov, Viktorija Stamatovska, Ljupka Necinova, Nastia Ivanova, Stanka Damyanova*
Sensor analysis of functional biscuits 56
- Nataliya Ryabchenko*
Influence of packaging on the quality of soft brine cheese fortified with seaweed additive 63
- Aliona Dikhtyar, Natalia Fedak, Natalia Murlikina*
Research of high oleic sunflower oil properties under the hydrothermal effect 70
- Mariia Zemelko, Valeriy Mank, Oleh Chervakov*
Influence of chocolate frosts on their qualities and usage in food industry 80
- Anastasiya Chorna, Oksana Shulga, Larisa Arsenieva, Nataliya Hrehirchak, Kateryna Zusko, Serhii Riabov, Serhii Kobylinskyi, Ludmila Goncharenko*
Antibacterial biodegradable films for foods 88

Зміст тому 5 2016 рік

Харчові технології

№ 1

- Тамара Носенко, Ірина Левчук, Володимир Носенко, Тамара Королюк*
Вплив попередньої мікрохвильової обробки насіння ріпаку на склад і антиоксидантні властивості пресової ріпакової олії
- Олеся Прісс*
Вплив теплової обробки антиоксидантами на утилізацію активних форм кисню впродовж зберігання солодкого перцю
- Юрій Посудін*
Розсіювання лазерного випромінювання частинками молока
- Валерій Сукманов, Вікторія Кійко*
Високий тиск у технологіях молока і м'якого сиру
- Гьоре Наков, Вікторія Стаматовска, Люпка Несінова, Настя Іванова, Станка Дамянова*
Сенсорний аналіз функціональних бесквітів
- Наталія Рябченко*
Вплив пакування на якість м'яких розсільних сирів, фортифікованих добавкою з морських водоростей
- Альона Діхтярь, Наталя Федак, Наталя Мурликіна*
Вивчення властивостей олії соняшникової високоолеїнового типу за умов гідротермічного впливу
- Марія Земелько, Валерій Манк, Олег Черваков*
Вплив складу шоколадних глазурей на їх властивості і використання в харчовій промисловості
- Анастасія Чорна, Оксана Шульга, Лариса Арсеньєва, Наталія Грегірчак, Катерина Зусько, Сергій Рябов, Сергій Кобилінський, Людмила Гончаренко*
Антибактеріальні біодеградабельні плівки для харчових продуктів

Issue 2

*Dimitar Dimitrov, Tatyana Yoncheva,
Vanyo Haygarov*

Methanol content in grape and fruit brandies: a major indicator for authenticity and safety 237

Aslihan Demirdöven, Taner Baysal
Inactivation effect of microwave heating on pectin methylesterase in orange juice 248

*Lyudmila Vinnikova, Andrey Kishenya,
Irina Strashnova*

Lactic acid bacteria compositions for application in the meat industry 262

*Inna Pylypenko, Liudmyla Pylypenko,
Elena Sevastyanova,*

Evgeniy Kotlyar, Ruslana Kruchek
Epiphytic and regulated microbial contaminants of food vegetable raw materials and products 272

Valerii Mank, Tetyana Polonska
Use of natural oils as bioactive ingredients of cosmetic products 281

*Oleksandr Rozhno, Olena Podobiy,
Vira Yurchak*

Rheological properties of gelatine solutions for production of gluten-free pasta 290

Issue 3

Yuriy Posudin

Spectroscopic analysis of honey 437
*Tamara Nosenko, Valeriy Mank,
Yaroslava Zhukova, Alyona Cherstva*
Composition and properties of partially hydrolyzed sunflower protein isolates 451

Olusegun A. Olaoye
Spoilage volatiles and sensory properties of a grilled stick meat product inoculated with *Pediococcus acidilactici* FLE07 as starter culture. 462

Svitlana Bazhay-Zhezherun, Tetiana Romanovska, Mariia Antoniuk

Improving the nutritional value of grains by biological activation 476

N 2

*Дімітар Дімітров, Тетяна Іончева,
Ваньо Хайгаров*

Вміст метанолу у виноградних і плодкових бренді: основний показник оригінальності та безпеки

Асліхан Демірдовен, Танер Байсал
Інактивувальний ефект мікрохвильового нагрівання на пектинметилестеразу в апельсиновому соці

*Людмила Віннікова, Андрій Кишеня,
Ірина Страшнова*

Композиції лактобактерій для застосування в м'ясопереробній промисловості

*Інна Пилипенко, Людмила Пилипенко,
Олена Севастьянова, Євгеній Котляр,
Руслана Кручек*

Епіфітні і регламентовані мікробні контамінанти харчової рослинної сировини і продуктів

Валерій Манк, Тетяна Полонська
Застосування природних олій в якості біологічно активних інгредієнтів косметичних засобів

*Олександр Рожно, Олена Подобій,
Віра Юрчак*

Дослідження реологічних властивостей розчинів желатину для виробництва безглютенових макаронних виробів

N 3

Юрій Посудін

Спектроскопічний аналіз меду 437
*Тамара Носенко, Валерій Манк,
Ярослава Жукова, Альона Черства*
Склад і властивості частково гідролізованих соняшникових білкових ізолятів

Олусагун А. Олаойе
Дослідження органолептичних властивостей смаженого м'яса, засіяного закваскою культури *Pediococcus acidilactici* FLE07, і летких з'єднань, які впливають на його якість

Світлана Бажай-Жежерун, Тетяна Романовська, Марія Антонюк

Підвищення харчової цінності зерна шляхом біологічного активування

- Ana Kalušević, Ana Salević, Radovan Đorđević, Mile Veljović, Viktor Nedović*
Raspberry and blackberry pomaces as potential sources of bioactive compounds 485
- Teodora Atanasova, Miroslava Kakalova, Lyubomir Stefanof, Maya Petkova, Albena Stoyanova, Stanka Damyanova, Mykola Desyk*
Chemical composition of essential oil from *Rosa Damascena* mill., growing in new region of Bulgaria 492
- Olga Rybak*
Milk fat in structure formation of dairy products: a review 499
- Nadezhda Zhilinskaia, Julia Bazarnova, Aleksandr Shleikin, Liudmyla Peshuk, Oleg Galenko*
Using of bioinformatics and computer morphometry in study of *Fusarium* spp. causing potato dry rot. 515
- Olivier Hirwa, Innocent Nyagahungu, Clement Bitwayiki*
Ethanol production from mucilage and pulp of processed coffee 523
- Nina Raichuk, Olena Podobiy*
Technology features of using gums in a creation of gel bases. 531
- Nilgün Öncül, Şeniz Karabıyıklı*
Mechanism of antibacterial effect of plant based antimicrobials 541
- Issue 4**
- Valerii Sukmanov, Andrii Marynin, Halyna Dubova, Anatolii Bezusov, Valentina Voskoboinik*
Study of aroma formation from lipids of the fruit raw material 629
- Eugenia Boaghi*
Impact of treatment with oxidative bleaching agents on walnut (*Juglans Regia* L.) shell chromatic parameters 644
- Galina Selyutina, Oksana Gapontseva*
Component composition of radish root essential oil 653
- Ана Калушевич, Ана Салевич, Радован Джорджевич, Міле Велйович, Віктор Недович*
Малинові і ожинові вичавки як потенційне джерело біологічно активних речовин
- Теодора Атанасова, Мирослава Какалова, Любомир Стефанов, Мая Петкова, Албена Стоянова, Станка Дамьянова, Микола Десик*
Хімічний склад ефірної олії з дамаської троянди (*Rosa Damascena* Mill.), вирощеної в нових регіонах Болгарії
- Ольга Рыбак*
Молочний жир у формуванні структури молочних продуктів
- Надежда Жилінская, Юлія Базарнова, Александр Шлейкін, Людмила Пешук, Олег Галенко*
Використання біоінформаційного аналізу і комп'ютерної морфометрії для вивчення *Fusarium* spp, які викликають суху картопляну гниль
- Олів'єр Хірва, Інносент Хягахунгу, Клемент Бітванскі*
Виробництво етанолу з продуктів переробки кавових плодів
- Ніна Райчук, Олена Подобій*
Особливості технології застосування камедей для створення гелевих основ
- Нілгюн Онкюл, Шеніз Карабійіклі*
Механізм антимікробної дії рослинних антибактеріальних препаратів
- N 4**
- Валерій Сукманов, Андрій Маринін, Галина Дубова, Анатолій Безусов, Валентина Воскобойник*
Дослідження процесу утворення аромату з ліпідів плодової сировини
- Євгенія Боагі*
Вплив обробки окисними вибілювальними речовинами на колірні параметри шкаралупи волоського горіха (*JuglansRegia* L.)
- Галина Селютіна, Оксана Гапонцева*
Компонентний склад ефірної олії коренеплоду редьки

- Habibeh Azizi, Vahid Hakimzadeh, Hossein Alizadeh Golestani*
Purification of Raw Sugar Beet Juice by Electrocoagulation
Viktoria Ostapenko
Analysis on application of different grape varieties in the production of icewine.
A review
667
- Stanka Damyanova, Silvia Mollova, Albena Stoyanova, Oleksii Gubenia*
Chemical composition of *Salvia officinalis* L. essential oil from Bulgaria
Tijani Akeem Olumide, Bakare Henry Adegoke, Oke Emmanuel Kehinde, Oyedeji Ajibola Bamikole
Effect of processing parameters on the proximate composition and sensory characteristics of breadfruit “Elubo”
678
- Andgela Dyakonova, Victoria Stepanova*
Usage of the nut raw materials and chia seeds to improve fatty acid composition of the smoothies
701
- Anatolii Ukrainets, Vasyl Pasichniy, Maksym Polumbryk, Maniefa Polumbryk*
Effect of collagen based protein isolate «Belkozine» on biological value of boiled sausages
713
- Valerii Mank, Oksana Tochkova, Oksana Melnyk, Oleksandr Bessarab*
Relaxation behavior of aqueous dispersion polysaccharides.
724
- Biotechnology, microbiology**
Issue 1
- Nilgün Öncül, Şeniz Karabiyikli*
Persistence and survival of some food borne pathogens in neutralized unripe grape products
96
- Olusegun A. Olaoye, Abiodun A. Onilude, Stella C. Ubbor, Anna N. Agiriga*
Microbiological quality during storage of pork balangu inoculated with nisin producing *Lactococcus lactis* subsp. *lactis*
109
- Anatolii Ukrainets, Vasyl Pasichniy, Yulia Zheludenko, Svitlana Zadkova*
Oleoresins effect on cooked poultry sausages microbiological stability
124
- Хабібех Азізі, Вахід Хакімзадех, Хоссеїн Алізадех Голестані*
Очищення соку з цукрових буряків електрокоагуляцією
Вікторія Остапенко
Аналіз вибору сортів винограду для технології крижаних вин
- Станка Дамянова, Сільвія Моллова, Албена Стоянова, Олексій Губеня*
Хімічний склад ефірної олії шальвії (*Salvia officinalis* L.) з Болгарії
Тіяні Акім Олуміде, Бакарє Генрі Адегоке, Оке Еммануел Кехінде, Ойедейі Аїбола Баміколе
Вплив параметрів переробки на склад і сенсорні характеристики хлібного дерева «Елубо»
Анджела Д'яконова, Вікторія Степанова
Використання горіхової сировини і насіння чіа для покращення жирнокислотного складу напоїв смузі
Анатолій Українець, Василь Пасічний, Максим Полумбрик, Манефа Полумбрик
Вплив колагенового білка «Білкозин» на біологічну цінність варених ковбас
- Валерій Манк, Оксана Точкова, Оксана Мельник, Олександр Бессараб*
Релаксаційна поведінка водних дисперсій крохмалю
- Біотехнологія, мікробіологія**
N 1
- Nilgun Öncül, Şeniz Karabiyikli*
Ніглум Онкул, Шеніз Карабійіклі
Стабільність і виживання деяких харчових патогенів в нейтралізованих незрілих виноградних продуктах
Олусегун А. Олаойе, Абіодун А. Онілуде, Стелла С. Уббор, Анна Н. Агіріга
Мікробіологічна якість під час зберігання страви балангу зі свинини, щепленої *Lactococcus lactis* subsp. *lactis*
Анатолій Українець, Василь Пасічний, Юлія Желуденко, Світлана Задкова
Вплив олеорезинів на мікробіологічну стабільність варених сосисок з м'яса птиці

Issue 2

Demet Kocatepe, Gökay Taşkaya, Hülya Turan, Yalçın Kaya

Microbiological investigation of wild, cultivated mussels (*Mytilus galloprovincialis* L. 1819) and stuffed mussels in Sinop–Turkey.

Izzet Turker, Gokhan Domurcuk, Mehmet Tokatli, Hilal Isleroglu1, Banu Koc

Enhancement of microbial transglutaminase production from *Streptomyces* sp.

Lubov Musiy, Orysia Tsisaryk, Iryna Slyvka, Oleg Galenko

The influence of technological parameters of creams fermentation on formation of functional peculiarities of cultured butter

Processes and equipment of food productions

Issue 1

Mariia Shynkaryk, Oleh Kravets

Mathematical modelling of the separation of suspension process on the filter with self-purifier filter element

Yaroslav Kornienko, Serhiy Hayday, Andrii Liubeka, Oleksandr Martynyuk

Kinetic laws of the process of obtaining complex humic-organic-mineral fertilizers in the fluidized bed granulator

Natalia Tkachuk, Oleksandr Shevchenko

Effects of osmotic pressure environments lethal effects on the level of microorganisms in the conditions of evacuation

Valentyn Petrenko, Mykola Pryadko, Yaroslav Zasyadko, Mariya Miroshnyk

Modeling of heat transfer in free down flowing laminar liquid films with development wavy structure at the regime of evaporation from the interface

Issue 2

Taras Pogorilyy

Non-stationary sucrose diffusion mass flow calculation for sucrose solution cells from the «larger sugar crystal–larger sugar crystal sucrose solution–less sugar crystal sucrose solution–smaller sugar crystal–massecuite» system cells depending on the boiling sugar massecuite time.

N 2

Демет Косатеє, Гьокай Ташкає, Хуля Туран, Ялчин Кая

Мікробіологічне дослідження диких, культивованих (*Mytilus galloprovincialis* L. 1819) і фаршированих мідій

Іззет Туркер, Гокан Домурджук, Мехмет Токатлі, Хіلال Іслероглу, Бану Кос

Оптимізація виробництва мікробної трансглутамінази із *Streptomyces* sp. *Любов Мусій, Оріяся Цісарик, Ірина Сливка, Олег Галенко*

Вплив технологічних параметрів ферментації вершків на формування функціональних властивостей кислотовершкового масла

Процеси та обладнання харчових виробництв

N 1

Марія Шинкарик, Олег Кравець

Математичне моделювання процесу розділення суспензії на фільтрі із самоочисним фільтрувальним елементом

Ярослав Корнієнко, Сергій Гайдай, Андрій Любека, Олександр Мартинюк

Кінетичні закономірності процесу гранулоутворення комплексних гуміново-органомінеральних добрив у грануляторі з псевдозрідженим шаром

Наталія Ткачук, Олександр Шевченко
Впливи осмотичних тисків середовищ на рівень летальних ефектів в умовах вакуумування

Валентин Петренко, Микола Прядко, Ярослав Засядько, Марія Мирошник

Моделювання теплообміну у вільно стікаючих ламінарних плівках з розвинутою хвильовою структурою в режимі випаровування з вільної поверхні

N 2

Тарас Погорілий

Розрахунок нестационарних дифузійних масових потоків сахарози для комірок міжкристалічних розчинів сахарози системи: «більший кристал цукру–розчин сахарози більшого кристалу–менший кристал цукру–розчин сахарози меншого кристалу–уфель» в залежності від часу уварювання цукрового утфелю

<i>Oleksandr Bessarab, Oleksandr Obodovich, Vitalii Sydorenko</i>	368	<i>Олександр Бессараб, Олександр Ободович, Віталій Сідоренко</i>	
Intensification of mass transfer processes in gas-liquid media by discrete – pulse energy input method		Інтенсифікація процесів масоперенесення в газово-рідких середовищах дискретним – імпульсним методом введення енергії.	
<i>Djamalutdin Chalaev, Nina Silnyagina, Oleksii Shmatok, Oleksandr Nedbailo</i>	376	<i>Джамалутдін Чалаєв, Ніна Сильнягіна, Олексій Шматок, Олександр Недбайло</i>	
Heat transfer enhancement in a corrugated tube heat exchanger		Підвищення ефективності теплопередачі в трубчастому теплообміннику з гофрованими трубами	
Issue 3		№ 3	
<i>Eduard Biletskyi, Olena Petrenko, Dmytro Semeniuk</i>	550	<i>Едуард Білецький, Олена Петренко, Дмитро Семенюк</i>	
Three-dimensional model of non-Newtonian fluid flow in the rectangular channel		Тривимірна модель течії неньютонівської рідини в прямокутному каналі	
<i>Igor Litovchenko</i>	560	<i>Ігор Литовченко</i>	
Modeling work furnace recirculating heating gases for tunnel baking ovens		Моделювання роботи топки з рециркуляцією гріючих газів для тунельної хлібопекарської печі	
Issue 4		№ 4	
<i>Yurii Zmievskii, Yuliia Dziačko, Valerii Myronchuk, Ludmyla Rozhdestvenska, Alexander Vilenskii, Ludmyla Kornienko</i>	739	<i>Юрій Змієвський, Юлія Дзяцько, Валерій Мирончук, Людмила Рождественська, Олександр Віленській, Людмила Корнієнко</i>	
Fouling of polymer and organic-inorganic membranes during filtration of corn distillery		Забруднення полімерних та органічно-неорганічних мембран при розділенні післяспиртової зернової барди	
<i>Nataliia Dunaievska, Mykola Chernyavskiy, Taras Shchudlo</i>	748	<i>Наталія Дунаєвська, Микола Чернявський, Тарас Щудло</i>	
Co-combustion of solid biomass in pulverized anthracite-coal firing boilers		Використання твердої біомаси в факельних котлах що спалюють антрацит	
<i>Pavlo Zasiadko, Mykola Priadko</i>	765	<i>Павло Засядько, Микола Прядко</i>	
Thermocouple errors in temperature measurements and validation of CFX and FLUENT models of natural gas combustion		Помилки прямих вимірювань температури термопарами та валідація CFX і FLUENT моделей спалювання природного газу	
<i>Yaroslav Korniyenko, Serhii Haidai, Andrii Liubek, Serhii Turko, Oleksandr Martynuk</i>	781	<i>Ярослав Корнієнко, Сергій Гайдай, Андрій Любека, Сергій Турко, Олександр Мартинюк</i>	
Modelling of pulsating mode of fluidization when obtaining organic-mineral fertilizers		Моделювання пульсаційного режиму псевдозрідження під час одержання органічно-мінеральних добрив	
Economics and Management		Економіка і управління	
Issue 1		№ 1	
<i>Alexandr Asmalovskij, Tomáš Sadílek</i>	186	<i>Александр Асталовській, Томаш Саділек</i>	
Food quality perception in the Czech Republic: trial study results		Сприйняття якості харчових продуктів в Чеській Республіці	

Issue 2
Oleksandr Yatsenko
Methodical bases of rating of investment appeal of Ukraine rural areas . 387

Issue 3
Jakia Sultana Jothi, M. Burhan Uddin
Are public perceptions precise towards the status of quality and safety of commercial brands of noodles? 568

Tomáš Sadílek
System of quality labels in the European Union 579

Food chemistry

Issue 2
Iliana Nikolova, Marin Marinov, Petja Marinova, Atanas Dimitrov, Neyko Stoyanov
Cu(II) complexes of 4- and 5- nitro-substituted heteroaryl cinnamoyl derivatives and determining their anticoagulant activity 326

Life safety
Issue 1
Olga Evtushenko, Alina Siryk, Petro Porodko
Development of the occupational safety in the food industry with regard for the risk-based approach 174

N 2
Олександр Яценко
Методичні засади рейтингової оцінки інвестиційної привабливості сільських регіонів України

N 3
Ждакія Султана Джутхі, М. Бурхан Уддін
Суспільне сприйняття рівня якості і безпечності комерційних брендів локшини
Томаш Саділек
Система якості маркувань харчових продуктів у Європейському Союзі

Харчова хімія

N 2
Ліана Ніколова, Марін Марінов, Петя Марінова, Атанас Дімітров, Нейко Стоянов
Комплекси 4- і 5-нітрозаміщених гетероарильних цинамоїлпохідних з Cu(II) і визначення їхньої антикоагулянтної активності

Безпека життєдіяльності

N 1
Ольга Євтушенко, Алина Сірик, Петро Породько
Підвищення рівня безпеки праці в харчовій промисловості з урахуванням ризико-орієнтованого підходу

Наукове видання

Ukrainian Food Journal

**Volume 5, Issue 4
2016**

**Том 5, № 4
2016**

Підп. до друку 27.12.2017 р. Формат 70x100/16.
Обл.-вид. арк. 15.20. Ум. друк. арк. 15.05.
Гарнітура Times New Roman. Друк офсетний.
Наклад 100 прим. Вид. № 11н/16.

НУХТ. 01601 Київ–33, вул. Володимирська, 68

Свідоцтво про державну реєстрацію
друкованого засобу масової інформації
КВ 18964–7754Р
видане 26 березня 2012 року.