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10.2	FRI–LCR-1-BFT(R) SAT–LB-P-2-BFT(R)	Biotechnologies and Food Technologies
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BIOTECHNOLOGIES AND FOOD TECHNOLOGIES

Content

FRI–LCR-1- BFT(R)-03

SENSORY EVALUATION AND RHEOLOGICAL BEHAVOIR OF YOGURTS PREPARED FROM GOAT MILK[1]

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***Abstract**: Goat milk production is a dynamic and growing industry that is fundamental to the wellbeing of hundreds of millions of people worldwide and is an important part of the economy in many countries. The aim of the present paper is scientific development of new technologies for goat milk yogurt with improved sensory and rheological properties. Set-yoghurts produced from goat and cow milk were examined fresh and after cold storage for sensory quality and rheological properties, in accordance with the ISO (Official Methods of Analysis of AOAC International). Rheological investigations consisted of the determination of apparent viscosity and drawings of flow curves. In comparison to cow milk yoghurt, goat milk yoghurt had a better consistency, and was more acceptable sensorialy. The apparent viscosity of goat milk yoghurt was more and its flow curve was characterized by a smaller hysteresis loop area than these of yoghurts from cow milk. The reported results on sensory evaluation and rheological behavoir of goat milk yoghurt could guide industry to develop new goat dairy products with improved quality.*

***Keywords:** sensory attributes, rheology, goat milk, youghurt, health benefits.*

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SAT–LB-P-2-BFT(R)-01

INFLUENCE OF SPIRULINA AND KELP ALGAE ON THE DEGREE OF INCREASE IN DOUGH VOLUME

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Abstract: *Bread is a product of high consumption in Bulgaria. Various additives are used to improve bread quality, and in recent years addition of seaweed is a common practice. Most authors pay attention to the nutritional value of algae-enriched bread. There are not many studies revealing algae influence on the properties of semi-finished products (and in particular, the yeast dough).*

The purpose of the present study is to investigate the influence of 4% Spirulina platensis and Kelp algae added to bread recipe on the degree of increase in yeast dough volume during the fermentation.

It was found that both the duration of the fermentation and sample composition influence the dough volume. After 3 hours of fermentation, an increase in the volume was observed in the control sample - 3.0 times, in the Kelp-enriched dough - 3.4 times. Tthe most significant being the increase in the Spirulina plantesis-enriched sample - 3.6 times. At 4 hours duration of the fermentation, in all the samples tested volumes decreased, the most pronounced in Spirulina plantesis enriched sample - 0.7 times, and the least significant in the sample with Kelp - 0.2 times. However, the volume of the enriched samples remains higher than that of the control sample.

Keywords: *Kelp, Spirulina platensis, algae, bread, dough volume*

ВЪВЕДЕНИЕ

Хлябът е продукт със сравнително висока и постоянна консумация както в България, така и в други страни по света. На съвременния етап основна цел при неговото производство е повишаване на хранителната ценност и подобряване на качеството му. Широко застъпена практика в много страни в света е това да се постига посредством обогатяването на хляба с морски водорасли.

Големият интерес към хранителните продукти, обогатени с водорасли, личи от многобройните публикации на редица автори (Cornish, M. & Garbary, D. (2010), Harnedy, P. & FitzGerald, R. (2011), Holdt, S. & Kraan, S. (2011), Hafting, J., Craigie, J., Stengel, D., Loureiro, R., Buschmann, H., Yarish, C., Edwards, M. & Critchley, A. (2015), Tiwari B, & Troy, D. (2015), Fleurence, J. & Levine, I. (2016)).

Menezes и съавтори (2015) изследват влиянието на зелени водорсли *Cladophora spp*. и *Ulva spp*. (добавени в количество 2,5; 5,0 и 7,5% спрямо масата на брашното) върху хранителната ценност и калорийната стойност на пшеничен хляб. Те установяват, че добавянето на макроалгална биомаса води до увеличаване на съдържанието на протеини до количество 16 - 18% и на фибри от 1 до 2% .

Burcu A. и колектив (2016) си поставят за цел да повишат хранителната ценност на хляба, приготвен от бяло брашно, като използват ценните компоненти, които съдържат водораслите *Spirulina platensis*. В проучването си към брашното за приготвяне на пшеничен хляб те добавят 10% *Spirulina platensis*. Резултатите от проведеното изследване сочат, че добавянето на водораслите води до повишаване на протеиновото съдържание от 7.40% до

11.63%. Освен това авторите изтъкват, че обогатяването на хляба със *S. platensis* води до повишаване на количествата на калций, магнезий и желязо съответно до 721.2; 336.6 и 41.12 ppm в сравнение с контролната проба хляб, който съдържа 261.7 ppm калций, 196 ppm магнезий и 8.72 ppm желязо.

В свое изследване García-Casal и съавтори (2009) обогатяват пшеничен хляб с кафяви, зелени и червени водорасли, съответно *Sargassum, Ulva* и *Porphyra*. Те стигат до извода, че най-ефективни за повишаване на антиоксидантната активност, съдържанието на полифеноли и желязо в хляба са кафявите водорасли.

Според Podkorytova (2004) и Sukhoveeva (2006) червените водорасли също са ценен ресурс, който може да намери приложение в хлебопроизводството, тъй като са много богати на витамини от В-комплекса и на полиненаситени мастни киселини – арахидонова и ейкозапентаенова.

Установено е (Velasco-González, 2013), че добавянето на 2% водорасли *Sargassum* в прахообразна форма към брашното води до увеличаване добива на мокър глутен и може да бъде използвано за подобряване на хлебопекарните свойства на слаби брашна.

От така представения обзор става ясно, че повечето автори насочват вниманието си към възможността за повишаване на хранителната и биологична ценност на хляба посредством добавка на водорасли. Не са много изследванията, разкриващи влиянието им върху свойствата на тестените полуфабрикати (и в частност – на маяното тесто при двуфазен метод на приготвяне на хляба). Увеличаването на обема на тестото е в пряка зависимост от газообразуващата и газозадържащата му способност. Отделеният по време на алкохолната ферментация въглероден диоксид предизвиква разпъване на глутеновите ципи и това води до увеличаване на обема на ферментиращото тесто. При увеличението на обема допълнителното опъване на протеиновите ципи се отразява положително върху структурата на тестото и шупливостта на готовия продукт - хляба. Ето защо е налице връзка между степента на увеличение на обема на тестото по време на ферментация и качеството на хляба.

Целта на настоящата разработка е да се проучи влиянието на водорасли *Spirulina platensis* и *Kelp,* добавени в количество 4% спрямо масата на брашното, върху степента на увеличение на обема на маяното тесто по време на ферментация.

МАТЕРИАЛИ И МЕТОДИ

Опитен материал

За целите на експерименталните изследвания тестото се замесва от пшенично брашно тип 500, което се характеризира със следните стойности по по–важните качествени показатели: влага – 12,81%; съдържание на мокър глутен – 27,07%; отпускане на глутена – 6 mm; титруема киселинност - 2°H; диастатична активност – 282 mg малтоза; водопоглъщаемост – 58 cm^3/100 g брашно.

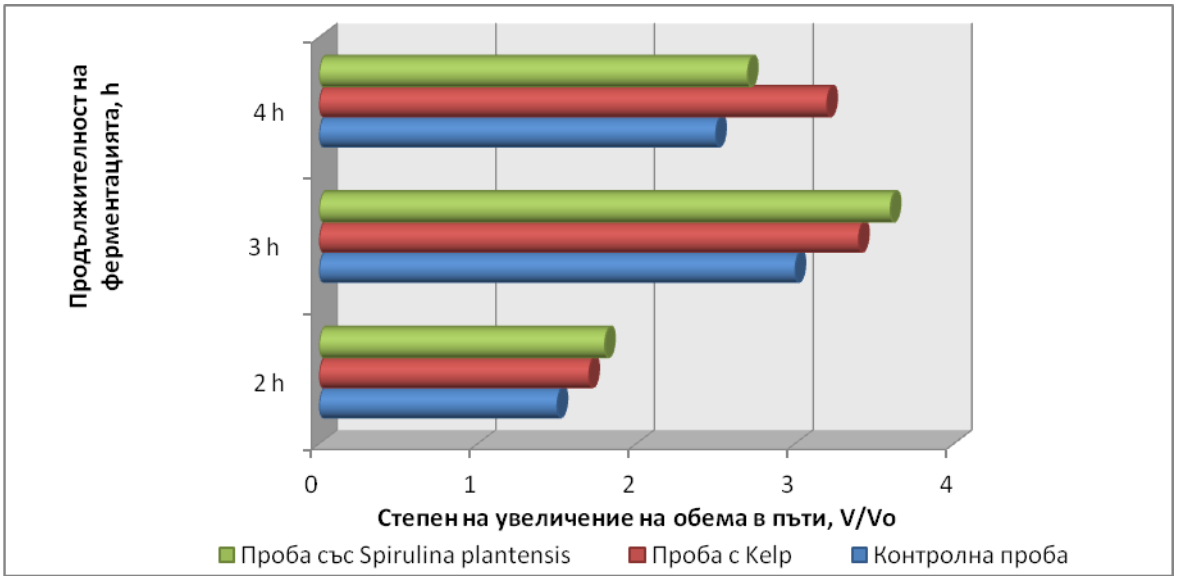
Пробите маяно тесто се приготвят при съотношение на брашно и вода 1:1. За замесване на пробите се използва питейна вода, загрята до температура 32 °C. Към така приготвената смес се добавя определено количество пресувана мая (900 g на 100 kg брашно). Ферментацията протича при температура 32°C за време 4 часа. За целите на настоящата разработка са приготвени и изследвани проби маяно тесто, както следва: контролна проба – приготвена само от брашно тип 500, вода и пресувана мая; а също и обогатени проби, в състава на които освен посочените суровини, са включени съотвтно зелени микроводорасли *Spirulina plantesis* и кафяви макроводорасли *Kelp* в количество 4% спрямо масата на брашното.

Метод

Степента на увеличение на обема на маяното тесто се определя като отношение между обема на тестото след ферментация (V) и обема му преди ферментация (Vo). За целта ферментацията на тестото се провежда в градуиран съд (Vangelov, A., 1993). Проследяват се промените, които настъпват в степента на увличениет на обема маяното тесто при продължителност на ферментацията 2, 3 и 4 h.

ИЗЛОЖЕНИЕ

Резултатите, получени при изследване на степента на увеличение на обема на маяното тесто, са представени на фиг. 1.



Фиг. 1. Степен на увеличение на обема на маяното тесто по време на ферментация при използването на добавки от водорасли *Spirulina platensis* и *Kelp*

Установи се, че върху обема на пробите оказва влияние както продължителността на ферментацията, така и състава им. След хомогенизиране на суровините всички проби тесто имат еднакъв обем – 250 cm^3. При контролната проба, приготвена без добавка на водорасли (само с мая), след ферментация в продължение на 2 h тестото увеличава обема си 1,5 пъти. При 3 и 4-часова ферментация тези стойности са съответно 3,0 и 2,5 пъти. При всички изследвани проби най-значително увеличение на обема се установява на третия час на ферментацията - през този период се извършва активно пъпкуване на дрождевите клетки, свързано с активен дихателен процес. С по-нататъшното увеличаване на продължителността на ферментацията обемът на тестото постепенно намалява. До голяма степен газообразуването в тестото и интензивността на протичане на ферментацията зависят от диастатичната активност на брашното. Наличието на активна амилаза е необходимо условие за перманентното образуване на ферментиращи захари в тестото, т. к. собствените захари в брашното (0,6 – 1,8% на с.в.) осигуряват едва около 30% от газообразуването. Диастатичната активност на използваното брашно е в нормални граници – 282 mg малтоза/10 g брашно. Това говори за наличието на достатъчно активни амилолитични ензими в тестото. Те осигуряват постепенно разграждане на нишестето до малтоза, която в последствие под действие на малтазата се разгражда до глюкоза, която дрождите ферментират до етилов алкохол и въглероден диоксид и по този начин се увеличава обема на тестото по време на ферментация.

Включването на водорасли в рецептурата на маяното тесто подобрява газообразуващата и газозадържащата му способност. Указание за това е по-високата степен, в която се увеличава обемът на обогатените проби в сравнение с контролната.

Когато към суровините по рецептурата допълнително се прибавят определените количества водорасли *Spirulina plantesis* и *Kelp* в прахообразна форма се наблюдава по-интензивно газообразуване. При обогатените проби се отчита и по-добра газозадържаща способност. След двучасова ферментация получените стойности са близки, но все пак по-високи в сравнение с тези при контролната проба.

При по-голяма продължителност на ферментацията (3 часа) обемът на обогатните проби се увеличава осезаемо. Най-голям ръст се отбелязва при обогатената със *Spirulina plantesis* проба маяно тесто – 3,6 пъти, докато пробата, обогатена с *Kelp*, увеличава обема си 3,4 пъти. Получените резултати се обясняват с факта, че аквакултурите съдържат ценни биологично активни вещества - витамини, минерали и свободни аминокиселини, които служат като хранителен субстрат за дрождите и това

поражда стимулиращ ефект по отношение на газообразуването. Експерименталните резултати свидетелстват и за заздравяване на глутеновия скелет, респективно – за по-продължително и по-добро задържане на отделения по време на ферментацията въглероден диоксид.

В края на съзряването на тестото (след 4 h) при всички изследвани проби се наблюдава намаление на обема. При пробата, обогатена с кафяви водорасли *Kelp* се наблюдва спад от 0,2 пъти, докато при тестото, приготвено със *Spirulina plantesis,* е налице спад с 0,9 пъти спрямо обема, отчетен при тричасова ферментация. Непрекъснатото образуване на въглероден диоксид във ферментиращото тесто постепенно повишава налягането в газовите мехурчета. Настъпва момент, когато това налягане превишава здравината на белтъчните ципи, газът започва да преминава през стените на шуплите и излита от тестото, в резултат на което обемът на тестото спада. Прави впечатление, че след двучасова и тричасова ферментация обемът на пробата със *Spirulina plantesis* е по-висок от този на тестото с добавка на водорасли *Kelp*, но при четиричасова продължителност на ферментацията тази тенденция не се проявява. Вероятно в случая това се дължи на заздравяване на глутеновите ципи, благодарение на факта, че кафявите водорасли съдържат вещества, които имат способността да модифицират реологичните свойства на продуктите и да формират устойчива пространствена структура.

Независимо от установения спад, обемът на обогатените проби остава по-висок от този на контролната проба при всяка една продължителност на ферментацията. Прави впечатлиние, че темпът на снижение на обема при различните проби е различен. При пробите, обогатени с *Spirulina plantesis,* той е по-ясно изразен. Според He и Hoseney (1992) увеличението на обема по време на ферментация зависи основно от това до каква степен изтъняват протеиновите ципи, преди да се скъсат.

ИЗВОДИ

Получените експериментални резултати показват, че влагането на добавка от водорасли *Spirulina plantesis* и *Kelp* в количество 4% спрямо масата на брашното при замесване на маяното тесто води до по-съществено увеличаване на обема на тестото по време на ферментация. След 3 h ферментация при всички проби се наблюдава увеличение на обема: при контролната проба – 3,0 пъти, при тестото, обогатено с *Kelp* – 3,4 пъти, а най-значително е увеличението при пробата, обогатена със *Spirulina plantesis* – 3,6 пъти. С увеличаване на продължителността на ферментацията до 4 часа, при всички изследвани проби се отчта спад на обема, като най-ясно изразен е той при пробата със *Spirulina plantesis* – 0,7 пъти, а най-незначителен при пробата с водорасли *Kelp* – 0,2 пъти. Независимо от това, обемът на обогатените проби остава по-висок от този на контролната проба. Това от своя страна говори за по-интензивно протичане на ферментацията и за образуване на по-големи количества въглероден диоксид в обогатените проби. Като се има предвид, че допълнителното опъване на протеиновите ципи на тестото по време на ферментация се отразява благоприятно върху структурните свойства и шупливостта на хлебната средина, може да се обобщи, че посредством включването на водорасли *Spirulina plantesis* и *Kelp* в рецептурата се постига подобряване на качеството на хляба.

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SAT–LB-P-2-BFT(R)-02

ENVIRONMENTAL IMPACT ASSESSMENTS OF CO_2 EMISSIONS OF POLLUTANTS PRODUCED USING DIFFERENT TRANSPORTATION FLEETS FOR "GREEN" DAIRY SUPPLY CHAIN DESIGN

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Abstract: *This study represents a continuation of the optimization approach for short-term design of "green" products portfolio of three echelon "green" supply chain (GSC) of the production complex from the dairy industry. The approach takes into consideration three main subjects - products manufacturing, SC management and environmental impact. The latter involves environmental impact assessments of wastes produced along the chain and released in air and water. They are evaluated in terms of costs such as the best trade-off between environmental and economic performance of the designed green products portfolio to be achieved. The approach is extended by including additional environmental impact assessments for the CO_2 emissions produced during transportation of raw material and products when fleets with different payload capacity and fuel engines are used. The latter aims to show how this factor influences designing the optimal environmental dairy products portfolio and they can be used in the decision-making process.*

Key words: *GSC management, Products' portfolio design, Environmental impact assessments, CO_2 emissions, Transportation fleets, Optimization*

INTRODUCTION

The production of milk and dairy products occupies a significant share of the European Union's economy (European Commission, 2016). However, their realization is related to the release of significant quantities of pollutants into the environment. One of the most effective ways to increase their sustainability is by applying the Life Cycle Analysis principles in the optimal design of so called "green" supply chains. It includes optimization of all activities along the chains from the supply of raw materials through the products production to the end users and the transport of raw materials and products, while meeting the environmental (Djekic, I. et al., 2014; Sharma, V., et al., 2015; Palmieri, et al., 2017) and/or economic (Jouzdani et al., 2013; Glover et al., 2014; Chen et al., 2014) requirements. However, the most of developed approaches consider different aspects of dairy GSCs in terms of environmental impact and economic performance where some level of trade-off is satisfied and they are focused on the impact only of the CO_2 emissions produced during transportation (Validi, S., et al., 2014).

Recently, Kirilova and Vaklieva-Bancheva, (2017) have developed an optimization approach for production portfolio design of a GSC for curd production. It involves a broader objective function including, along with environmental impact assessments of CO_2 impact associated to the

energy consumed and generated during transportation, and assessments for each production task accounting for associated wastewater (including these from the used raw material). The optimization criterion is defined in terms of money such as to find the best tradeoff between the total profit of the dairy complex and the costs incurred for the environmental impact due to its operation.

The aim of the present study is an extention of the approach of Kirilova and Vaklieva-Bancheva, (2017) by including additional environmental impact assessments for the CO_2 emissions produced during transportation of raw material and products when fleets with different payload capacity and fuel engines are used. The latter aims to show how this factor influences designing the optimal environmental dairy products portfolio and they can be used in the decision-making process.

EXPOSITION

1. General formulation of the optimization problem

The approach of Kirilova and Vaklieva-Bancheva, (2017) is outlined below. It has been developed to plan the activities in three eshelon SC including milk suppliers, dairies and markets to satisfy, in a short term, a certain consumer demand for a group of products. As a result of its implementation the optimal green production portfolio of the production complex, satisfying trade-off between environmental and economic objectives is found. The approach includes three interconnected models for: (i) description of the products production; (ii) SC design; and (iii) description of the SC environmental impact. The latter is assessed in terms of two areas:

1). Wastewater generated at each processing task of the dairy production, including these related to the raw material used;

2). CO_2 emissions related to: the energy consumption by the dairies and the transport of raw material and products between suppliers, dairies and markets.

➢ Needed data

In order to develop the mathematical models three groups of data should be known:

- *raw material and products data* - the composition of used raw material and target products.
- *SC data* – data for the production system; markets' demands; capacities of the milk suppliers; selling prices of milk and products; production costs, distances between milk suppliers, dairies and markets; transportation costs; fleets' capacities.
- *environmental impact data* - related to the environmental impact of pollutants obtained from the implementation of the SC activities with respect to two areas of impact - air and water. For assessments indicators as BOD_5 for the wastewater and CO_2 for the air emissions of pollutants are used.

➢ Control variables

- *Binary variables* to structure SC;
- *Continuous variables* to transfer the raw material from suppliers to the dairies and products form the dairies to the markets.
- *Continuous variables* for key compound concentration in the used raw materials.

➢ Mathematical models

***SC* mathematical description**

- *Material balance equations for the subsystems suppliers-dairies and dairies-markets* – they prevent from accumulation of raw materials in the suppliers and products in the dairies;
- *Equations for determination of the quantities of raw materials* required from each dairy to produce the planned quantities of products.

Dairy production modeling

It includes dependencies for the composition of used raw materials and products, as well as an equation for the target product yield as a function of the composition of the key compound. The model also provides a connection between the production tasks using size factors calculated.

Environmental impact modeling

The environmental impact model includes dependencies for the two type of pollutants:

- BOD_5 associated with wastewater produced during realization of the production tasks and pre-processing of used raw materials. It depends on concentration of the key compound of the raw materials used.
- CO_2 related to the energy consumed during the dairy production for the raw materials processing.
- CO_2 associated with the fuel combustion during the transport of raw materials and products. It depends on the payload capacity and the type of the used fleets as well as the distances in km.

CO_2 emitted from the fleets to transport 1 kg standardized whole milk and 1 kg curd/km is:

$$TMCO_2 = 2 \cdot \frac{TCO_2}{VCm}, \quad \left[\frac{\text{kg CO}_2}{\text{km.kg milk}} \right] \quad TPCO_2 = 2 \frac{TCO_2}{VCp}, \quad \left[\frac{\text{kg CO}_2}{\text{km.kg curd}} \right] \qquad (1)$$

where TCO_2 is the amount of CO_2 emissions produced by fuel combustion, [kg CO_2/ km]. $TMCO_2$ and $TPCO_2$ easy can be calculated based on data about the energy content of 1 liter fuel [MWh/l], the CO_2 emissions produced by fuel combustion [kg CO_2/MWh] and the fuel consumption [l/km], and the payload capacity of the fleet used - VCm [kg] and VCp [kg].

- **Constraints**

- for realization of the production portfolio in the time hosizon;
- for the capacity of suppliers of raw materials;
- for the capacity of the markets for realization of planned quantities of products;
- for the environmental impact costs that have to be paid for treatment of the pollutants.

- **Optimization criteria**

A single-objective optimization criterion is used F_{Profit}, [BGN]. It represents the difference between the production profit and all costs including the environmental ones, as follows:

$$F_{Profit} = F_R - (F_{P\_Cost} + F_{M\_Cost} + F_{T\_Cost} + F_{BOD\_Cost} + F_{CO_2\_E\_Cost} + F_{CO_2\_T\_Cost}). \qquad (2)$$

where F_R is the revenue from the sale of the products at the markets; F_{P_Cost} is the total production costs for the dairy complex; F_{M_Cost} is the total costs incurred by the dairy complex for purchasing the necessary quantities of milk from suppliers for the products production; F_{T_Cost} is the total costs for the transportation of the milk and products between milk supply centers, dairies and markets; F_{BOD_Cost} is the total BOD_5 costs paid for treatment of the wastewater generated during production of the products; $F_{CO_2\_E\_Cost}$ is the total CO_2 emissions costs associated with the energy consumed by pasteurization process; $F_{CO_2\_T\_Cost}$ is the total CO_2 costs associated with emissions of pollutants generated during milk and product transportation.

The latter term of the optimization criterion (2) (the rest terms are given in detail in Kirilova and Vaklieva-Bancheva, 2017) is:

$$F_{CO_2\_T\_Cost} = \sum_{i=1}^{I} TCO_2 cost \cdot \left(TMCO_2 \cdot \sum_{s=1}^{S} Y_{i,s} \cdot SDis_{i,s} + TPCO_2 \cdot \sum_{p=1}^{P} \sum_{m=1}^{M} X_{i,p,m} \cdot MDis_{i,m} \right) \qquad (3)$$

where $TCO_2 cost$ is the cost for CO_2 due to the transportation of milk and products, [BGN/kg CO_2]. $SDis_{i,s}$, and $MDis_{i,m}$ are the distances between supply centers, dairies and markets, [km] $TMCO_2$ and $TPCO_2$ are calculated using Eq. (1). $i \in 1...I$, $s \in 1...S$, $p \in 1...P$, $m \in 1...M$ are data sets about the dairies, suppliers, products and markets.

A detailed description of the represenetd above optimization approach with the included models for: i) describing the products production; ii) planning the activities in SC; iii) describing the environmental impact of SC are given in detail in Kirilova and Vaklieva-Bancheva, (2017).

2. Case study

In order to found how the fleets used (with different payload capacity and fuel engines) influences the optimal environmental dairy products portfolio design, the represented above approach of Kirilova and Vaklieva-Bancheva, (2017) is implemented on a real case study comprising production complex for production of two types of curd in one technology over the time horizon of one month. SC includes two milk suppliers, two dairies for the products production and two markets for the realization of the produced products. All data needed for the optimal environmental dairy products portfolio design are given in detail in Kirilova and Vaklieva-Bancheva, (2017). Here, only data needed for determination of the environmental impact assessments for the CO_2 emissions produced during transportation of raw material and products using fleets with different payload capacity and fuel engines are given.

In Table 1, the distances between supply centers, dairies and markets are presented. In Table 2, data about the energy content of 1 liter fuel [MWh/l], the CO_2 emissions produced by fuel combustion [kg CO_2/MWh] and the fuel consumption [l/km], and the payload capacity of the fleets used - VCm [kg] and VCp [kg] are listed (https://autoline.info;http://1automarket.ru/en/; https://www.mercedes-benz.com/en/mercedes-benz/vehicles/trucks/fuel-comparison-tests-in-europe/; http://www.cngas.co.uk/cngvehicles.php).

The latter are needed for calculation of the CO_2 emissions generated during transportation of raw material and products $TMCO_2$ and $TPCO_2$, using different type of fleets.

Taking into account the data given in Table 1, Table 2 and data about the CO_2 cost due to transportation which is 1 BGN/kg CO_2, the environmental costs related with transportation of raw material and products using different type of fleets can be obtained.

Table 1. Distances between suppliers, dairies and markets in SC.

Distance, [km]				
	Supplier 1	Supplier 2	Market 1	Market 2
Dairy 1	41	36	226	92
Dairy 2	31	61	238	89

Table 2. Data about the fleets.

Type of fleet	Type of fuel	Payload capacity, [l] or [kg]	Energy of fuel combustion, [MWh/l]	CO_2 amount, [kg CO_2/MWh]	Fuel consumption, [l/100km] or [kWh/100km]
Milk tanker truck	Gasoline	2500	0.008056	249	32.2
	Diesel	2000	0.0095833	267	23
Refrigenerator truck	Diesel	4000	0.0095833	267	23
	Electro	3575	-	0.46	88
	LPG	1500	0.00702778	227	14
	Gasoline	1000	0.008056	249	11

RESULTS AND DISCUSSIONS

Eight optimization problems for all possible combinations of the fleets data used for transportation of raw material and products are formulated and solved using GAMS optimization software. The obtained results for the optimal green products portfolios are given in Table 3. One can see that Product 1 is only produced in the Dairy 1, while Product 2 is produced in both dairies. The latter is produced in 20 times greater quantity in Dairy 1 than in Dairy 2. Moreover, the two dairies supply the necessary quantities of raw material only from Supplier 2. Form the data listed in Table 3, it also can be seen that the optimal green products portfolios differ only in the values of the

provided by the suppliers' quantities of milk for Dairy 2 and the quantities of the Product 2 produced in the Dairy 2 respectively.

Table 3. Results for optimal production portfolios obtained at eight combination of fleets used for transport of raw material and products.

Optimal "green" product portfolio				**Optimal "green" product portfolio**			
Combination 1 *Milk tanker - diesel and refrigenerator truck - diesel (VCm=2000 l; VCp=4000 kg)*				***Combination 2*** *Milk tanker - diesel and refrigenerator truck - gasoline (VCm=2000 l; VCp=1000 kg)*			
Market 2		Supplier 2		Market 2		Supplier 2	
dairy1.product1	7704	dairy1	165881	dairy1.product1	7704	dairy1	165881
dairy1.product2	34591	dairy2	6568	dairy1.product2	34591	dairy2	861
dairy2.product2	1649			dairy2.product2	216		
Combination 3 *Milk tanker - diesel and refrigenerator truck -LPG (VCm=2000 l; VCp=1500 kg)*				***Combination 4*** *Milk tanker - diesel and refrigenerator truck - electro (VCm=2000 l; VCp=3575 kg)*			
Market 2		Supplier 2		Market 2		Supplier2	
dairy1.product1	7704	dairy1	165881	dairy1.product1	7704	dairy1	165881
dairy1.product2	34591	dairy2	6427	dairy1.product2	34591	dairy2	9326
dairy2.product2	1613			dairy2.product2	2341		
Combination 5 *Milk tanker - gasoline and refrigenerator truck - diesel (VCm=2500 l; VCp=4000 kg)*				***Combination 6*** *Milk tanker - gasoline and refrigenerator truck - gasoline (VCm=2500 l; VCp=1000 kg)*			
Market2		Supplier2		Market 2		Supplier 2	
dairy1.product1	7704	dairy1	165881	dairy1.product1	7704	dairy1	165881
dairy1.product2	34591	dairy2	11314	dairy1.product2	34591	dairy2	5200
dairy2.product2	2840			dairy2.product2	1305		
Combination 7 *Milk tanker - gasoline and refrigenerator truck - LPG (VCm=2500 l; VCp=1500 kg)*				***Combination 8*** *Milk tanker - gasoline and refrigenerator truck - electro (VCm=2500 l; VCp=3575 kg)*			
Market 2		Supplier 2		Market 2		Supplier 1	Supplier 2
dairy1.product1	7704	dairy1	165881	dairy1.product1	7704	dairy1	165881
dairy1.product2	34591	dairy2	11162	dairy1.product2	34591	dairy2 3175	11619
dairy2.product2	2802			dairy2.product2	3714		

In Fig. 1 all costs values, corresponding to the eights optimal green products portfolios are shown.

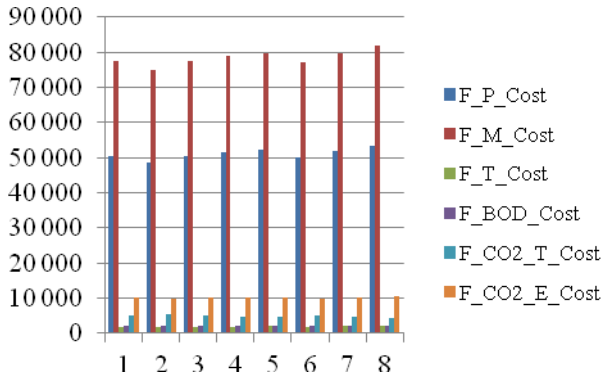

Fig.1. Costs values for the eight combinations of the fleets.

Fig. 1 shows that the costs of purchasing raw material and the production costs have the largest share in the total costs and the environmental costs and transport costs are significantly lower than the rest ones.

One can see in Fig. 2 that combinations 2 (milk tanker with diesel fuel and refrigenerator truck with gasoline fuel) results in the highest environmental costs, while combination 8 (milk tanker with gasoline fuel and refrigenerator truck with electro engine) corresponds to the lowest. The latter leads to the highest optimal green production portfolio, respectively (see Fig. 3).

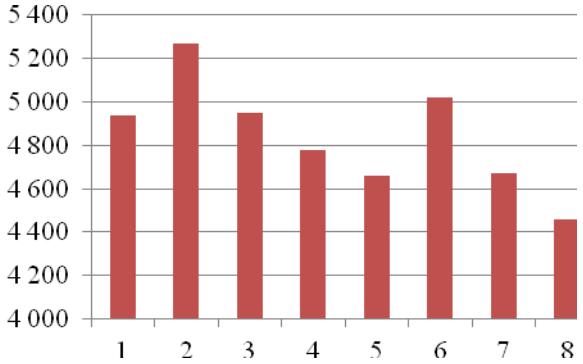

Fig. 2. Environmental transportation costs values for the eight combinations of the fleets.

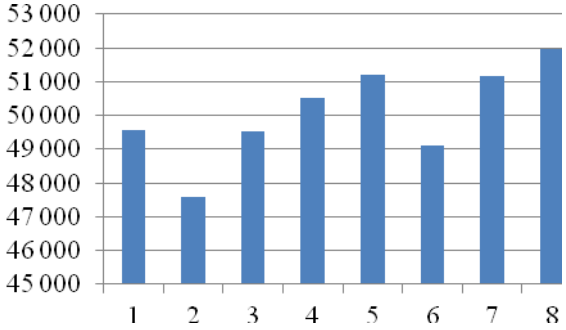

Fig. 3. Optimal "green" production profits for the eight combinations of the fleets.

CONCLUSIONS

The study represents an implementation of the approach of Kirilova and Vaklieva-Bancheva, (2017) for optimal green production portfolio design of dairy supply chain for eight combinations of fleets with different payload capacity and fuel engines. The obtained results have shown that the combination of milk tanker with diesel fuel and refrigenerator truck with gasoline fuel leads to the optimal green production portfolio with the greatest environmental impact.

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SAT–LB-P-2-BFT(R)-03

DETERMINATION OF RHEOLOGICAL PROPERTIES WITH FARINOGRAF And EXTENSIGRAF OF BIO-FORTIFIED FLOUR

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Abstract: *Rheological properties of dough are very important indices for product development in terms of product quality and process efficiency. There are several ways to evaluate the rheological behaviors of the dough, one of them is using farinographc and extensographic.The aim of this research was to examine the impact of agronomic bio-fortification on the rheological properties of flour obtained from wheat variety Radika. In this research are included 7 samples obtained by adding high quality chelate fertilizers at different stages of wheat growth: Fe soil (1), Fe soil + foliar (2), Fe foliar (3), Control (4), Zn soil (5) , Zn soil + foliar (6) and Zn foliar (7). From farinograph data for water absorption it is concluded that all variants have approximate values with minimal differences compared with variant 4. According to the data obtained for the level of softness, it is concluded that the dough for all variants are with medium quality. According to the qualitative number, all variants fall into the quality level B2, with exception of variant 5 which belongs to quality level C1. The results obtained from the extensigraf have shown that variant 1,2 and 7 has higher value of extensibility of the dough compared to variant 4, while variant 5,6 and 3 have lower values.The greatest resistance is measured in variant 2, and the lowest value for variant 5. Higher values were found in variants 1, 6 and 7, but variant 3 has a lower energy value compared to variant 4. Highest value the ratio (esistance / exstensibility) was measured in variant 1 and 3, and the lowest in variant 5. Higher values were found in variants 6 and 7 compared to variant 4. From the farinographc analysis it can be concluded that the application of iron and zinc chelating fertilizers did not have a significant effect on the technological quality of the flour. From extensographic analysis is ascertained influence from application of iron soil, iron soil + foliar and zinc foliar wherein for variants 1,2 and 7 are obtained flour with higher extensibility, resistance and energy.*

Keywords: *bio-fortification, rheological, farinograph and extensigraf*

INTRODUCTION

In recent years there have been significant changes in terms of the desire of food consumers to buy and consume healthier foods, higher quality foods, with lower prices and more exotic foods. Individual food producers must respond quickly to consumer demands in order to remain competitive in the food industry. The plant food provides a range of nutrients essential for human consumption, yet, in most parts of the world, the main raw materials derived from agricultural crops are often deficient in terms of some nutrients such as zinc and iron.

Biofortification is the process by which the concentration of micronutrients as zinc, iron, manganese, etc increases, in agricultural products, especially the cereals. The genetic biofortification uses specially grown cultures that will be able to accumulate (absorb) more zinc and other micronutrient elements from the soil in the nutrient parts of the grains (Ryan, E., 2010). Agronomic biofortification involves the use of fertilizers with higher concentrations of zinc and other micronutrients. It also provides a short-term and efficient approach that will provide an

increase in the concentration of Zn / Fe in the soil and wheat grains, using Zn / Fe fertilizer or NPK fertilizer enriched with Zn or Fe (Cakmak, I ., 2008).

However, accepting biofortificated crops on one hand from the consumers and on the other hand the producers in the milling and bakery industry is another issue that needs to be paid special attention. Taking into account that in the Republic of Macedonia no research was conducted in the field of biofortification, the purpose of this research is to investigate the influence of zinc and iron chelating fertilizers on the rheological properties of flour obtained from the wheat variety Radika.

MATERIAL AND METHODS

Material

Plant material

The variant of the type "Radika" soft wheat (*Triticum aestivum*), was used as a plant material in this research.

Location and setting experiment

On the lands belonging to the Agricultural Institute in Skopje (Macedonia), in the testing economy "Dolno Lisiche", during the production year 2012/2013, a test was placed according to the method of accidental bloc system, with 7 variants, three time repeated, while the testing parcel being of 30 m² size. The distance between the variants and the repeating procedures was 50 cm. The procession of the parcel was a standard one by bringing the plowed layer in condition of normal sowing. The sowing was conducted manually with 600-650 life-able grain/m².

Application of fertilizer

The following variants are included in the test of this research:

- Fe application in soil (variant 1)
- Fe application in soil and foliar (variant 2)
- Fe foliar application (variant 3)
- Control – without fertilizing (variant 4)
- Zn application in soil (variant 5)
- Zn application in soil and foliar (variant 6)
- Zn foliar application (variant 7)

Basic characteristics of the fertilizers

Yara Vera™ Amidas is a highly qualitative granular fertilizer which contains nitrogen and sulfur. The nitrogen is mostly available in the form of urea. The sulfur is available in the form of sulfate and is totally water-soluble. The ratio between the nitrogen and sulfur is from 7 towards 1.Nutrichem folifer-Fe EDTA chelate product, which is used for a foliar nutrition of the plants.Yara Vita Rexolin is a product for prevention of a shortage of zinc formulated in the form of EDTA chelate. Containing 15% and 148 grams of zinc per kilogram a product can be used for soil or foliar application.

Period of application of fertilizer

The nutrition of the wheat is conducted in the following stages of development:

1. Germination stage-fertilizing with NPK(9:15:15) 200 (kg/h) soil at the variants 1,2,3,4,5,6 and 7. Fe EDTA 10 (kg/h) soil apllication with the variants 1 and 2. Zn EDTA 20 (kg/h) soil apllication with the variants 5 and 6.

2.Tillering stage- applied Yara Vera Amidas 160 (kg/h) soil at the variants 1,2,3,4,5,6 and7.

3. Booting stage- Yara Vera Amidas 100 (kg/h) soil at the variants 1,2,3,4,5,6 and 7.

4. Booting stage- Fe EDTA 1 (kg/h) foliar at the variants 2 and 3. Zn EDTA 1kg/h(0.1%) foliar at the variants 6 and 7

5. Heading and flowering- Fe EDTA 1(kg/h) foliar at the variants 2 and 3.Zn EDTA 1kg/h(0.1%) foliar at the variants 6 and 7

6. Flowering Fe EDTA 1 (kg/h) foliar at the variants 2 and 3. Zn EDTA 1kg/h(0.1%) foliar at the variants 6 and 7

The foliar fertilizing was conducted by a dorsal sprinkler, with 3 liters of solution (mixture) with the variants 2 and 3 at the early morning hours.

Methods

The grinding of wheat from each variant is performed with a laboratory mill from the BRABENDER company.

Determination of the rheological properties of the biofortificated dough is carried out with the pharynograph and extensograph from the company BRABENDER.

-pharographic analysis with the method AACC 54-21 (American Association for Cereal Chemistry - AACC 1995) the following parameters were examined:

- water absorption%, degree of softening (Fj), quality number and quality group.

- Extensographic analysis with the method AACC 54-10 (American Association for of Cereal Chemistry - AACC 1995) and the measured parameters were:

extensibility (mm), resistance (Ej), relative number and energy (cm^2)

All parameters are measured after 45, 90 and 135 min of the rest time. Grinding and testing of the flour is carried out in the farinological laboratory of "Zito Luks AD" - Skopje.

RESULTS AND DISCUSSION

Farinological studies of the quality properties of flour

The physico-chemical properties of food (rheological properties, physical properties, stability, taste) determine the quality of food and are an important factor for the consumer when coosing the product. The most important factors are the production conditions and the raw materials used for production (Nakov, G., 2018).The quality of the flour is tested by physical and chemical methods. The physical characteristics of the dough have a major influence on the quality of ready-made bakery products. The determination of the quality of the flour with the farinograph is based on the registration of a change in the physical properties of the dough during a particular mixing time, which depends mainly on gluten. It is actually a dynamometer that measures the resistance of the dough that produces the dough on the mixer blades when it is absorbed in the container. From the obtained farinographic curved graphs for wheat flour, are obtained data related to the absorption capacity, the degree of softening the dough during the filling, and also the quality number and the quality group (Wheat and Flour Testing Methods, 2004).

Table 1. Determination of the physical properties of wheat flour with Farinograph

Farinograph data	1	2	3	4	5	6	7
Water absorption %	65.4	64.5	64.5	64.7	65	64.2	64.9
Level of softness (Fj)	80	100	95	110	115	90	95
Qualitative number	54.4	48.6	49.6	48.8	43.4	53.3	52
Qualitative level	B_2	B_2	B_2	B_2	C_1	B_2	B_2

An important technological feature for the baking industry is the degree of softening the dough, expressed in Farinoghraphic units (in Fj). If the degree of softening is greater, the flour, i.e. the dough is harder to tolerate fermentation and vice versa. It is considered that the 75 Fj softening grade flour is of good quality, from 75 to 125 Fj with medium and over 125 Fj of poor quality. The more value is lower, the dough has better quality.

The technological quality of the flour, based on farinograph is evaluated in three quality groups. To quality group A belong strong flours with optimal baking ability; to quality group B belong middle flours with good baking characteristics, while to quality group C belong weak flours, ie. with poorer quality and lower absorption power (Albrecht, T., 2010).

From the results obtained for water absorption it is concluded that all variant have approximate values with minimal differences with regard to variant 4. The degree of softening the dough for all varieties is within the limits of 80 to 115 Fj accordingly, and this dough belongs to the dough group with medium quality. As for the quality number variants 1, 2, 3, 4, 6 and 7, it belongs to the quality group B2, while the flour of variant 5 belongs to the quality group C1.

With the extensograph, are examined the physical properties of the dough and its reaction to resting and mechanical processing i.e. are measured the extensibility and the resistance. The obtained results complement the image of the flour quality obtained with the examination of the Farinograph (Žeželj, M., 2005; Kalugerski, G., 2006).

Table 2. Determination of the physical properties of wheat flour with an extensograph.

Extensigraf data	1	2	3	4	5	6	7
Extensibility (mm)	181	170	130	161	152	150	170
Resistance (Ej)	100	140	100	80	65	95	100
Value the ratio (esistance / exstensibility)	0.5	0.8	0.8	0.5	0.4	0.6	0.6
Energy (cm^2).	36	45	24	26	21	28	36

From the results presented in Table 2, it is noted that the varieties 1, 2 and 7 have higher spreadability of the dough compared to variant 4, while variant 5, 6 and 3 have lower values.

The highest resistance and energy were measured in variant 2, and the lowest value for variant 5. In the other variants, higher values were found in relation to variant 4, with the exception of variant 3 having a lower energy value compared to variant 4.

As for the ratio, the highest values were measured in variant 2 and 3, and the lowest in variant 5. For variants 6 and 7, higher values have been found, compared with variant 4.

CONCLUSION

Rheological methods are used to determine the technological quality of wheat and the quality of wheat flour, which is the basic raw material of the mill and bakery industry. The results of these tests have a direct relationship to the quality of the product.

On the basis of the obtained results of the research for determining the effects of agronomic bio-fortification, it can be concluded that the application of zinc and iron chelating fertilizers does not have a significant effect on the examined Farinographic parameters.

From extensographic analysis is ascertained influence from application of iron soil, iron soil + foliar and zinc foliar wherein for variants 1,2 and 7 are obtained flour with higher extensibility, resistance and energy.

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SYNTESIS OF MECHATRONIC FUNCTION MODULES DRIVES OF FLOW TECHNOLOGICAL LINES IN FOOD PRODUCTION

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Abstract: *The tasks were considered, which are related to the working bodies for the artificial food products movement according to the specified movement law and their positioning in the intermediate positions of the kinematic cycle. The actuators dynamics characteristics and control system of power part of positional electro-pneumatic actuators were researched. The methods of mathematical and computer modeling, and methods of solving ordinary differential equations and partial differential equations and method of correlation analysis were used. In the obtained results of modeling the kinematic load and the pressure of the working position pneumatic actuator, clearly observed that the inertial component increases in 4 stages (braking), during the narrowing the exhaust section of the working cylinder of the positional pneumatic actuator. The results of mathematical modeling for positional pneumatic actuators with the condition of changing the section of the exhaust hole allowed to track all the kinematic characteristics of the actuator. The obtained results allow to assign to the working body the law of motion, approximated to the optimal on the speed of action, not exceeding at the same time the maximum permissible dynamic influences for a moving artificial product.*

Keywords: *functional, module, packing, electro-pneumatic actuator, accuracy.*

INTRODUCTION

In recent years, a rather complicated process of optimal control of actuators of technological equipment for food production has been studied by many authors (Krivts I., Krejnin G., 2006). The authors took the various assumptions in order to simplify the mathematical description of the work of tracking and positional actuators (Janiszowski K., Kuczyński M. 2007). For a long time, this approach was justified, but over time, the productivity of mechatronic functional modules as part of technological equipment has increased significantly. In this connection, many control models of positional actuators with rational kinematic and dynamic parameters have become unacceptable for practical use (Virvalo T., 2016). Therefore, modulation of the moving process of artificial products by pusher on the basis of a position pneumatic actuator taking into account the real boundary conditions, as well as dynamic processes in the pneumocylinder, is relevant.

The main ways of packing artificial products in polymer films are revealed: the placement of the product in a pre-made package and fastening it with clips; the placement of the product in the sleeve, which is formed from roll packaging material; the placement of the product between two

films and the formation of a package with four seams; the wrapping of the product with a polymeric film (Gavva O., 2017).

The analysis of the existing equipment for the packaging of artificial and small artificial foods, showed the priority of using polymeric packaging materials for a number of economic, environmental and protective parameters (Richard E., Hurmuzlu Y., 2015). There are modules with linear displacement actuators in the composition of the collision mechanisms in the studied packaging machines (PMs), the most common mechatronic functional modules (MFMs) feeding the food product to the packaging area. The main ways of packing artificial products in polymer films are: placing the product in a pre-made package and fastening it with clips; placement of the product in the sleeve, formed from roll packaging material; placement of the product between two films and the formation of a package with four seams; wrapping the product with a polymeric film (Kinyckyi Y., 2008).

The tasks of the study

The tasks of the following studies are:

- the modeling of piston movement law of the pneumocylinder with an initial difference in air pressure, approximating to the optimal speed. In this case, the loads movement on the fixed flat is considered a collision mechanism with a positional pneumatic actuator.
- using the mathematical modeling to study the cases of smoothing the acceleration function at the moment of disengagement of the driving force, which allows to change smoothly the working parameters of the positional pneumatic actuator.
- the creation of the simulation model of the positional actuator, with taking into account the cases of functions smoothing of the of the analogue of speed and analogue of acceleration.
- the description of the method of choosing the initial movement stage (in the coordinate x), with taking into account the possible reduction of the actuating mechanism productivity.

EXPOSITION

Materials

The materials were chosen the positional actuators of packaging machines. The aim of the study was chosen the dynamics of electro-pneumatic positional actuators. The analysis of the working bodies motion laws of the initial kinematic link of the collision mechanisms was carried out for the technological schemes of the MFM movement of artificial products and the group (layer) of artificial products into the formed sleeve of the packaging material.

MFM formation characteristics of artificial products packaging

The operations of forming the artificial products packaging are connected to the work of the MFM elements according to the laws of motion, which determine the required productivity of the packaging machine. As an researched positional actuator, for the given layout of Fig. 1, MFM was chosen on the basis on pneumo actuator of positional type.

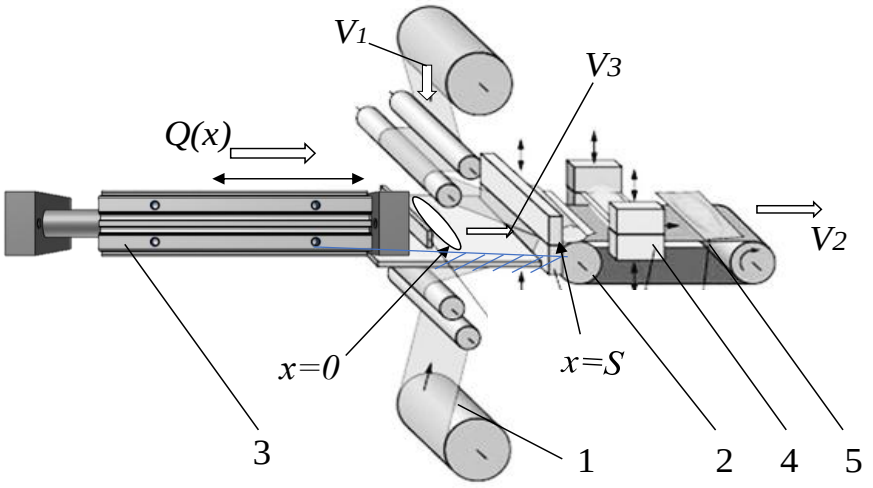

Fig. 1. General scheme of the technological module for the packaging of food products:

1—functional mechatronic module (FMM) supply of packaging material; 2 - functional device for formation of transverse joints and cutting off finished packages; 3 - FMM movement of products into the sleeve; 4 - FMM forming a longitudinal seam; 5 - FMM withdrawal of finished packages; x - coordinate of movement of a piston (m); V - speed of movement of a piston (m / s); Q(x) - acceleration of movement of the piston; P_1 - pressure in the piston chamber of the pneumocylinder (Pa); P_2 - pressure in the ventricular chamber of the pneumocylinder (Pa); t -time movement (sec).

Methods of mathematical and computer modeling, methods of solving ordinary differential equations and differential equations in partial derivatives were used to study the dynamics of compressed air in the cavities of the pneumocylinder. In the study of the layout of MFM packaging machines, the theory of automated control of electropneumatic position drives is used.

Thus the resultant of all resistance forces at I, II and III stages of the kinematic links movement:

$$P(x) = P_{pak} + \left(m_{pak} + m_n\right)\ddot{x} + m_{pak} gf + p_a\left(F_1 - F_2\right) \quad (1)$$

The resultant of all resistance forces at stage IV:

$$P(x) = P_{pak} + m_n\ddot{x} + p_a\left(F_1 - F_2\right) \quad (2)$$

m_{pak} - is the mass of the product; m_{pak} =0.5 kg; P_1, P_2 - is pressure of the piston and stomach cavity(Pa), $F_{1,2}$ - is square of the piston pneumocycline (m^2); f = 0.3 coefficient of friction; pa - atmospheric pressure; P_{pak} - is the dynamic load of the pneumocylinder(N); g=9.81 (m/sec^2) - free fall acceleration; m_n - is the mass of the piston.

Consider the law of movement of the leading link as a part of the mechatronic FD. It requires:

-to find the time T (on) of load movement in the optimal speed of the two-stage mode to set the required value of x (lk) of load movement at the first stage I in a four-stage mode;

-to determine the equations on the basis of the obtained value x(Ik), describing the kinematic parameters of the moving load at first stage in the four-stage mode, and also the final conditions for this stage;

-to consider the load movement as a three-stage and to determine the shutdown time of the driving force and the total time of movement. In this case, the final coordinates for the stages I and III of the three-stage mode of motion coincide with the final coordinates for stages I and IV of the four-stage mode of movement;

-to determine the equations describing the load movement at II and IV stages, and then at III stage for a four-stage mode of motion.

This sequence of tasks is connected with determining the initial and final coordinates of the load movement for each stage and with the searching for integration constants.

The time T_{on} of the load movement at optimal speed in two-step mode is determined by the method.

$$T_{on} = \sqrt{\frac{2S}{gf\left(1-\left(\mathrm{m_{pak}}\mathrm{g}\, f\,/\,\mathrm{Q}\right)\right)}} \quad (3)$$

where S is value of load movement (piston stroke); *f* is the coefficient of friction between the bearing surface of the load and the displacement flat.

Fig. 2 shows the graphs of the dependence of kinematic parameters from the time of movement of an artificial product in the implemented mode and the pressure change in the working cavities of the pneumocylinder (the power part of the position actuator).

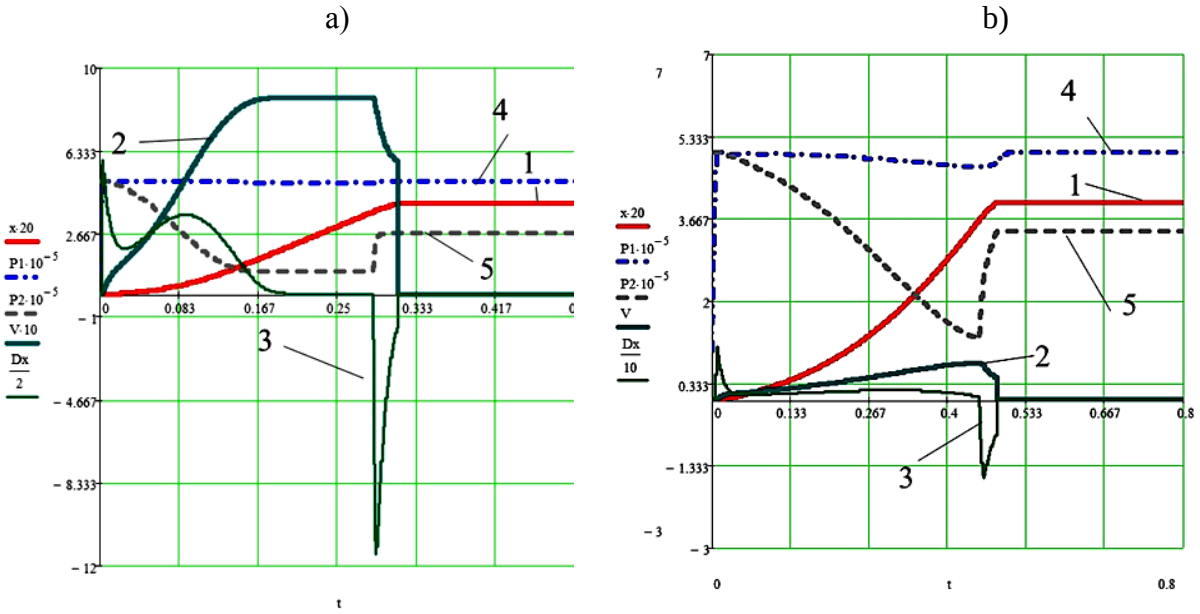

Fig. 2. Results of simulation of the kinematic load and pressure of the working position pneumatic drive with the power part: 1 - change of coordinate of movement; 2 - change of speed; 3 - change of acceleration; 4 - change in pressure in the piston chamber; 5 - change in pressure in the vent chamber of the pneumocylinder; diameter of the piston 25 mm; rod diameter 12 mm;

a) pipeline diameter 10 mm; effective cross-sectional area $f^{e}_{1}=7.854\times10\text{-}5\ m^2$;

b) pipeline diameter 6 mm; effective cross-sectional area $f^{e}_{1}=2.827\times10\text{-}5\ m^2$;

CONCLUSION

The output link movement of the experimental MFM, the pneumo-cylinder rod of the electro-pneumatic positional actuator are implemented and mathematically described. The conditions of the initial difference of air pressure are taken into account. The mathematical description of the rod movement law, which is optimal for the speed of action, is obtained. In the obtained results, it is clearly observed that when the exhaust section of the working cylinder of the positional pneumatic actuator is narrowed, the value of the inertial component at stage 4 (deceleration) increases. In addition, given the complexity of the working environment, - compressed air - it is necessary to apply the additional parameters: viscous friction coefficients of the working kinematic pair of piston-rod, resistance coefficients in the exhaust section in the implementation of the fourth stage of motion.

The movement of products on a fixed reference flat by a mechanism of collision with an electro-pneumatic positional pneumatic actuator with consideration of the control system is researched.

The proposed analytical dependences allow:

- to set the working body the law of translational motion, approximating to the optimal speed, without exceeding the maximum permissible dynamic load for the moving load;
- to move the artificial product from the initial position to the final in the shortest possible time for the pneumatic actuator;
- to analyze the existing structures of operating actuators with pneumatic actuators.

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QUALITY CHARACTERISTICS OF HONEY: A REVIEW

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Abstract: *Honey is a sweet natural product, which is produced by bees generally from the nectar of flowers and sweet deposits from plants. It is a complex mixture that contains nutrients and bioactive compounds such as carbohydrates (primarily fructose and glucose), enzymes, proteins, amino acids, organic acids, minerals, vitamins, aromatic substances, polyphenols, pigments, beeswax, and pollen that contribute to its color, smell and flavor. The composition and quality of honey is variable and it depends mainly on the botanical source of nectar from which it is obtained, but also depend on the geographic location, seasonal and climatic conditions, processing type and storage. Due to its special composition, honey is a functional food, which is consumed for its effects on human health, with antibacterial, antioxidant, anti-inflammatory and antimicrobial properties, as well as wound and sunburn healing effects. Honey is used in pure form after little or minimal processing as liquid, crystals or other types. The uses of honey as food include flavourant and sweetener in honey cookies, dairy products and fruit juices, as well as industrial production of beverages by mixing with alcohol. In this review, the physical properties and nutritive chemical composition thoroughly reviewed to underscore the quality of honey.*

Keywords: *Honey, Quality, Nutritive chemical composition, Physical properties.*

INTRODUCTION

Honey is one of the most widely sought products due to its unique properties, which are attributed to the influence of the different groups of substances it contains (Buba, F., Gidado, A. & Shugaba, A., 2013).The bees collect the sweet juices from various honey plants, process them in their digestive systems, and then store them in wax honeycombs, which are collected by beekeepers (Jovanović, N 2015).

Codex Alimentarius Commission defined honey as the natural sweet substance, produced by honeybees from the nectar of plants or from secretions of living parts of plants, or excretions of plant-sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in honeycombs to ripen and mature. The EU definition states that honey is only honey according to the definition when it is produced by *Apis mellifera* honeybees (Buba, F., Gidado, A. & Shugaba, A., 2013; Bradbear, M., 2009).

Honey may be categorised according to its origin (blossom honey, honeydew honey, monofloral honey, multifloral honey), the way it has been harvested and processed (comb honey, strained honey, chunk honey, extracted honey, pressed honey, crystallised or granulated honey,

creamed honey), and its intended use (table honey, industrial or bakers' honey) (Bradbear, M., 2009; Alvarez-Suarez, M.J., Gasparrini, M., Forbes-Hernández, Y.T., Mazzoni, L. & Giampieri, F., 2014.

Honey is a supersaturated solution of sugars mainly comprised of D-fructose, D-glucose, sucrose, maltose and higher sugars (~80% of solid mass). A wide range of minor constituents is also present in honey such as alkaloids, flavonoids/isoflavones, glycosides, phenolics, peptides/proteins, certain enzymes (invertase, amylase and glucose oxidase), carotenoid-like substances, organic acids, Maillard reaction products, vitamins, and minerals (Aurongzeb, M. & Azim, M. K., 2011; Manyi-Loh, E.C., Clarke, M.A. & Ndip, N.R., 2011; do Nascimento, S. A., Marchini, C.L. , de Carvalho, L. A. C., Araújo, D. F.D., de Olinda, A.R. & da Silveira A.T., 2015; Mannina, L., Sobolev, A.P., Di Lorenzo, A., Vista, S., Tenore, G.C. & Daglia, M., 2015).

The physicochemical properties of honey are an important indicator of the quality and origin of honey. The physicochemical characteristics of honey depend on the flowers used by the honeybees, as well as regional, beekeeping practices and environmental climatic variations. The physical properties and chemical composition of honey from different sources have been carried out by many researchers. The major quality criteria of interest are moisture content, sucrose content and reducing sugars content, pH value, electrical conductivity, ash content, free acidity, diastase activity and hydroxymethyl furfural (HMF) content (Ahmed, M., Khiati, B., Meslem A., Aissat, S. & Djebli, N., 2014; Jovanović, N., 2015; Ajibola, A., 2015; Bogdanov, S., Ruoff, K. & Oddo, L., 2004).

EXPOSITION

Chemical composition

The composition of honey varies from floral source to origin. Natural honey contains more than 300 bioactive substances, but it is mainly composed of water and sugars, primarily fructose and glucose, which accounts for 95–99% of honey dry matter, and about 4–5% of fructo-oligosaccharides (Ajibola, A., 2015). Besides fructose (38%) and glucose (31%), other identified sugars include maltose, sucrose, maltulose, turanose, isomaltose, laminaribiose, nigerose, kojibiose, gentiobiose and oligosaccharides (Ajibola, A., 2015; Ahmed, M., Khiati, B., Meslem A., Aissat, S. & Djebli, N., 2018).

According to Janevski, S., 2007, the composition of honey includes: 76% sugars (34% glucose, 40.5% fructose, 1.9% sucrose) and 5.5% other carbohydrates. Acacia and chestnut honey have a very high fructose content, rapeseed honey is distinguished with a higher proportion of glucose. The fructose/glucose ratio in various honey samples was the subject of studies conducted by a large number of researchers (Vahčić, N. & Matković, D., 2009). Primorac et al. (2009), found slightly higher fructose content (32.4%) than glucose (31.0%) in samples of honeydew honey from Croatia, while in Macedonia higher glucose content (36.8%) than fructose (33.6%) was found in the Macedonian samples. Ahmed et al. (2014) established that the content of glucose and fructose in four honey samples from different parts of western Algeria ranges from 21.45-28.26 g/100 g and 25.20-37.64 g/100 g, respectively.

Water is the second most important ingredient of honey and its content may vary from 15 to 23%. Water content influences some characteristics of honey (viscosity, specific weight, maturity, flavor and crystallization, specific gravity), and depends on the climatic conditions, the bee variety, the bee colony strength, the humidity and the air temperature in the hive, the processing and storage conditions, as well as the botanical origin of honey (Vahčić, N. & Matković, D., 2009; do Nascimento, S. A., Marchini, C.L. , de Carvalho, L. A. C., Araújo, D. F.D., de Olinda, A.R. & da Silveira A.T., 2015; Marković, M., 2014). The quantity of water in the honey is not constant due to its hygroscopicity and it changes during storage depending on the humidity of the air. It can be said that the water content in honey is an important parameter in determining its quality and its durability because it determines its stability and microbiological spoilage resistance during storage (Vahčić N. & Matković D., 2009). The higher the water content, the greater the chance of fermentation (Jovanović, 2015).

Honey contains a number of acids which include amino acids (0.05-0.1%) and organic acids (0.57%, range: 0.17-1.17%). Honey contains different free amino acids including: lysine, proline and tryptophan. The major amino acid in honey is proline (50–85%), and accepted as a criterion for the maturity of honey (Bogdanov, S., Ruoff, K. & Oddo, L., 2004; Janiszewska, K., Aniołowska, M. & Nowakowski, P., 2012). Primorac et al. (2009) determined the proline content within the range of 512.9 to 877.5 mg/kg in honeydew honey originating in Macedonia, while in Croatian honeydew honey samples significantly lower content of proline was found (261.7-749.7 mg / kg).

Batinić, K. & Palinić, D. (2014), quoting the findings of several scientists, stated that proteins and amino acids in honey can be of animal origin (from bees) and from plant origin (from pollen). According to some scientists, most of the protein in honey is derived from salivary glands with which bees process nectar and honeydew and turn them into honey, while according to the rest, the majority of proteins originate from protein-rich pollen (10 – 35%). Another possible source of protein is the nectar containing a minimum amount of protein (Marković, M., 2014; Vahčić, N. & Matković, D., 2009; Mendešević, N., 2014). The protein content in honey ranges from 0-1.7%, and honeydew honey contains more protein than nectar honey. During longer storage or heating, the amino acids condense with sugars creating yellow and brown products, leading to darkening of the honey (Batinić, K. & Palinić, D., 2014).

Organic acids are other important group of compounds in honey. In honey the main acid is gluconic acid, which is found together with the respective glucono-lactone in a variable equilibrium. Other acids that have been identified in honey include acetic, butyric, citric, formic, lactic, maleic, malic, oxalic, and succinic acids (Ball, W. D., 2007; Bogdanov, S., Ruoff, K. & Oddo, L., 2004; Ahmed, M., Khiati, B., Meslem A., Aissat, S. & Djebli, N., 2018). The organic acids are responsible for the acidity of honey and contribute largely to its characteristic taste (Aurongzeb, M. & Azim, M.K., 2011). Honey is deceptively acidic, as the high sugar content tends to mask the acidity in the taste. The average pH of honey is 3.9 (with a typical range of 3.4 to 6.1) (Ball, 2007; Manyi-Loh et al., 2011). These values prevent the development of microorganisms that require neutral or basic pH values, significantly limiting the spectrum of potentially contaminating microorganisms (do Nascimento, S. A., Marchini, C.L. , de Carvalho, L. A. C., Araújo, D. F.D., de Olinda, A.R. & da Silveira A.T., 2015). Darker types of honey are usually more acidic, and the storage of honey increases its acidity. Acacia, chestnut and meadow honey are characterized by a low concentration of organic acids, while dark honey is characterized by higher acidity (Vahčić, N. & Matković, D., 2009).

Honey contains different quantities of minerals ranging from 0.02 g/100 g to 1.03 g/100 g (Popov-Raljić, J., Arsić, N., Zlatković, B., Basarin, B., Mladenović, M., Laličić-Petronijević, J., Ivokov, M. & Popov, V., 2015), that varies depending on the particular botanical origin, pedoclimatic conditions and extraction technique (Hernández, O.M., Fraga, G.M.J.M, Jiménez, I.A., Jiménez, F. & Arias, J.J., 2005). The dominant element in honey is K, comprising approximately one-third of total mineral content. The blossom honey has lower mineral content than honeydew honey. Macro mineral elements, such as K, Ca, and Na, as well as trace minerals, such as Fe, Cu, Zn, and Mg, play a critical role in biological systems. In the literature there are reports of a correlation between dark honey color and the contents of Fe, Cu, Mg and other mineral substances (Aurongzeb, M. & Azim, M. K., 2011; Popov-Raljić, J., Arsić, N., Zlatković, B., Basarin, B., Mladenović, M., Laličić-Petronijević, J., Ivokov, M. & Popov, V., 2015). Vitamins C, B1 (thiamine) and B2 complex like riboflavin, nicotinic acid, B6, and panthothenic acid are also found in honey (Aurongzeb, M. & Azim, M. K., 2011; Ajibola, A., 2015; Ahmed, M., Khiati, B., Meslem A., Aissat, S. & Djebli, N., 2018)

One of the characteristics that differentiate honey from other sweeteners is the presence of enzymes. Honey naturally contains small amounts of enzymes that are introduced into honey by the bees during various phases of the honey manufacturing process (https://www.honey.com/files/general/refguide.pdf; Batinić, K. & Palinić, D., 2014). The predominant enzymes in honey are diastase (amylase),which digest starch to maltose and is relatively stable to heat and storage; invertase (saccharase or α-glucosidase), which catalyses the conversion of sucrose to glucose and fructose; and glucose oxidase, which regulate the production

of hydrogen peroxide H_2O_2. The invertase also catalyses many other sugar conversions and is mainly responsible for the sugar patterns of honey. Other enzymes such as catalase and acid phosphatase, are generally present in lesser amounts. While enzyme type is fairly uniform across honey varieties the amount of enzyme present can vary widely. Enzymes play an important role in honey and contribute to its functional properties (Buba, F., Gidado, A. & Shugaba, A., 2013; https://www.honey.com/files/general/refguide.pdf; Batinić, K. & Palinić, D., 2014).

Because polyphenols are present in all plants, they are also found in honey. Honey contains complex mixtures of polyphenols depending on the climate, region, soil, pollution levels, storage and many other factors. These differences are possible because certain polyphenols are specific to particular plants and hence are found only in honey produced by bees from those plants (Predescu, C., Papuc, C. & Nicorescu, P., 2015). Polyphenols in honey are mainly flavonoids (e.g. quercetin, luteolin, kaempferol, apigenin, chrysin, galangin), phenolic acids and phenolic acid derivatives. These are compounds known to have antioxidant properties (Tomás-Barberán, F.A., Martos, I., Ferreres, F., Radovic, B.S. & Anklam, E., 2001; Singh, P. M., Chourasia, R. H., Agarwal, M., Malhotra, A., Sharma ,M., Sharma, D. & Khan S., 2012). The content of flavonoids is 0.5% in pollen, 10% in propolis and ≈ 6 mg/kg in honey (Pyrzynska, K. & Biesaga, M., 2009). According to Jovanović, N., 2015 the the content of flavonoids in honey ranging between 60 and 460 mg/100 g.

Some types of honey contain very small quantities of bitter substances. These include glycosides, alkaloids, polyphenols, and terpenoids. According to Bradbear, N., 2009 several types of plants (*Agave* spp., *Datura* sp., *Euphorbia* sp., *Senecio* sp.) produce a bitter taste when used for honey.

Hydroxymethylfurfural (HMF) is a chemical compound, a breakdown product of of simple sugars (such as fructose) that is formed slowly and naturally during the storage of honey, and much more quickly when honey is heated (Bradbear, N., 2009). Several factors influence the levels of HMF, such as temperature and time of heating, storage conditions, pH and type of honey, thus it provides an indication of overheating and storage in poor conditions (Ahmed, S., Sulaiman, A.S., Baig, A. A., Ibrahim, M., Liaqat, S., Fatima, S., Jabeen, S., Shamim, N. & Othman, H. N., 2014). Many studies confirmed that the content of HMF increases with heating and storage (Batinić, K. & Palinić, D., 2014; Vahčić, N. & Matković, D. 2009). When honey is subjected to high temperatures, inadequate storage conditions or addition of invert sugar, the HMF content increases and it is one of the most common degrading products in honey, indicating its aging (do Nascimento, S. A., Marchini, C.L. , de Carvalho, L. A. C., Araújo, D. F.D., de Olinda, A.R. & da Silveira A.T., 2015). A disproportionately high content (more than 100 mg/kg) can be indicative of honey falsification (Batinić, K. & Palinić, D., 2014; Vahčić, N. & Matković, D., 2009).

Physical characteristics

The chemical composition of honey affects several of its physical characteristics (crystallization, viscosity, hygroscopicity, electrical conductivity, optical properties, surface tension, color) (Ball, W.D., 2007; Batinić, K. & Palinić, D., 2014). The physical appearance of honey varies with the methods of extraction, processing, packaging and preservation (Ajibola, A., 2015).

Freshly extracted honey is a viscous liquid food, and its viscosity depends on the various honey constituents. Hence, the viscosity is greatly influenced by the composition of honey, mainly its water content (Ajibola, A., 2015). In contact with the air, honey absorbs water, a phenomenon known as hygroscopicity. The water content absorbed depends on the relative humidity of the air. The hygroscopicity of honey is conditioned by the large amount of sugar. This process can increase the amount of water in the surface layer of the honey that can affect its quality during storage (fermentation) (Bartulović, M., 2015). Honey will absorb moisture from air at a relative humidity of about 60%. Another factor affecting the physical appearance of honey is surface tension, which is influenced by the colloidal substances in the honey, a reflection of the honey's botanical origin. The surface tension and high viscosity of honey cause the foaming appearance of honey (Ajibola, A., 2015).

Honey is a supersaturated glucose solution and it spontaneously enters a state of balance by crystallizing the excess glucose in the solution. Glucose loses water (becomes glucose

monohydrate) and passes in crystalline form. Water, previously bound to glucose, becomes free, increasing the water content of uncrystallised parts of the honey. Honey therefore becomes prone to fermentation and spoilage. The fructose remains in liquid form and forms a thin layer around the glucose crystals. Honey changes colour, it becomes brighter, it is no longer translucent, and changes its taste (Batinić, K. & Palinić, D., 2014). Glucose crystallizes very easily and quickly, while in fructose it is more difficult. The consequence is a not fully-crystallized honey. If there is a higher glucose content in honey, that honey crystallizes rapidly (e.g., meadow, mountain, clover honey). In acacia honey, there is a higher fructose content and therefore this type of honey crystallizes only after long storage (Jovanović, N., 2015). The speed of honey to crystallize depends not only on its composition, but also on the presence of catalysts, like seed crystals, pollen grains and pieces of beeswax in the honey (Erez, E. M., Karabacak, O., Kayci, L., Fidan, M. & Kaya, Y., 2015).

Colour is the physical property perceived most immediately by the consumer. The determination of colour is a useful classification criterion for honeys (Bogdanov, S., Ruoff, K. & Oddo, L., 2004). The colour of liquid honey varies from clear and colourless, yellow, amber to dark amber or black. The colour varies with honey's origin, age, and storage conditions, but transparency or clarity depends on the amount of suspended particles such as pollen. Other honey colours are bright yellow (sunflower), reddish undertones (chest nut), greyish (eucalyptus) and greenish (honeydew). Heat also affects the physical appearance of honey, including colour, crystallization, taste, and fragrance. In fact, natural honey becomes dark in colour when heated (Ajibola, A., 2015).

The electrical conductivity of honey is very small and depends on the mineral, organic acid and protein content of honey. Therefore, electric conductivity is a parameter which is often used in routine honey quality control, and can be considered a valid criterion for determining the botanical origin of a honey sample (Bogdanov et al., 2004). The greater the content, the greater the value of electrical conductivity. The usual values range from 0.39-0.76 mS/cm. Chestnut honey and honeydew honey have high electrical conductivity, while acacia and meadow honey have lower conductivity (Batinić, K. & Palinić, D., 2014; Jovanović, N., 2015; Bartulović, M., 2015).

Aqueous honey solution is optically active, i.e. capable of rotating the polarized light angle (Šarić, G., Matković, D., Hruškar, M. & Vahčić, N., 2008; Bartulović, M., 2015). Optical activity is a function of the proportions of individual carbohydrates in the honey. Fructose rotates the plane of polarized light to the left, and glucose, all disaccharides, trisaccharides and higher oligosaccharides to the right (Vahčić, N. & Matković, D., 2009). Because of the higher fructose mass fraction, nectar honey rotates the polarized light angle to the left, i.e. it has negative optical activity. On the other hand, because of its higher oligosaccharide mass fraction (mainly melecitose and elose), honeydew rotates the polarized light angle to the right, i.e. it has positive optical activity (Šarić, G., Matković, D., Hruškar, M. & Vahčić, N., 2008).

Honey has a characteristic microflora that can be of primary and secondary origin. It can be said that honey is an environment that allows the growth and reproduction of microorganisms. If the sugar concentration is above 20%, microorganisms do not grow. Under certain conditions, when the water content in honey is above 20%, osmophilic yeasts can grow and cause fermentation processes. Fermentation happens due to two reasons: hydroscopy and the presence of osmophilic and other types yeasts that sustain high concentrations of sugar (Bartulović, M., 2015).

CONCLUSION

The physicochemical properties of honey are an important indicator of the quality and origin of honey. The physical properties and chemical composition of honey from different sources have been carried out by many researchers.This paper presents an overview of the quality characteristics that honey has on the basis of data from the available literature. In its chemical composition, honey is a mixture of carbohydrates (mainly glucose and fructose) and water, and a smaller content of organic acids, minerals, vitamins, enzymes, proteins, polyphenols and other substances. The chemical composition of honey affects of its physical characteristics such as crystallization, viscosity, hygroscopicity, electrical conductivity, optical properties, surface tension, and color.

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BASIC PHYSICO-CHEMICAL STUDIES OF ORANGE-COLORED SNOW (RAZGRAD, BULGARIA)

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Abstract: *Snow can be found in other colors besides white. In this paper orange-colored snow sample collected from Razgrad, Bulgaria was evaluated. The specific purposes of the present study are to characterize the physical and chemical composition of the melted snow-water sample. Snow was analyzed for acidity (pH), total solids, total suspended solids, total dissolved solids, basic anions: chloride (Cl^-), nitrites (NO_2^-), nitrates (NO_3^-), sulfides and hydrogen sulphide. These parameters indicated high concentrations of total solids and total suspended solids in the snow-water. The acidity (pH) was 5,1. According to the above analyses, the possible sources of the particles in the snowfall should be soil and ground dust and co al-burning.*

Keywords: *Orange-colored snow, Physical and chemical characterisations, Physical indicators, Chemical indicators.*

ВЪВЕДЕНИЕ

Снегът е валеж под формата на множество ледени кристали (снежинки) и образуваните от него натрупвания по земната повърхност. Жизненият цикъл на снега започва в атмосферата, където при подходящи условия се формират снежинките. Снежните кристали се образуват, когато малки свръхохладени облачни капчици с диаметър около 10 μm започват да замръзват. Капките замръзват в присъствието на аерозолна частица, която да послужи за ядро. Такава роля могат да играят частици глина, пустинен прах или биологична материя. Ледените кристали нарастват до размер в порядъка на милиметри, падат като валеж и се натрупват на земята, претърпяват структурни промени на място и накрая се стопяват, свличат или сублимират (Vekilska, B., 1991).

Снегът успява особено ефективно да привлече и задържи към себе си миниатюрните частици на замърсителите във въздуха – отделяни например с газовете от автомобилите, при изгаряне на твърдите горива, от различните промишлени производства. Информацията за замърсяването на снега има важно екологично значение, защото снегът попада директно по растенията и те могат да бъдат замърсени. Освен това при топенето снежните води се оттичат повърхностно в реки и езера, вливат се в подземните води, а също така се отлагат в почвата. Информацията за замърсеността на снежната покривка е индиректен показател за състоянието на атмосферния въздух (Galitskaya, I.V., & Rumyantseva, N.A., 2012).

Поради наличието на прах, пясък или други замърсители във въздуха, снегът може да е оцветен в цвят, различен от белия – червен, оранжев, кафяв. Един известен пример за това е оранжевият и жълт сняг, паднал върху Сибир през 2007 г. (Helmenstine, A.M., 2017).

През февруари 2015 г. в Челябинск е валял син сняг. Тогава е установено, че причина за синия цвят е боя за яйца, случайно попаднала във вентилационната система на цех за производство на хранителни оцветители (http://www.dnesplus.bg/News.aspx?n=823302).

Фиг. 1. Син сняг в град Челябинкс

В град Омск, два пъти през 2012 г. и на 31.01.2018 г. е валял черен сняг (http://vreme.to/pages/news/11214.html?backto=). Установено е, че става дума за емисии от ТЕЦ, който в студеното време работи на пълна мощност.

На 23.03.2018 г. в част от Източна Европа - Румъния, Молдова, Украйна, Русия и на много места в Северна България, валя оранжев сняг. В Северна България необичайното явление е наблюдавано в много населени места - Шумен, Силистра, Исперих, Дулово, в села край Русе, Плевен, Видин, за което съобщиха много медии (https://www.24chasa.bg/novini/article/6778666).

Оранжев сняг валя и в град Разград, образуващ пласт в снежната покривка, покрит отгоре с бял сняг (Фиг. 2).

Фиг. 2. Пласт оранжев сняг от снеговалежа в град Разград на 23.03.2018 г.

От националния институт по метеорология и хидрология към БАН (Balgarska akademiq na naukite) обясниха, че обикновено при такава циркулация на въздушните маси, каквато се реализира в Средиземноморието с циклона от 22 март 2018 г., в по-високата част на атмосферата се изнася прах от прашни бури в пустинята от Северна Африка. Вграждайки се в облачността и минавайки от югозапад над Балканите, пада като валежи под формата на оцветен дъжд или сняг (https://nova.bg....). От брегове на Северна Африка топлите въздушни маси донесоха ситен пясък. Шуменската хидрометеорологична обсерватория съобщи, че киселинността на взетите снежни проби е неутрална, а в утайката не са открити вредни химикали.

Преди да стигнат до България най-често прашните бури минават през южните острови на Гърция. На остров Крит буквално всичко е пожълтяло. Високата концентрация на пясък във въздуха от около 500 $\mu g/m^3$ му придава оранжево-червен оттенък (https://www.24chasa.bg/novini/article/6778666).

По данни на националната обсерватория в Атина честотата на подобни явления през последните 20 години се е увеличила двойно, а интензивността им – с 50 %. Причина, според

специалистите, е разширяването на пустинните райони в Северна Африка и увеличаване на количеството прах, пренасян от вятъра.

Целта на нашето проучване е да се изследват някои основни физико-химични показатели на оранжевия сняг, паднал в град Разград на 23.03.2018 г., което да даде представа за вида и източника на причинителя на оцветения валеж.

ИЗЛОЖЕНИЕ

Взети са снежни проби в чисти пластмасови съдове (Фиг. 3). Съхранявани са в хладилник при 0-4 ºС и е извършен анализ на твърдите и течни фази на снега по някои основни физико-химични показатели.

Фиг. 3. Разкриване на пласта оранжев сняг и пробовземане

Физични показатели

- Външен вид.

Резултат: Снегът е зърнообразен, във вид на ледени гранули.

- Мирис.

Резултат: Снегът и снежната вода са без специфичен такъв.

- Цвят. Основен показател за замърсяването на водата е нейния цвят. Той се обуславя от разтворените в нея соли и органични съединения.

Резултат: Цветът на изследвания сняг и снежната вода е оранжев.

- Мътност. Този показател характеризира наличието на пясък, глина, хумус, планктон, водорасли и други вещества във водата.

Резултат: Снежната вода е мътна, неясна, кална. Следователно съдържа голямо количество от някои от горепосочените вещества.

- Прозрачност. Прозрачността на водата се определя от количеството органични и минерални вещества във водата. Мътността и прозрачността са визуални качества на водата, основаващи се на проникващата светлина.

Резултат: Снежната вода е напълно непрозрачна (Фиг. 4).

Фиг. 4. Снежна вода

Определяне на общ сух остатък - общо. Същността на метода се състои в изпаряване на определен обем вода и полученият остатък се изсушава при 105 °C (Todorova, S., 2015).

Резултат: Изследваната проба е с много високо съдържание на общ сух остатък - общо = 1468 mg/dm^3.

Определяне на суспендираните (неразтворени) вещества – общо. Методът се основава на задържането върху филтър на суспендираните (неразтворени) частици, съдържащи се в определен обем вода, и определяне на тяхната маса след изсушаване при 105 °C (Todorova, S., 2015).

Фиг. 5. Утайка от суспендираните (неразтворени) вещества в снежната вода

Общо неразтворените вещества са частици, намерени във водния стълб, които са по-големи от 2 микрометъра (органични и неорганични). Частиците, по-малки от 2 микрометъра, се считат за разтворени твърди вещества. Прави впечатление по-високото съдържание на суспендираните (неразтворени) вещества върху филтъра (Фиг. 5). Мътността и общите суспендирани частици са свързани. Колкото повече присъстващи във водата твърди вещества, толкова по-малко прозрачна е тя. Увеличението на мътността може да се посочи като потенциално замърсяване (https://pure-h2o-learning.eu/bg/.

Резултат: Суспендираните (неразтворени) вещества – общо в пробата сняг = 1157 mg/dm^3.

Определяне на разтворени вещества – общо. Определен обем филтрат от изследваната вода се изпарява на водна баня и остатъкът се суши при 105 °C до постоянна маса (Todorova, S., 2015).

Резултат: Количеството разтворени вещества – общо в пробата = 258 mg/dm^3. Прекомерните общо разтворени вещества могат да упражнят токсични ефекти в зависимост от техните йонни свойства. EPA, USPHS и AWWA препоръчват горна граница от 500 mg/dm^3 в повърхностните води (https://pure-h2o-learning.eu/bg/).

Оценката на основните физико-химични показатели е направена на базата на Наредба №4 за характеризиране на повърхностните води от 14.09.2012 г. (Naredba № H-4 ot 14.09.2012 g.).

Химични показатели

- **Определяне на pH**

Стойността на pH е определена потенциометрично с pH-метър TM6.

Стойностите, спрямо които се оценява киселинно-алкалния състав на валежите, по данни на НИМХ (Balgarska akademiq na naukite), са:

pH<5 – киселинни, 5≤pH≤6 – неутрални, pH>6 – алкални.

Средномесечните стойности на pH за месец март 2018 г., измерени в метеорологична станция Разград, са 5,4<pH<5,6. т.е. в рамките на неутралните стойности.

Резултат: На снежната вода е измерено pH 5,1.

Следователно е с неутрална реакция. Нашите резултати съвпадат с измерените в Шуменската хидрометеорологична обсерватория стойности, според които киселинността на снежните проби е неутрална (https://www.24chasa.bg/novini/article/6778666).

- **Окисляемост на водата** - основен показател за съдържащите се във водата органични и лесно окисляеми неорганични вещества. Изразява се с количеството кислород необходим за окисляването на органичните примеси в даден обем вода.

Перманганатна окисляемост (Метод на Кубел). Методът се основава на окисляването с калиев перманганат в сярнокисела среда на съдържащите се в изследваната вода органични и неорганични вещества (Todorova, S., 2015).

Резултат: Перманганатната окисляемост на изследваната проба = 7,68 mgO_2/dm^3.

- **Определяне на нитрити**

Методът се основава на диазотирането на сулфаниловата киселина в кисела среда, от присъстващите в изследваната вода нитрити, и реакцията на получената сол с α-нафтиламин, при което се получава червеновиолетово азобагрило. Светлинната абсорбция на разтвора се измерва при λ = 520 nm (Todorova, S., 2015).

Резултат: Съдържанието на нитрити в пробата = 0,01 mg/dm^3.

- **Определяне на нитрати**

Нитратите в присъствие на концентрирана трихлороцетна киселина образуват с натриевия салицилат сол на нитросалициловата киселина, оцветена в жълт цвят. Светлинната абсорбция на разтвора се измерва при λ = 410 nm (Todorova, S., 2015).

Резултат: Съдържанието на нитрати в пробата = 1,56 mg/dm^3.

- **Определяне на хлориди по аргентометричния метод.** В неутрална или слабо кисела среда хлорните йони се утаяват при титруване с разтвор на сребърен нитрат. Като индикатор се използва разтвор на калиев хромат, който реагира с излишъка сребърни йони, променяйки цвета на разтвора от лимоненожълт в оранжевочервен (Todorova, S., 2015).

Резултат: Съдържанието на хлорни йони = 14,8 mg/dm^3.

От киселите замърсители в отлаганията хлоридите са най-силно представени. В един сравнителен анализ Hristova and all., (2016) докладват много по-ниски средни стойности на хлорни аниони във валежни проби у нас и в чужбина – от 0,16 mg/dm^3 до 4,9 mg/dm^3. Но както е известно, процесите на самоочистване на атмосферата при суха депозиция са много по-неефективни, в сравнение с мократа депозиция от валеж (Hristova i dr., 2016). Примесите се задържат в атмосферата и това обяснява по-високите концентрации в последващия валеж.

Редът, по който се изменя концентрацията на анионите, установен в нашето изследване, е $Cl^- > NO_3^- > NO_2^-$ и е обратен на този в литературния източник (Hristova, E., Veleva, B., Korsachka, M., & Valcheva, L., 2016).

- **Определяне на сулфиди и сероводород по йодометричния метод, изчислено като сероводород.**

H_2S - може да има органични и неорганични производни (Todorova, S., 2015).

Резултат: В снежната проба не е установено наличие.

ИЗВОДИ

• Според гореспоменатите анализи, възможните източници на частиците в снеговалежа може да бъдат почвени и земни прахове и изгаряния.

• Тъй като суспендираните (неразтворени) вещества – общо са в големи количества в снега, то въздухът е бил сериозно прахово замърсен преди или по време на снеговалежа.

• Валежът на 23.03.2018 г. не е киселинен. От киселите замърсители в отлаганията най-силно представени са хлоридите.

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SAT–LB-P-2-BFT(R)-08

COMPARISON OF ALEXA 488, DR110 AND FITC CONJUGATED TO ANTIBODY FOR MICROSCOPIC ASSAYS[2]

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Abstract: *The fluorescent dyes DR110 and Alexa 488 were obtained. Synthetic fluorescent dyes that are conjugated to antibodies are useful tools in microscopic imaging. Alexa 488, DR110 and fluorescein 5(6)-isothiocyanate (FITC) were compared in applications using various conjugates with anti-sheep IgG antibody. Antibody-fluorescent dye conjugates with variety degree of labelling were obtained. Their fluorescence characteristics were observed by fluorescence spectrophotometer and fluorescence microscope. Brightness, photobleaching and background of the fluorescent conjugates were examined. Alexa 488 labeled antibody has brighter fluorescence and negligible photobleaching and background in microscopic assays, then DR110 and last FITC dye.*

Keywords*: Alexa 488, DR110, FITC, anti-sheep IgG antibody, fluorescent conjugates, microscopy.*

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SAT–LB-P-2-BFT(R)-09

USE OF ESSENTIAL OILS IN DAIRY PRODUCTS 4. ESSENTIAL OIL OF OREGANO (*ORIGANUM VULGARE* L.)

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Abstract: *There are dairy products developed with an enriched composition through the addition of limseeds, sesameseeds, out flakes, honey, and essential oil of oregano (Origanum vulgare* L.*).*

The effect of the additives on the process of the acidifying, syneresis, and the development of lactic acid bacteria was researched. It was found that they are good for the lactic acid process. The prepared products have very good organoleptic properties and can be successfully used for the purposes of functional food.

Keywords: *dairy products, titratable acidity, syneresis, lactic acid bacteria*

INTRODUCTION

Food is important to maintain and protect human health. A lot of traditional products (milk, fruits, vegetables, etc.) contain components with potential health benefits. New ones based on these food are being developed in a way increasing or joining the useful components because of their benefits or desirable physiological effects. Today the functional food based on milk takes up two-thirds of the total volume of such foods on the market as dairy foods with naturally balanced composition of the essential nutrients such as proteins, fats, carbohydrates, minerals, and enzymes. In the lactic acid products might be used: probiotics, dietary fibers (soluble and insoluble), vitamins, mineral elements, polyunsaturated fatty acids, essential oils, antioxidants, inulin, lactulose, etc. (Betored, E. et al. 2011, Cardarelli, H. et al. 2007, Kajiwara, S. et al. 2002, Panesar, P. S. 2011, Roberfroid, M. B. 2002).

In our previous work (Damyanova, St. et al. 2011) dairy products containing linseed and sesame seeds, oat flakes, and honey were prepared and examined. It was found that the products

have the properties of functional food and the additives have positive effect on the development of lactic acid process.

Interest in recent years is the use of essential oils in food products in order to increase their absorption by the human body, to enrich the composition, to improve the aroma, to prolong the durability, etc. (Barros, C. et al. 2012, Cleff, M. B. et al. 2010, Deliu, I. et al. 2017, Georgiev, E. & Stoyanova, A. 2006, Gutierrez, J. et al. 2009, Kačániová, M. et al. 2012, Thabet, H. et al. 2014).

The results from our previous studies (Kostova, I. et al. 2014) show that the essential oil of oregano has got antimicrobial activity but it does not inhibit the development of the lactic acid bacteria in dairy starter cultures.

The purpose of this work is to develop and examine dairy products with enriched composition by adding linseed, sesame seeds, oat flakes, oregano oil and honey.

EXPOSITION

Materials and methods

The studies were conducted in laboratory conditions with cow milk which was obtained from Razgrad region, northeastern Bulgaria.

The physicochemical parameters of raw milk (fat, solids-nonfat (SNF), density, added water, protein) were determined by the milkanalyzer EKOMILK Company BULTEH 2000.

The microbiological parameters of the raw and pasteurized milk were tested by conventional methods (Slavchev, D. et al. 2003).

The fermented milk product with set coagulum (control) was prepared by a classical technology with the symbiotic starter culture of the strains *Lactobacillus delbrueckii subsp. bulgaricus* and *Streptococcus thermophilus* purchased by the company Selur Pharma Ltd.

The control sample was obtained by traditional technology for yogurt (Dimitrov, T. et al. 2008).

The samples studied (№ 1 to 3) were prepared by traditional technology by adding: oat flakes (6%), linseed (4%), sesame seed (2%) and honey (4%) (№ 1); essential oil (№ 2); the combination of the ingredients of the first and second examined samples (№ 3).

The additives used were market purchased; the essential oil of oregano was prepared in laboratory conditions (Kostova, I. et al. 2014). The amount of the oil is 0.8 mg/kg of final product, which was consistent with the known literal data and our previous studies (Georgiev, E. & Stoyanova, A. 2006, Kostova, I. et al. 2014).

The prepared dairy products were analyzed for chemical, microbiological and organoleptic characteristics:

- The lactic acid process dynamics was monitored by determination of titratable acidity (°T) (Dimitrov, T. et al. 2008, Slavchev, D. et al. 2003).
- Microbiological research - total number of viable lactic acid bacteria - *Lactobacillus delbrueckii subsp. bulgaricus* and *Streptococcus thermophilus* were carried out by growing on the synthetic medium M17 and MRS (Merck) methodology of IDF (IDF-Standard 122C: 1996, IDF-Standard 149A: 1997).
- The organoleptic assessment of lactic acid products was carried out according to BNS 15612-83 (BNS (Bulgarian National Standard) 15612-83**)**.

RESULTS AND DISCUSSION

The milk used for the experimental work meets the requirements of raw cow milk (Commission Regulation (EC) No853/2004, Regulation № 4 the Ministry of Agriculture and Food 2008). Figure 1 presents the dynamics of the lactic acid process.

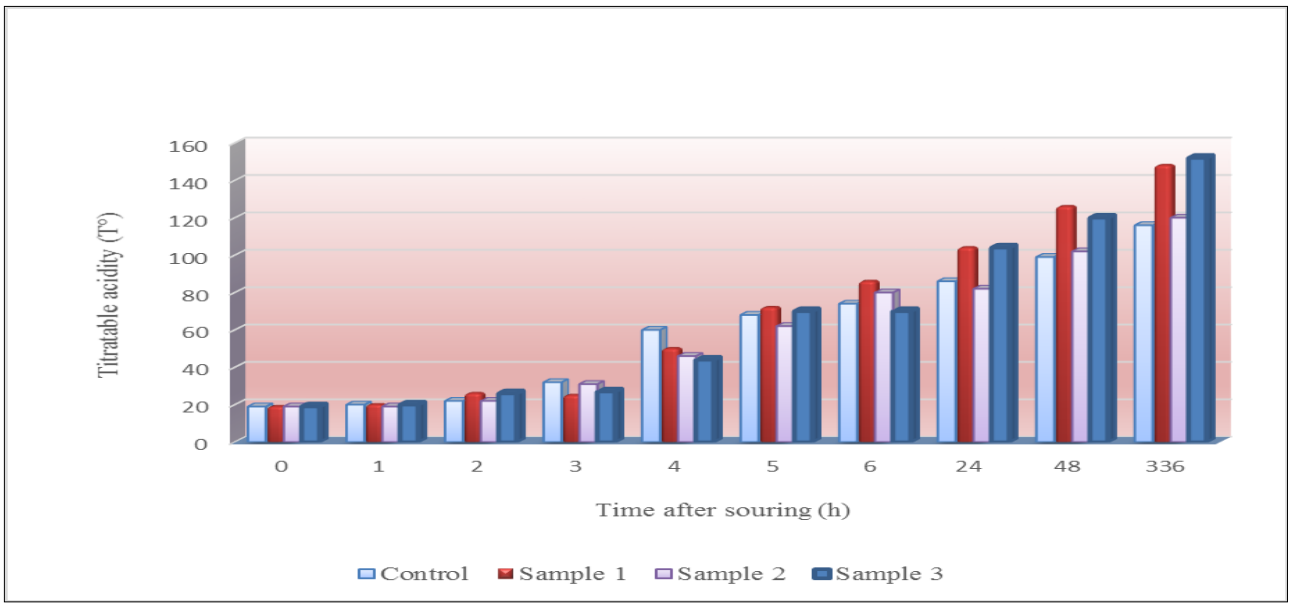

Fig. 1. Dynamics of lactic acid formation

The experiments conducted show increasement of the titratable acidity for all four samples as a result of lactic acid bacteria metabolism. More active lactic process was found in the samples with additives when they were combined with oregano oil. For these samples the tendency of increased acidity was maintained until the end of study period of 336 hours (14 days of the storage). The titratable acidity was higher than the control. The acid formation in samples with added essential oil was the same as for the control sample.

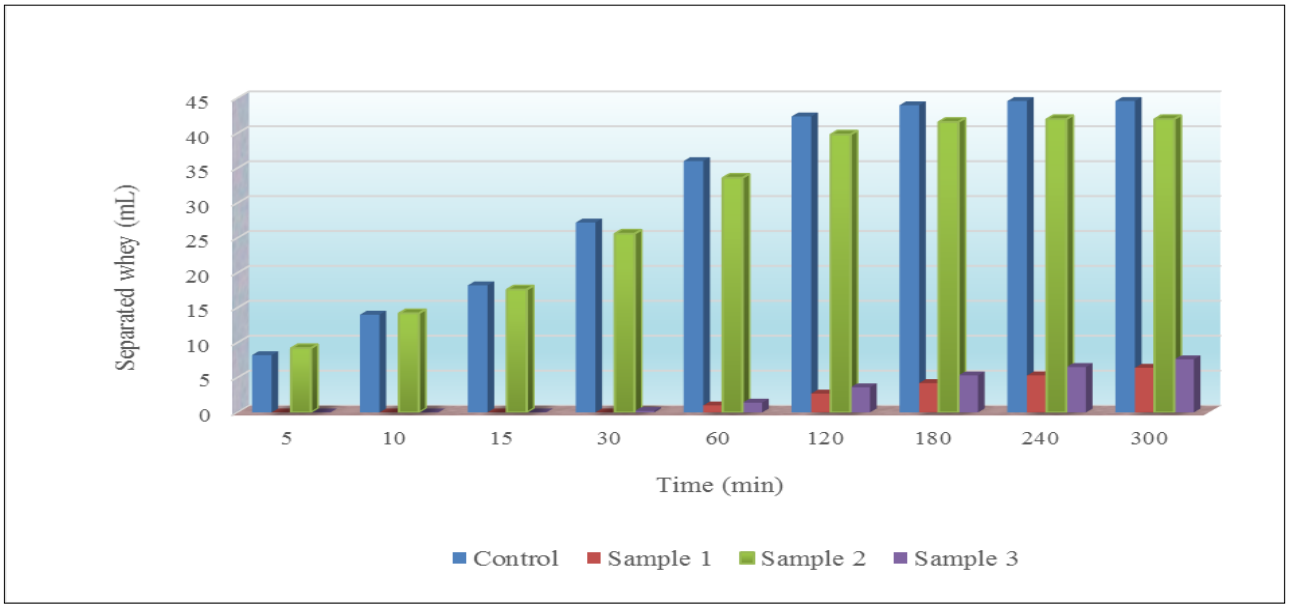

Fig. 2. Syneresis of the fermented milk products

Figure 2 presents the results for the values of the syneresis of the prepared dairy products. The amount of the separated whey for 5 hours was highest in the control sample (44.6 mL) and in the milk with oregano oil (42 mL). Significantly less whey was separated in sample № 1 (6.4 mL) and in sample №3 (7.6 mL), because of the ability of oat flakes and seeds to connect the water that leads to reduction of the aqueous phase of the milk.

The effect of the additives on development of lactic acid bacteria *Lactobacillus delbrueckii* subsp. *bulgaricus* and *Streptococcus thermophilus* in the tested products are shown in Figures 3 and 4.

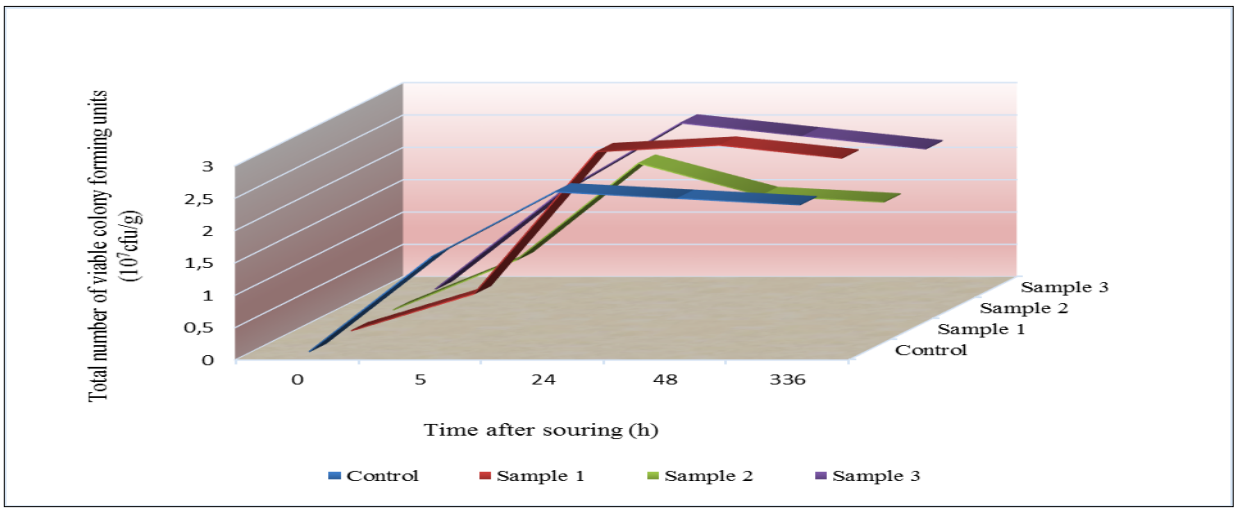

Fig. 3. The growth dynamics of *Lactobacillus delbrueckii* subsp. *bulgaricus*

It was obvious from the data obtained that with the exception of the dairy product with oregano oil, in all other samples during the first 24 hours the cells of *Lactobacillus delbrueckii* subsp. *bulgaricus* grow actively. After 1st day and to 14th day, the number of the viable cells was kept relatively the same as in the dairy products with additives, in combination with the oregano oil (No 1 and 3) it was higher in comparison with the control. This is probably confimed with the higher content of the nutrients needed for the development of the lactic bacteria. The results obtained correspond to the prescribed values for the titratable acidity (Fig. 1).

In the samples examined the number of the viable cells of *S. thermophilus* was increased to 48th hour. Then the growth speed was kept relatively unchanged till the end of the study period and the number of cells slightly decreases (Fig. 4). The lactic acid bacteria *S. thermophilus* develops fast growth speed in the samples with the additives and they reach the highest number in combination of all additives and the essential oil (sample №3).

The oregano oil inhibits to a certain extent the development of lactic acid bacteria *L. delbrueckii* subsp. *bulgaricus* and *S. thermophilus* that is related to its antimicrobial activity (Georgiev, E. & Stoyanova, A. 2006).

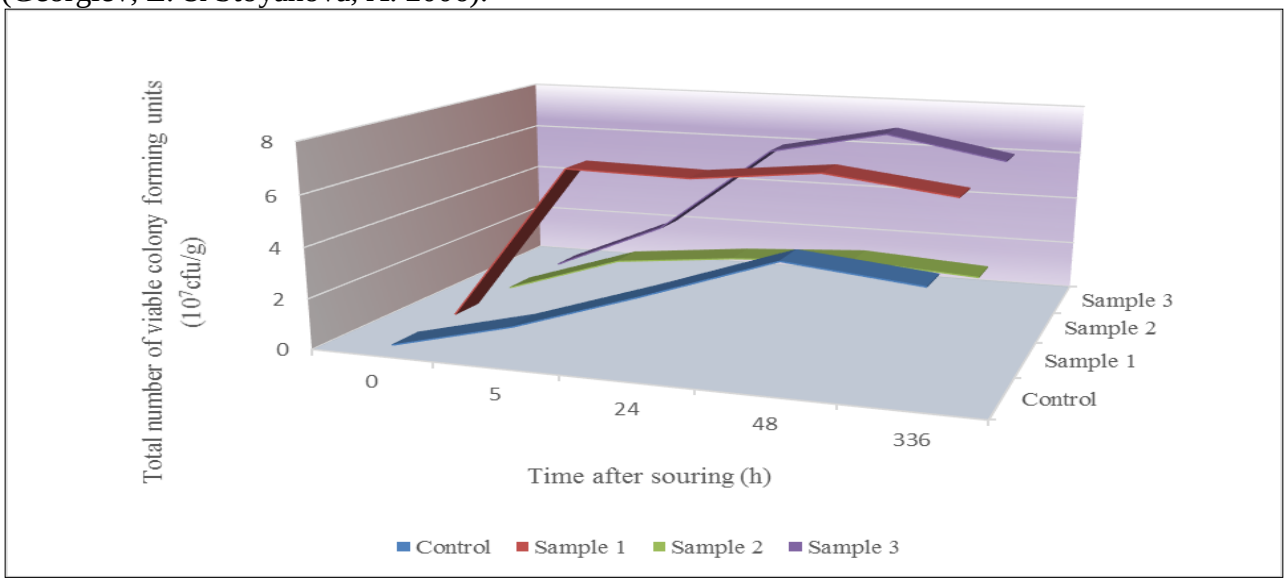

Fig. 4. The dynamics of cell growth of Streptococcus thermophilus

The data from the qualification of the prepared dairy products according to their organoleptic parameters are presented in Table 1. The products obtained were characterized as very good and balanced lactic acid taste, thick and smooth coagulum, homogeneous consistence and structure.

Table 1. Organoleptic indicators

Parameters	Control Sample	№ 1	№ 2	№ 3
Surface	smooth	smooth	smooth	smooth
Colour	white with cream-coloured shade	white with cream-coloured shade	white with cream-coloured shade	white with cream-coloured shade
Type of coagulum	thick, smooth	thick, smooth	thick, smooth	thick, smooth
Structure after cutting	smooth surface with slight serum separation	smooth surface without serum separation	smooth surface with slight serum separation	smooth surface without serum separation
Consistency after whipping the coagulum	homogeneous, like cream	homogeneous, like cream	homogeneous, like cream	homogeneous, like cream
Taste and flavor	tasty specific lactic acid	tasty specific lactic acid with a hint of the used nuts and honey	tasty specific lactic acid with a hint of oreganf	tasty specific lactic acid with a hint of the used nuts and honey, and oregano

CONCLUSION

Dairy products with added oat flakes, sesame seeds, linseeds, honey and essential oil of oregano (*Origanum vulgare* L.) has been prepared. The combination of these additives affects adversely on the speed of lactic acid process, syneresis, and their organoleptic parameters. The products acquired the specific for the fruits of oregano taste and aroma.

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SAT–LB-P-2-BFT(R)-10

THE INFLUENCE OF INDUSTRIAL AND FACIAL WATER ON THE FIFTH CHANNEL SITUATION IN THE CITY OF BITOLA

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Abstract: *The concept of sustainability in urban waste water management is more commonly used and has a primary focus on ways to the environmental protection, public health and water resources (Ibrahimali A., 2014).*

The fifth channel is located in the City of Bitola and is filled with mountain water - Siva Voda. Half of the fecal wastewater from the City of Bitola and the village of Kravari and the industrial wastewater from the factory for yeast and alcohol, the beer factory, the factory for production of paper and cardboard packaging, the „Kiro Dandaro" printing plant and the Sugar Factory flow in it.The measuring points are along the fifth channel: Measuring point 1 - fifth channel at the exit from Bitola, Measuring point 2 - fifth channel at the village of Kravari, Measuring point 3 - fifth channel before it enters the Crna River. For determining the condition of the water, the following physical chemical parameters were examined in the fifth channel: the water temperature determined by a digital thermometer, turbidity (opacity) was determined by turbidimeters, suspended solids, dissolved oxygen, biological oxygen consumption (BOD), chemical oxygen consumption (COD) and together organic carbon (TOC) was determined with UV PASTEL - tool for directly reading of the values. All examinatios are conducted in March and September. By summarizing the results obtained, it can be concluded that the largest pollution is in the Measuring point 2, which is more pronounced in September. The value of BOD is 370mg / L, TOC is 72,0 mg / L in the same measuring place and the same month. This situation is due to the increased concentration with organic pollution in the Measuring point 2. Therefore, it is preferable to temporarily clean the channels and purify the wastewater in order to protect the environment.

Keywords: *Fifth channel, waste water, environmental pollution*

INTRODUCTION

Water is essential to all living organisms. According to Dalmacija, B., 2000, the water once used and untreated is returned to the aquatic system, it is wastewater. Such wastewater poses a threat to the environment and a favorable environment for the development of microorganisms (Belič, S., Belič, A., Rajkovič, M., 2007). The subject of this research is the water from the Fifth canal located in the city of Bitola. This canal is filled with mountain water from the river Siva Voda, which is a river with low water level, and into it flows half of the fecal wastewater from the city Bitola and the village the Kravari and the industrial wastewater. The aim of this research is to determine the quality of the water in the Fifth channel and its proper management.

MATERIAL AND METHODS

Work Material

The work material used in this study is water from the fifth channel. The measuring points were selected along the fifth channel. Measuring point 1 MM1 of the fifth channel is the section where the wastewater flows from: the Beer Factory, Yeast and Alcohol Factory, the Printing Factory "Kiro Dandaro", the Factory for production of paper and cardboard packaging and part of the waste from the City of Bitola. Measuring point 2 MM2 is the fifth channel in which the waste faecal waters flow from the village of Kravari. The measuring point 3 MM3 is the fifth channel in which the waste from septic tanks and livestock farms near the village of Egri is discharged. The water samples were taken in March and September and was made physical-chemical analysis.

Methods of work

The following analyzes were made for the examination of physical-chemical parameters: the water temperature determined by a digital thermometer, turbidity (opacity) was determined by turbidimeters, suspended solids, dissolved oxygen, biological oxygen consumption (BOD), chemical oxygen consumption (COD) and together organic carbon (TOC) was determined with UV PASTEL - tool for directly reading of the values.

RESULTS AND DISCUSSION

In order to obtain a realistic picture of the current state of water quality in the fifth channel,were analyzed the physical and chemical parameters , which are shown in Table 1.

Table 1. Physical- chemical parameters of the water from the fifth channel in March and September

Measuring Points	MM1	MM1	MM2	MM2	MM3	MM3
	March	September	March	September	March	September
Water temperature [^{0}C]	10,4	20,5	10,9	20,0	10,2	16,0
Turbidity NTU	20,2	34,1	28,2	102	37,5	18,9
Suspended substances. mg/L	201	42,5	14,6	142	27,0	46,5
pH	6,60	6,60	6,78	6,34	6,53	6,54
O_2 mg/L	5,05	1,08	2,66	0,0	9,68	0,0
BOD mg/L	12,4	13,4	11,7	370	16,8	13,4
COD mg/L	28,4	36	31,0	1140	36,0	34,5
TOC mg/L	11,6	10,8	9,5	72,0	11,2	10,4

Each outside work it was measured the temperature of the water. The water temperature is correlated with seasonal variations. The highest value of the temperature is expressed in MM1 20,5 ^{0}C in September and the lowest in MM3 10,2^{0}C in March. According to Lokoska, L., 2004, the temperature limits the activity of microorganisms.

The first visual impression about the state of the water is the turbidity. The highest value was detected at the measuring point 2 102 NTU month of September as a result of the discharge of communal wastewater from the village of Kravari. With the departure of the fifth channel from the settlements and the value of the turbidity decreases. Lowest value is recorded at the measuring point 3 18,9 NTU.

Suspended substances determine the presence of organic and inorganic substances in the water. The highest value is determined at the measuring point 1, 201mg / L in March as a result of heavy rainfalls and increased soil erosion.

According to Dalmacija, B., 2000, there is a regulating mechanism in the aquatic ecosystem that controls the pH value of the water. And in our measurements there are not great variations in the pH value in all measuring points.

According to Mulev (2003), and Jovanov, D., 2012 the content of dissolved oxygen and water temperature influence the activity of microorganisms. The highest content of dissolved oxygen is recorded at the measuring point 3, 9.98 mg/L in March, as a consequence of the higher water level of the channel in the channel and the greater dilution of organic matter. The state of water at the measuring points 2 and 3 is alarming in September, where the dissolved oxygen content is 0.0 mg/L, the temperature is higher, and the metabolic activity of microorganisms is more pronounced. According to Adebayo, S.A. & Usman, L.A., 2009), BOD is correlated with the amount of organic matter present in the water. The highest value of BOD was found at the measuring point 2, 370 mg/L in September, where the amount of TOC is highest 72.0 mg/L. At the measuring point 2, there is a large metabolic activity by microorganisms for decomposition of organic matter. The highest value of COD was found at the measuring point 2, 1140 mg/L in September in all measuring points, as a result of the higher concentration of organic matter in the water from the canal.

The content of the total organic carbon according to Ivancev-Tumbas (2009), is an indicator of the present amount of organic matter in the water. The highest value is recorded at the measuring point 2, 72,0 mg/L, in September, where the content of dissolved oxygen content is the lowest 0,0 mg / L in the same month and the same measuring point.

CONCLUSION

From the conducted research of the water from the fifth channel where the industrial and fecal waste waters from the city of Bitola and the village of Kravari enter, the greatest burden on organic matter can be found in the measuring point 2. At the same measuring point and the content of BOD for degradation of the organic matter by the microorganisms is the largest, and the content of dissolved oxygen is the smallest. In this measuring place the greatest anthropogenic influence is felt, which is reduced by distancing the canal from the populated areas.

Therefore, this survey provides guidelines for conducting continuous cleaning of the channels and purification of industrial wastewater before being discharged into the canels.

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SAT–LB-P-2-BFT(R)-11

PAINTING WITH YEASTS ON CHROMOGENIC DIFFERENTIAL CULTURE MEDIA

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Abstract: *Arts-related science activities provide unique opportunities to engage students' strengths. Microbial art, or agar art, is artwork created by culturing microorganisms in certain patterns. Agar plates are used as a canvas, while pigmented bacteria and yeasts represent the paint. Chromogenic media are frequently used in direct and rapid identification of yeasts because different species produce unique colors on these media. This study was thus undertaken to investigate the ability (or inability) of some Candida, Rhodotorula, Saccharomyces, Saccharomycodes, Endomyces and Kluyveromyces species to grow on chromogenic yeast culture medium - HiCrome™ Candida Differential Agar. Living works of art on agar plates were created by "painting" with yeasts that express various colors in chromogenic medium. The intensity of growth and the characteristic pigmentation of each of the studied speciaes yeasts were determined.*

Keywords: *Microbial art, Agar art, Painting, Yeasts, Chromogenic differential media.*

ВЪВЕДЕНИЕ

Връзката на микробиологията с изкуството дава възможност за визуализация и комуникация на науката, а също и за различен вид научно творчество на студентите. Прилагането на „микробното изкуство" (microbio art), а именно рисуване с живи микроорганизми върху агарова среда, включва иновативни задачи, които да направят дисциплината по-атрактивна, да стимулират студентите за още по-задълбочени познания и да ги насърчат да мислят извън границите на даден обект (Todorova, S., Dimitrov, T., Ivanova, I., Muradov, H., Spiridonova, R., Nedelcheva, R., Nedelcheva, R., Stefanova, P., & Petrova, D., 2015).

Микроорганизмите с пигментите, които синтезират, са „живите бои'' за цветните рисунки. За направа на различните изображения, картини, рисунки, освен „живи бои", е необходимо и „платно". „Платното" са различните агарови хранителни среди.

Най-голям ефект постигаме при рисуване с дрожди на хромогенни хранителни среди.

Хромогенните хранителни среди са диференциално – диагностични среди от ново поколение, които позволяват бързо откриване и идентифициране на микроорганизмите. Това става възможно с помощта на хромогенни и флуорогенни съставки, включени в състава на хранителните среди. Хромогенните хранителни среди ни позволяват да открием специфични ензимни активности, характерни за отделна група или даже за отделен вид микроорганизъм.

Принцип на действие:

Микроорганизмите се идентифицират чрез ензимни реакции, които са специфични за вида им. Изследваният микроорганизъм съдържа ензим, който метаболизира безцветния хромогенен субстрат, като се образува специфично оцветен реакционен продукт.

Хромогенната среда променя цвета си (или флуоресцира) или колониите на съответния микроорганизъм се оцветяват в характерен за него цвят.

Това проучване е предприето за изследване на способността (или неспособността) на някои видове Candida, Rhodotorula, Saccharomyces, Saccharomycodes, Endomyces и Kluyveromyces да растат върху хромогенна среда за култивиране на дрожди - HiCrome ™ Candida Differential Agar. Определя се интензивността на растежа и характерната пигментация на всеки от изследваните видове дрожди. Чрез рисуване с дрождите, които изразяват различни цветове в хромогенната среда, се създават живите произведения на микробното изкуството върху агар. Крайният резултат е впечатляващ и запомнящ се и много малко хора могат да кажат, че са го правили.

ИЗЛОЖЕНИЕ

Дрожди

Дрождите са едноклетъчни гъби. Те са безхлорофилни, неподвижни, еукариотни микроорганизми.

Използвани са следните видове дрожди от колекцията на катедра „Биотехнологии и хранителни технологии“ във филиал Разград на Русенски университет „Ангел Кънчев“:

Saccharomyces cerevisiae - хлебните дрожди са едни от най-изучаваните в микробиологията. Развиват се в среди, съдържащи въглехидрати и причиняват алкохолна ферментация. Човекът използва тези организми от хиляди години в производството на хляб, вино, бира.

Candida utilis, Candida tropicalis, Rhodotorula rubra – се използват в получаването на микробиален белтък.

Candida albicans – могат да причинят кандидози.

Saccharomycodes Ludwigii – могат да причинят развала на хранителни продукти, по-специално на сулфитирани ферментирали напитки, като вино, сайдер.

Endomyces magnusii – гъбите от сем. *Endomycetaceae* нямат практическа стойност.

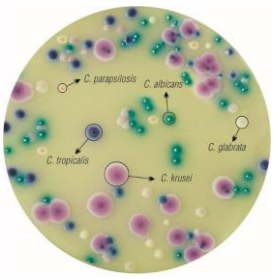
Klyuveromyces mara - изследвани са за потенциална употреба в биотехнологични производства, като на биогорива, едноклетъчни протеини, ензими и др.

Дрождите се съхраняват при 0-4 ºС в епруветки на наклонен агар на Сабуро.

Хромогенни хранителни среди

Богата палитра от различно оцветени дрожди се получава най-вече на хромогенни диференциални среди. Тези среди са предназначени за директна и бърза идентификация на дрождите, тъй като различните видове, най-вече *Candida,* произвеждат уникални цветове върху тях и лесно се разграничават помежду си. От друга страна многообразието от цветове прави хромогенните среди много подходящи за микробното изкуство при рисуване с дрожди.

HiCrome™ Candida Differential Agar дава възможност за селективна изолация и директна идентификация на дрождите от р. *Candida.* Хромогенният агент в средата позволява колониите на всеки вид да прорастват и да се оцветяват в характерния за него цвят (Фиг.1) (https://ridacom.com/en/products/view/5016).



Фиг. 1. Различни видове *Candida* на HiCrome™ агар с характерно оцветяване на колониите: *C. albicans* – зелен цвят; *C. tropicalis* – стоманено синьо до синьо; *C. krusei* – лилав цвят; *C. glabrata* – кремав до бял; *C. parapsilosis* - кремави колонии, подобни на *C. glabrata*

Цветовете на колониите на HiCrome агар трябва да се определят след 48 h (Shettar, S. K., Patil, A. B., Nadagir, S. D., Shepur, T. A., Mythri, B. A., & Gadadavar, S., 2012).

PP3010 – Colorex™ Candida

Тази среда е разработена с цел опростяване на изолацията и предполагаемото идентифициране на някои видове дрожди. Външният вид и диференциацията на *Candida sp.* е очевиден от отличителните цветове на колониите (Фиг. 2) (http://www.eolabs.com/product/pp3010-colorex-candida/). На тази среда единствено *C. glabrata* дава различно оцветяване в сравнение с HiCrome™ агар.

C. tropicalis→ метално сини *C. albicans→ зелени* *C. glabrata→лилави*

Фиг. 2. Характерно оцветяване на колониите на видове *Candida* върху PP3010 – Colorex™ Candida

CHROMagar™ Candida

CHROMagar Candida е диференциална хромогенна среда, предназначена да идентифицира *C. albicans, C. tropicalis* и *C. krusei* по цветовите и морфологични различия на колониите им. Колониите на *C. albicans* са зелени; колониите от *C. tropicalis* изглеждат тъмносини до метално сини; *C. krusei* имат розови колонии с белезникава граница. Други дрожди могат да развият светло- до тъмнолилави или кремави цветове (например, *C. glabrata*), според литературния източник (Ozcan, K., Ilkit, M., Ates, A., Turac-Bicer, A., & Demirhindi, H., 2010).

HardyCHROM ™ Candida

Хромогенна селективна среда, препоръчителна за изолиране и диференциране на дрожди. Различията в морфологията и цвета на колониите на тази среда позволява диференцирането на *C. albicans*, *C. tropicalis* и *C. krusei*. Съгласно литературния източник (https://catalog.hardydiagnostics.com/cp_prod/content/hugo/HardyCHROMCandida.html):

C. albicans – образува средноголеми, гладки, зелени до тъмно метало-зелени колонии за 48 h. Колониите изглеждат светлозелени след 24 h.

C. tropicalis – след 48 h колониите са средноголеми, гладки, сини до тъмносини с метален блясък, със син ореол. След 24 h колониите изглеждат сини до синьо-розови.

C. glabrata - средно големи, гладки, розови колонии, често с по-тъмно сиволилав център.

Други видове дрожди, например *C. parapsilosis*, обикновено имат малки, бели до розови колонии.

Candida ID chromogenic medium (CAID)

Тази среда е за идентифициране на *C. albicans, C. tropicalis, Candida lusitaniae, Candida kefyr* и *Candida guillermondii*. На CAID *C. albicans* има синьо оцветяване на колониите, за разлика от зеленото оцветяване на горепосочените хромогенни среди. Синият цвят е по-интензивен след 24 h култивиране върху средата. Колониите на *C. tropicalis, C. kefyr, C. lusitaniae* и *C. guillermondii* са розови и блестящи в рамките на 48 h. С изключение на два вида *Candida famata* и *Rhodotorula sp.*, другите изолирани видове дрожди са бели на CAID (Letscher-Bru, V., Meyer, M. H., Galoisy, A. C., Waller, J., & Candolfi, E., 2002). Авторите не са наблюдавали оцветяване на изолати *C. glabrata* и *S. cerevisiae*. Други автори (Fricker-Hidalgo,

H., Orenga, S., Lebeau, B., Pelloux, H., Brenier-Pinchart, M. P., Ambroise-Thomas, P., & Grillot, R., 2001) докладват розова пигментация на някои щамове за видове *Candida sphaerica, Candida pelliculosa, C. utilis, C. glabrata* и *S. cerevisiae.*

Никерсон Агар Bi.G.G.Y. (Nickerson Medium)

Диференцирането на дрождите в тази среда се основава на способността им да редуцират бисмутов хидрокси полисулфит. Доказано е, че най-силна редуцираща способност проявяват *C. albicans, C. krusei* и *C. tropicalis*. В кисела или неутрална среда, те образуват черни колонии, поради образуването на бисмутов сулфид (http://www.himedialabs.ru/m217-m217d).

C. albicans – колонии гладки, кръгли, кафяво-черни, без блясък, без дифузия на цвета в околната среда;

C. tropicalis – колонии гладки, тъмнокафяви с черни центрове, с блясък, дифузно затъмняване на средата след 72 часа.

ВЛ хранителен агар (Wallerstein Laboratory Nutrient Agar)

Тази среда е разработена от Green и Gray през 1950 г. Създаден е нов вариант с бромкрезол зелено, присъстващ в средата като оцветител и придаващ ѝ зелен цвят. Дрождите *Saccharomyces* поемат багрилото от средата и обикновено не го метаболизират, така че колониите им се оцветяват в зелено, а агаровата среда става бистра, непрозрачна. *Brettanomyces sp.* поемат бромокрезол зеленото, но е наблюдавано, че метаболизират багрилото. Затова техните колонии са с жълтеникав, белезникав цвят (http://brettanomycesproject.com/2009/03/wln-agar-medium/).

Агар арт

За създаване на уникалните рисунки с дрожди е използван хромогенен агар за Candida - HiCrome™. Предварително е предприето изследване на способността (или неспособността) на проучваните от нас видове *Candida, Rhodotorula, Saccharomyces, Saccharomycodes, Endomyces* и *Kluyveromyces* да растат върху хромогенната среда за култивиране на дрожди - HiCrome ™ Candida Differential Agar и определихме характерното им оцветяване. В нашето изследване при *C. albicans* (зелен цвят) и *C. tropicalis* (тъмносин цвят) (Фиг. 3) оцветяването напълно съвпада с дадената за средата характеристика на видовете (https://ridacom.com/en/products/view/5016). В литературата не открихме цветово описание на *C. utilis* на хромогенен агар за Candida - HiCrome™. Но на среда Candida ID, някои щамове от вида образуват розови колонии (Letscher-Bru V, Meyer MH, Galoisy AC, Waller J, Candolfi E. J Clin Microbiol. 2002 Apr; 40(4):1508-10.). В нашето проучване установихме, че при хидролизиране на хромогенните субстанции, този вид образува светлолилави колонии (Фиг. 3), различаващи се ясно от останалите два вида.

C. albicans *C. tropicalis* *C. utilis*

Фиг. 3. Оцветяване на видове *Candida* в проведеното изследване на HiCrome ™ Candida Differential Agar

Видовете *Rhodotorula* се характеризират с производството на каротеноидни пигменти в оранжево-червен цвят. Bellanger, A.-P., Grenouillet, F., François, N., Skana, F., & Millon, L. (2013) установяват, че два изолата *Rhodotorula* spp. не успяват да растат в субкултура върху хромогенна среда за дрожди и да образуват характерното оцветяване. Освен това две от четири налични в търговската мрежа хромогенни среди за дрожди са показали значителен инхибиторен ефект върху растежа на видовете *Rhodotorula*. Willinger, B., Hillowoth, C., Selitsch, B. & Manafi, M. (2001) докладват за *Rhodotorula mucilaginosa*, растящи като розови

колонии на среда Candida ID. В нашето изследване *R. rubra* имаше много добър растеж на HiCrome ™ Candida Differential Agar в типичното оранжево-червено оцветяване.

S. cerevisiae на Candida ID растат като бели незабележими колонии (Willinger, B., Hillowoth, C., Selitsch, B. & Manafi, M., 2001). В нашето изследване те имат тъмно розово оцветяване (Фиг. 4 (1)). *E. magnussii* също се оцветяват в тъмно розово (Фиг. 4 (2)), но имат по-сух и по-плътен растеж.

(1)   (2)

Фиг. 4. Оцветяване на *S. cerevisiae* (1) и *E. magnussii* (2) в HiCrome ™ Candida Differential Agar

K. mara образува големи, бели до кремави колонии с розов център (Фиг. 5 (1)), а *S. Ludwigii* растат много слабо, с малки, бели, незабележими колонии (Фиг. 5 (2)).

(1)  (2) 

Фиг. 5. Оцветяване на *K. mara* (1) и *S. Ludwigii* (2) в HiCrome ™ Candida Differential Agar

При рисуване върху Хромогенен агар за Candida - HiCrome™ петритата трябва да се инкубират в продължение най-малко на 48 часа, за да се постигне адекватно цветово развитие на дрождите. Цветовете се засилват с възрастта. И когато дрождите са посяти в рисунък, се получава нещо красиво и радващо окото, което много малко хора могат да кажат, че са правили (Фиг. 6, 7 и 8).

Фиг. 6. Рисунка с *C. tropicalis, R. rubra, S. cerevisiae* и *K. mara* на HiCrome ™ Candida Differential Agar от Мирела Атанасова

Фиг. 7. Рисунка с *C. albicans, C. utilis* и *C. tropicalis* на HiCrome ™ Candida Differential Agar от Нели Атанасова

Фиг. 8. Рисунки с *C. albicans, C. utilis, C. tropicalis* и *K. mara* на HiCrome ™ Candida Differential Agar от Севдалина Тодорова

ИЗВОДИ

Хромогенните среди дават възможност откриването и идентифицирането на микроорганизмите да става лесно, бързо и надеждно.

Хромогенните субстрати, включени в агара, се хидролизират от специфичните ензими на дрождите, което води до характерното оцветяване на различните видове дрожди и прави нашите рисунки многоцветни.

За първи път е определено оцветяването и растежа на видове *C. utilis, R. rubra, E. magnussii, S. Ludwigii, K. mara* на HiCrome ™ Candida Differential Agar.

Интензитетът и специфичността на цветовете са ясни и характерни и се засилват с възрастта.

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SAT–LB-P-2-BFT(R)-12

DETERMINATION OF FATTY ACID PROFILE OF SUNFLOWER OIL SAMPLES BY NMR ^{1}H SPECTROSCOPY

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Abstract: *Sunflower oil with a high content of oleic acid (Omega-9) and a sufficiently low content of polyunsaturated linoleic acid (Omega-6) is characterized by a lower nutritional value but greater chemical stability at high temperatures and in the presence of oxidizing agents, therefore, it has several advantages for the food and chemical industries, and also as a raw material for the production of biofuels. The determination of the TAG composition of oil is very important, because due to selection there is a large number of sunflower varieties. The spectra of oil samples extracted from seeds of various sunflower varieties were investigated by NMR ^{1}H spectroscopy to determine fatty acids composition. This method based on estimation and comparison the proton integral intensities of allylic and bis-allylic CH_2 groups with intensity of glycerol protons that allows to determine the amounts of these unsaturated fatty acids. Each oil sample obtained has its individual TAG profile determining its physicochemical properties and nutritional value. Method ^{1}H-NMR spectroscopy is rapid and non-destructive, so it is perspective for determination of oil fatty acid composition.*

Keywords: *Sunflower oil, Fatty Acid, Oleic Acid, Linoleic Acid, NMR Spectroscopy, Fatty Acid Profile.*

INTRODUCTION

Recently, sunflower varieties with a high content of oleic acid (more than 82%) have been becoming more popular with producers, traders and agricultural processors. According to published data, the seeds of ordinary varieties of sunflower contain only 27-40% of this acid. Oil with a high content of oleic acid (Omega-9) and a relatively low content of linoleic acid (Omega-6) is characterized by less nutritional value, but more technological one, since it more chemically inert under high temperatures and in the presence of oxidants and can be stored almost four times longer saving its properties compared to oils with a lower percentage of oleates (Lee, 2000). Further, oils with a high content of oleates are perspective sources for obtaining biofuel (biodiesel) in regions where the cultivation of rapeseed is unprofitable (Holt, 2016). Sunflower oil with a high content of oleic acid has become a serious competitor to olive oil in the world market, since it is much cheaper and not inferior to olive oil in the chemical composition, and, moreover, in some cases surpasses it. The growing popularity of sunflower hybrids with a high content of oleic acid causes of an increase

in acreage for cultivation them. That contributes to cross-pollination of hybrid and non-hybrid of sunflower varieties, therefore the fatty-acid profile of sunflower oil depends not only on the plant species, but also on the region where they are grown. The fatty acid profile of oils is the major factor influencing their chemical and physical properties and subsequently their various applications (Atanasova, 2016). Thus, the issue of express method to determine the fatty-acid composition of sunflower oil to use sunflower raw materials rationally is acute on the agenda. Due to their chemical composition sunflower lipids are very susceptible to oxidative processes owing to their degree of unsaturation, giving rise to the development of off-flavour and a decrease of nutritional quality and safety. Especially the more unsaturated fatty acids with bis-allylic methylene groups are susceptible to oxidation. One of the express and non-destructive methods for determination of fatty acid profile and oxidation products is NMR ^{1}H spectroscopy providing a straightforward approach to quantitative analysis of oils and enabling a simultaneous detection of different oxidation products in one single analysis. The common unsaturated fatty acids such as oleic and linoleic, in an oil can be quantified using NMR ^{1}H. This method utilizes the area per proton (determined by integration) and gives equations for determining the amounts of the unsaturated fatty acids. Up to now, NMR is not widely used in food control and in food industry.

The aim of this work was to study the triacylglycerols composition of some sunflower oil samples by NMR ^{1}H spectroscopy. Samples of oil obtained from seeds of different sunflower varieties, NMR ^{1}H spectroscopy, computer program ADVASP Analyzer for processing spectra data, a method for quantitative comparison of the integrated intensities of typical signals of groups containing hydrogen atoms in NMR ^{1}H spectra. Deuterated chloroform ($CDCl_3$) that is probably the most commonly used solvent in NMR experiments on fatty compounds and was used here to obtain the spectra depicted. The spectra of prepared solutions were recorded on a Varian VXR-300 spectrometer.

EXPOSITION

Some of shown spectra may contain minor impurities, which are visible in the spectra. The impurities and their signals are not discussed. All spectra were obtained at 300 MHz. For sake of consistency, the integration value of the secondary CH_2 protons of glycerol moiety in the triacylglycerol molecule was chosen as reference in most spectra and assigned the value that is a multiple of 4.00. Usually, the spectral range of 0-6 ppm is shown since it covers the range of chemical shifts in most fatty compounds. Besides serving as solvent, $CDCl_3$ is also the reference material for chemical shift values with residual chloroform giving a peak at 7.29 ppm, although the exact shift values of the same peaks can vary slightly from spectrum to spectrum. In accordance with IUPAC nomenclature, carbon atoms are counted from the carbon carrying the carboxylic acid or ester group in the fatty acid chain, with this carbon being C1 (see Fig. 1 and Fig. 2) The presence of few quantity of phospholipids in the oil does not significantly affect the results of interpretation of spectra.

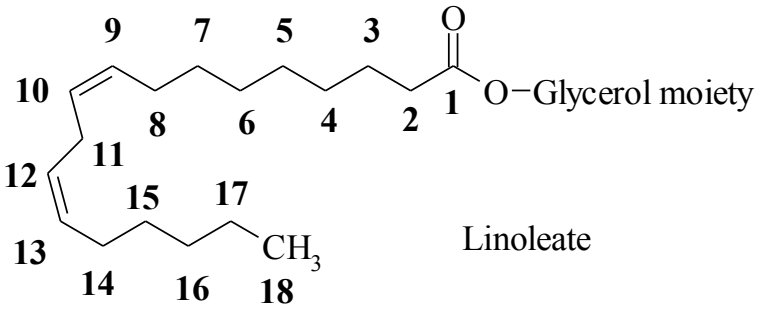

Fig. 1. General structure of linoleate

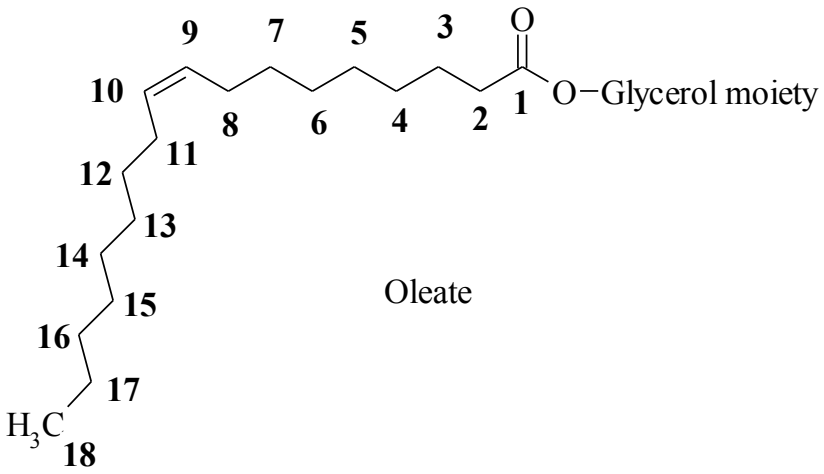

Fig. 2. General structure of oleate

Sunflower oil consists of 99.9% triacylglycerols and about 90% of them are represented by esters of oleic (Omega-9) and linoleic (Omega-6) acids. From consideration of NMR spectra in the literature various resonances can be assigned to specific chemical groups (see Table 1).

Table 1. Chemical shifts of protons in NMR spectra

Signal	Functional group	Chemical shift (ppm) of protons in oleic and linoleic esters of glycerin
1	$–CH_3$	0.96 – 0.82 (dd)
2	$–CH_2$-	1.43 – 1.16 (m)
3	$–CH_2$-C-CO_2	1.70 – 1.51 (m)
4	$–CH_2$-CO_2-	2.11 – 1.91 (m)
5	–C-CH_2-C=C-	3.38 – 2.21 (m)
6	–C=C-CH_2-C=C-	2.83 – 2.73 (t)
7	–C-CH_2-O-CO-C	4.21 – 4.08 (dd)
8	–C-CH_2-O-CO-C	4.36 – 4.22 (dd)
9	–CH(-C-O-CO-C-)$_2$ + C-HC=CH-C	5.43 – 5.13 (m)

Signal multiplicity: s, single; d, doublet; t, triplet; m, multiplet

The set of peaks at δ5.2 – 5.5 ppm arises largely from the ^{1}H nuclei attached to carbons involved in a double bond, usually referred to as olefinic. Signals at δ2.7 ppm arise from bis-allylic protons from the $–CH_2–$ group located between pairs of unsaturated bonds (see Fig. 3).

Peaks of allylic protons at C8, C11 for oleic acid C8, C14 for linoleic acid are located at about 2.05 ppm. In accordance with increasing in the percentage of linoleic acid in sunflower oil, the theoretical integrated values of the olefinic, allilyc and bis-allylic protons also increase while that of the high peak of CH2 group located at about 1.43 – 1.16 ppm decreases.

However, changes in the integrated intensity of proton signals at 1.43-1.16 ppm can not be used to estimate the number of CH_2 groups of fatty acid residues in the triacylgicerols, since signals of aliphatic solvents often used for extraction of oil from seeds are located in the same region.

To quantative determination unsaturated fragments of oleic and linoleic acid molecules , the integrated intensities of vinylic (H_v), allylic (H_a) and bis-allylic hydrogen (H_b) atoms in ^{1}H NMR spectra were used (see Fig. 3).

The ratio of the integral intensities of the signals of the hydrogen atoms of allylic (H_a), bis-allylic (H_b) groups and the tertiary hydrogen atom of the glycerol residue (H_g) is not a sufficient argument to make conclusions regarding the quantitative composition of fatty acids in sunflower oil, since the integrated intensities of allylic and bis-allylic protons can be significantly decreased

due to oxidation processes in the triacylglycerol molecules proceeding as a result of long-term storage of the oil. (Stephenson, 2005)

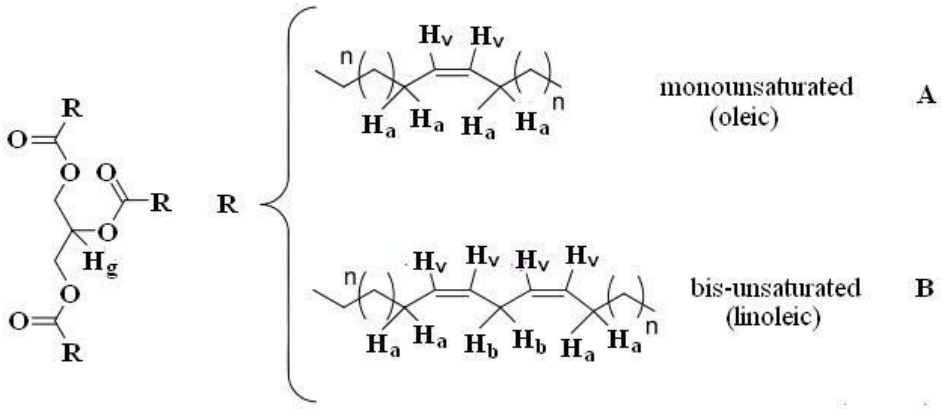

Fig. 3. General structure of triacylglycerides of sunflower oil.

Besides, in practice, it is often impossible to separate the signal of the tertiary hydrogen atom Hg of the glycerol residue from the signals of vinyl hydrogen Hv in the obtained spectra, that is, in the spectra the integrated signal intensity at 5.2 - 5.5 ppm depends on the total number of H_v and H_g atoms.

The results of the monitoring fatty acid composition by NMR ^{1}H spectroscopy confirm a progressive decrease in the contribution of linoleic acid throughout the store period. As result of the oxidative processes, at first, the ratios of relative intensities between bis-allylic protons (H_b) to allylic protons (H_a) decreased. Finally, peaks of bis-allylmethylene protons (H_b) almost disappeared.

With increasing storage time, the process becomes more and more complicated since primary oxidative products undergo further reactions forming volatile and non-volatile secondary products. Thus, the very small peak of aldehyde group is observed at δ9.74 ppm that is in according to literature (Wong, 2017).

Therefore, to determine the quantitative ratio of oleic and linoleic acids, it is necessary to compare the integrated intensities of the signals H_a at 1.95-2.07 ppm and H_b at about 2.75-2.85 ppm between themselves, relative to the secondary hydrogen atoms of the glycerol fragment at 4.1-4.3 ppm and the signals at 5.2 - 5.5 ppm, corresponding to the Hv and Hg atoms, taking into account the contribution of hydrogen atoms of each acyl residue (Vlahov, 1999).

It should be taken into account that the integral intensities of the hydrogen atoms of the CH_2 groups of the glycerol fragment and allylic group must be a multiple of four and the bis-allylic group must be multiple of two.

The NMR ^{1}H spectrum of the high-oleic oil obtained from sunflower seeds provided by Institute of Oilseed Crops of the Ukrainian Academy of Agricultural Sciences (IOC UAAS) is shown on Fig. 4. The spectrum of this sample demonstrates the presence of signals mainly oleates, and percentage of them is almost 95%. The content of linoleic acid detected by very weak typical signals at about 2.75-2.85 ppm does not exceed 1%.

In the spectrum of the sunflower oil sample № 2 (Fig.5), beside signals of oleic acid, peaks of polyunsaturated linoleic acid in the region of 2.75-2.85 ppm are identified exactly. The ratio of oleic and linoleic acids in this oil sample is 9:1, that is, the mass fraction of oleates reaches almost 89%, and of the polyunsaturated acids do not exceed 11%.

The ^{1}H NMR spectrum of the sunflower oil sample № 3 (see Fig. 6), obtained from sunflower seeds purchased in local markets, shows that the ratio of oleic and linoleic acids is 1: 2, that is, the oleic acid content in that sample is about 32%.

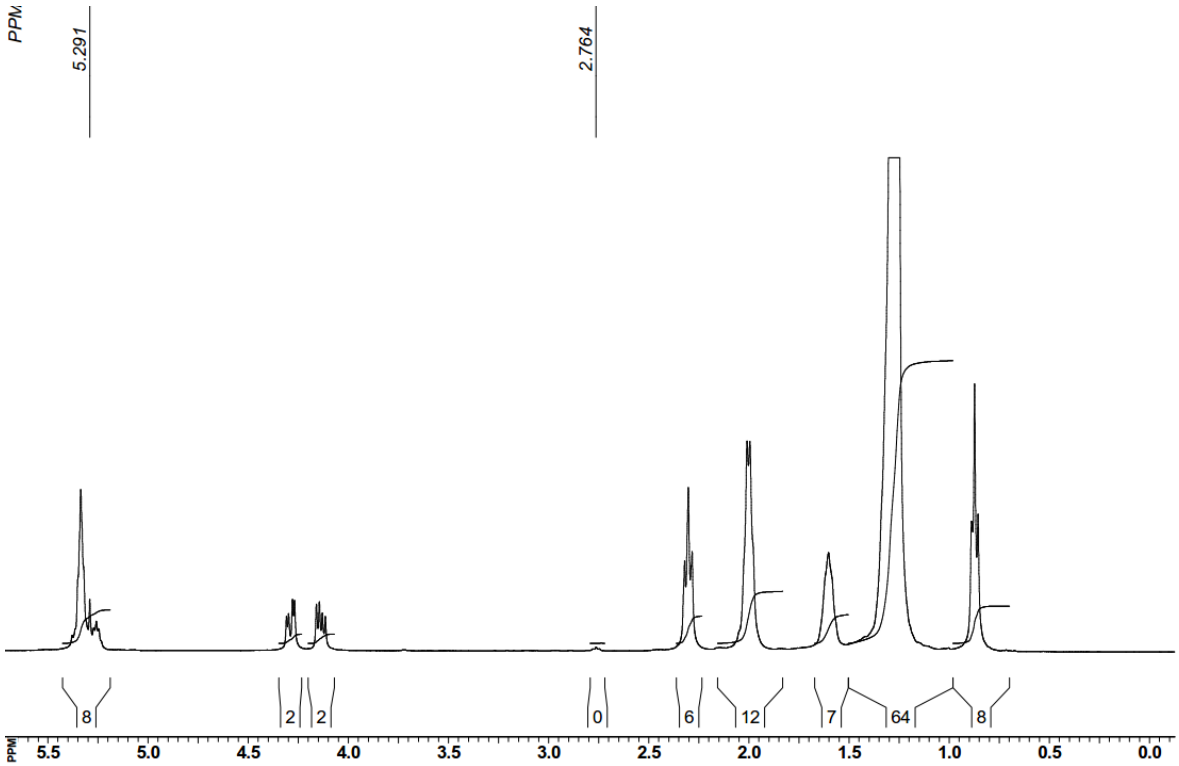

Fig. 4. NMR ^{1}H spectrum of high-oleic sunflower oil (sample №1)

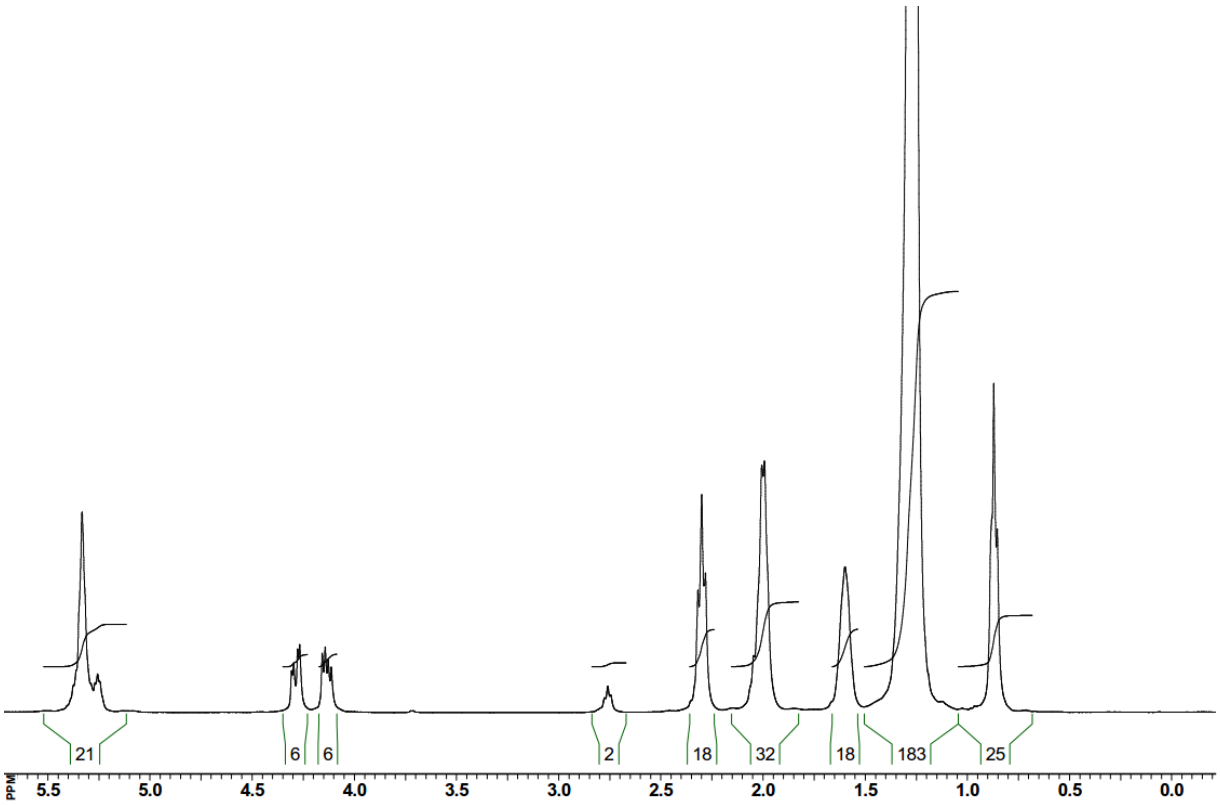

Fig. 5. NMR ^{1}H spectrum of the sunflower oil (sample № 2)

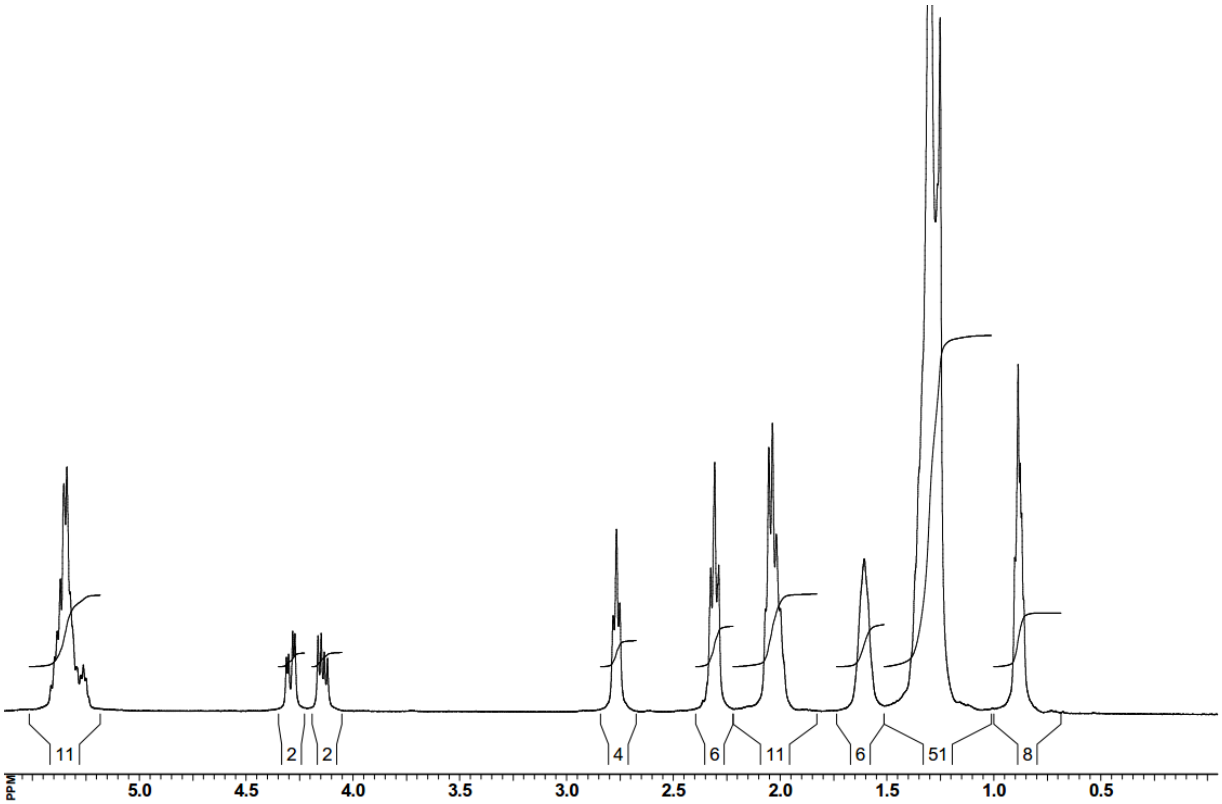

Fig. 6. NMR ^{1}H spectrum of the sunflower oil obtained from seeds bought in local markets (sample № 3)

CONCLUSION

The non-destructive and express method of NMR ^{1}H spectroscopy is a perspective tool for the quantitative determination of oleic and linoleic acids content in sunflower oil, that, under modern conditions of agricultural cultivation is characterized by a non-permanent fatty-acid composition, to aim of determination of the most optimal course for use of seed raw materials. NMR ^{1}H spectroscopy may be used as express and non-destructive method of estimation of sunflower oil quality.

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SAT–LB-P-2-BFT(R)-13

STUDYING THE BORROWING STRUCTURE OF BAKERY PRODUCTS

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Abstract: *Bakery products after mixing by working elements of various configurations are estimated by physical and chemical indicators, one of the important consumer qualities of bread is its freshness and porosity.*

Among the most important organoleptic characteristics of porosity the uniformity of the arrangement of pores and their size were determined. After mixing, the yeast dough should increase in volume, acquire a capillary-porous structure, in which pores will form gaseous fermentation products. Studies have been carried out on the influence of costs of specific work during mixing on the formation of the number of pores in the cereal product.

Porosity characterizes the important qualitative property of bread. Low porosity is usually characterized by bread from poorly-battered yeast dough. By means of enhanced mechanical processing of the dough, the specific work required for the batch increases and the qualitative parameters of the porosity of the finished product increase accordingly. The porosity and structure of the porosity of finished products were investigated, preliminary kneading the yeast dough with the working elemets of different configurations.

Keywords: *Mixing, Yeast Dough, Porosity, Structure, Distribution.*

INTRODUCTION

The mixing of the yeast dough was carried out on a kneading machine of continuous action, used to knead the screw, finger and cam working elements. After kneading the yeast dough, had been vibrated for 30 minutes and baked in the oven for about 12 minutes. Porosity was investigated using ImageJ software.

The porosity of bread is an important indicator of its quality. After mixing, the yeast dough should increase in volume, acquire a capillary-porous structure, in which pores will form gaseous fermentation products. For the formation of a dough with an elastic structure, it is required that the gluten proteins are elastic and envelop the whole grain of starch with a thin film. If the protein is insufficient or the gluten is not elastic, the dough will have a low gas-retaining capacity, which in turn will reduce the formation of porosity.

EXPOSITION

Investigations have been carried out on the influence of the costs of specific work during mixing on the formation of the number of pores in the bread product (Fig. 1). Porosity characterizes the important qualitative property of bread. Low porosity is usually characterized by bread from poorly-battered yeast dough. Due to enhanced mechanical processing of the dough, the specific work required for the batch increases and the qualitative parameters of the porosity of the finished product increase accordingly.

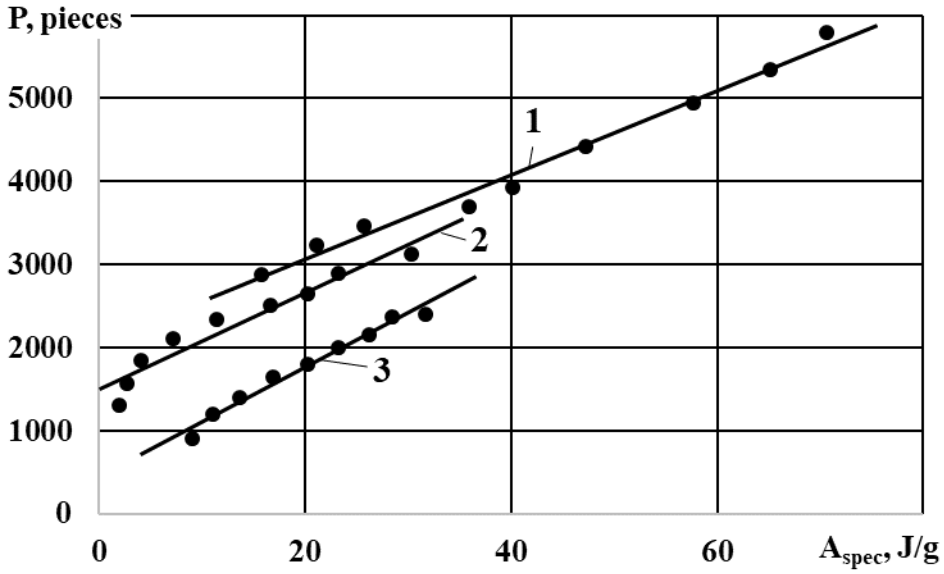

Fig.1. Investigation of quantitative indices of porosity of the finished product from the costs of specific work on mixing the yeast dough (1-Cam working element; 2-Screw working element; 3-Finger working element)

The processed experimental data shows that, with increasing costs of specific work on the batch, the number of pores in the finished product increases as well.

During the kneading of the yeast dough by the cam and the fingers, linear dependence is observed, while for the screw working elements, the curve has a degree of dependence. For the costs of the specific work of 20 J/g among the represented working elements, the greatest number of pores (3241 pieces) is formed when kneading the yeast dough by cam operating elements.

The influence of the specific work during the cam shaking by the working elements on the formation of the number of pores in the finished product is determined by the mathematical formula:

$$П = 50{,}6A_{spec} + 2056, \text{ pieces} \quad (1)$$

A_{spec} – the costs of the specific work on mixing the yeast dough, J/g.

The highest number of pores is 2884-5786 units formed during the kneading of the yeast dough by the cam operating aelements, there is an intensified mechanical treatment of the dough, the performance of the specific work reaches 15-70 J /g, in the process of kneading the dough does not rupture and shrinks, thus a quality batch is produced, the dough becomes elastic, gluten films hold off carbon dioxide and a fine-grained uniformly distributed pore structure is formed throughout the volume of the finished product.

The influence of specific work during mixing by screw working elements on the formation of the number of pores in the finished product is determined by the mathematical formula:

$$П = 58A_{spec} + 1501, \text{ peices} \quad (2)$$

A_{spec} – the costs of the specific work on mixing the yeast dough, J/g.

Indicators of the specific work during the kneading of the yeast dough vary in the range from 2 to 30 J/g, according to these values, the number of pores reaches 1311-3126 pcs. The process of mixing in this case takes place in a short time, as a result, the gaseous phase is represented by bubbles of air, the captured dough during the mixing is unevenly distributed in the volume of the finished product, increases the pore size but reduces their amount.

The influence of specific work during the kneading by the digital working elements on the formation of the number of pores in the finished product is determined by the mathematical formula:

$$П = 65{,}2A_{spec} + 460, \text{ pieces} \quad (3)$$

A_{spec} – витрати питомої роботи на замішування дріжджового тіста, J/g.

Expenditures of specific work during kneading by the finger work elements reach 9-31 J/g, low amount of pores (902-2410 units) in this case is explained by the fact that the components are

not equable mixed, mixing by the finger's working elements leads to a constant breakdown of the gluten of the dough, which does not have time to recover as a result of gluten films are not able to fully retain carbon dioxide necessary to further form the fine-grained porosity of the product.

Bakery products after mixing by working elements of various configurations are estimated by physical and chemical indicators, one of the important consumer qualities of bread is its freshness and porosity. Among the most important organoleptic characteristics of porosity were determined the uniformity of the arrangement of pores and their size. The porosity and structure of the porosity of the finished products (Fig. 2) was investigated, after having previously subjected to different configurations by the working elements of the yeast dough.

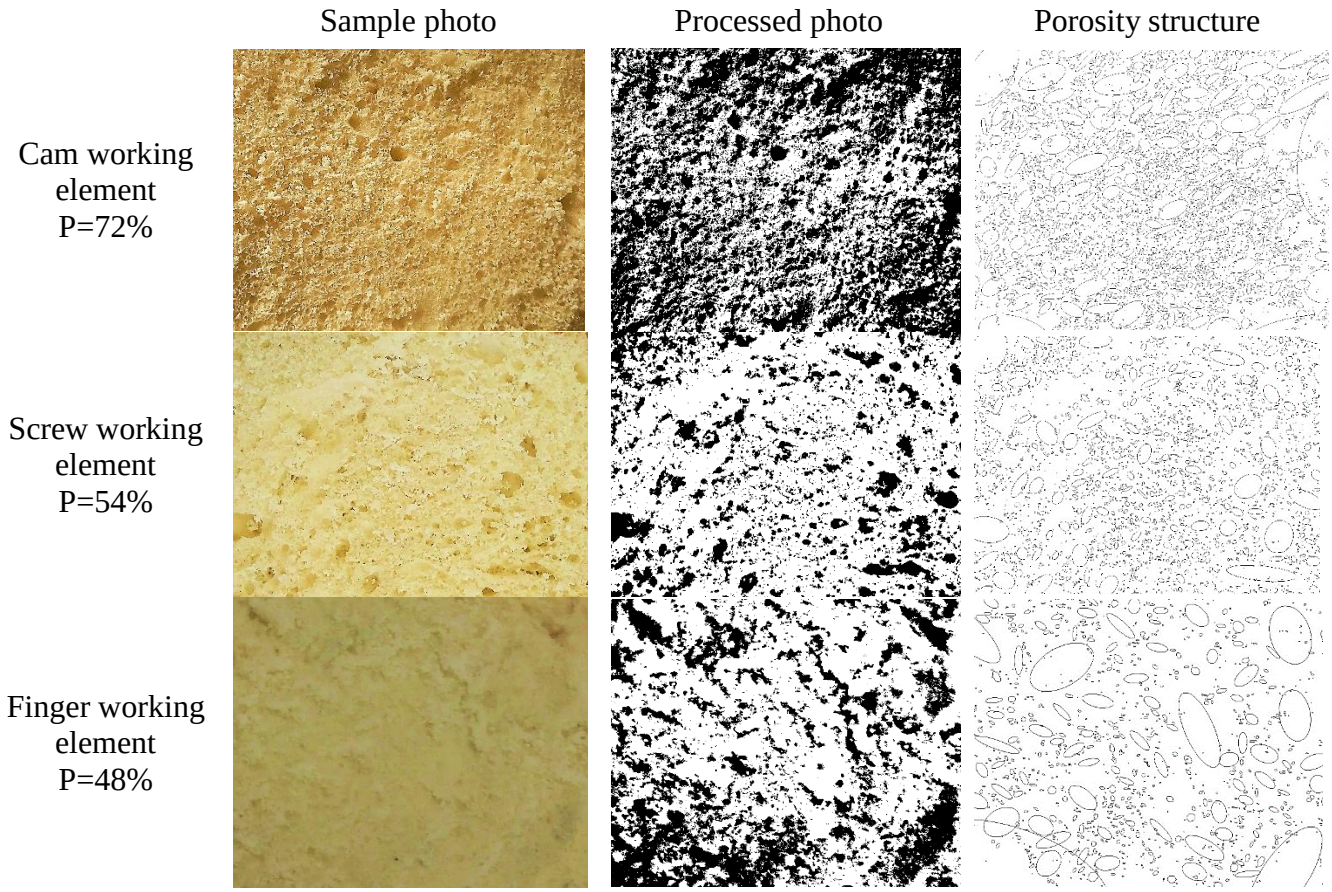

Fig.2. Structure of porosity of finished products after mixing by working elements of various configurations

The uniform fine-grained porosity of the finished product, P = 72%, is observed after mixing the yeast dough by the cam working elements, their mechanical effect improves the function of the microflora of the dough and maintains the elasticity of the surface, thereby increasing porosity and as a result, an increase in the volume of dough preform after baking and baking. The porosity of the finished product, after mixing with screw working elements, reaches 54%, reduced porosity indices are explained by the fact that some components of the dough at the first stage merged and in the future due to the rapid transport power of screw working elements did not have time to qualitatively pass the stage of actual kneading and plasticization. The mixing by the finger work elements resulted in damage to the gluten-free dough frame, resulting in a merger of small pores and the formation in some places of the volume of a large, unevenly distributed throughout the volume of the product, porosity of the bread P = 48%, and as a result of a decrease in the ' a large output of bread.

CONCLUSION

It has been established that with increasing energy consumption, the best dough mix takes place and more pores are formed. The influence of working elements of different configurations on qualitative indices of the finished product is investigated. It was found that the best porosity indices are observed when kneading the yeast dough by cam operating oelements. Indicators of porosity reach 72%. After mixing the yeast dough with the cam working elements a uniformly distributed fine-grained porosity is formed.

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SAT–LB-P-2-BFT(R)-14

INFLUENCE OF ELECTROPHYSICAL WATER TREATMENT ON THE PROCESS OF BEVERAGES SATURATION

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Abstract: *The content of carbon dioxide, which is actively used by producers of carbonated beverages as a preservative, acidity regulator and antioxidant, significantly affects the quality of finished products.*

The possibility of changing the ph value, which affects the balance between carbon dioxide, bicarbonate and carbonate during saturation, by electrophysical treatment of water was considered. Industry produces various variants of electrolysers, but they are not suitable for saturation of drinks. Therefore, the development of an appropriate design is an urgent task.

It is expedient to carry out the process of saturation simultaneously with the electrophysical treatment of pre-prepared (cooled and deaerated) water. The parameters that influence the efficiency of electrophysical treatment and the quality of finished products are the voltage, the voltage-ampere characteristic, the mutual placement of the electrodes, the duration of activation, the degree of mineralization of the solution. The influence of material of equipment, including electrodes, on the content of metals in the carbonated beverages is also taken into account. Electrodes in the process of operation should not experience electrochemical destruction. It is expedient to make an anode from a titanium, a cathode - from a corrosion resistant steel AISI 321.

Keywords: *Saturation, Beverage, Electrophysical treatment, ph value.*

INTRODUCTION

The non-alcoholic beverages market is one of the few that is showing positive dynamics in Ukraine. At the same time, sales of aerated diet and soft drinks are increasing, despite the warnings of doctors and scientists about the harm of such products for health (Shenkin, J. D., 2003; Malik, V.S., 2006).

An important stage in the production of carbonated beverages is their saturation - the saturation of the drink with liquid carbon dioxide at a certain temperature and pressure. The basis of this process is the ability of carbon dioxide to interact with water to form an aqueous solution.

By the level of saturation of carbon dioxide, the largest share on the market is concentrated in medium- and stronglycarbonated beverages. Such a structure of consumption is justified by the fact that carbon dioxide is actively used by non-alcoholic beverage producers as a preservative, acidity regulator and antioxidant (Solov'yeva, M. P., Karkh, D. A., CHugunova, O.V., 2017).

EXPOSITION

The content of carbon dioxide in beverages has a significant effect on the quality indicators of finished products, so looking for ways to intensify the saturation process is an urgent task.

For revealing of factors influencing saturation of water by CO_2, and intensification of this process, the scientific and scientific-technical literature for the last twenty years has been analyzed. Attention was paid to both the technical side of the process and the impact of products on consumer health.

The amount of gas G absorbed by the liquid phase

$$G = k \cdot F \cdot \Delta p \cdot \tau, \quad (1)$$

k – the absorption coefficient of carbon dioxide by water (may be 12,8, which corresponds to the solubility of 87 ml of gas in 100 mg of water); F – the phase contact surface, Δp – the difference of partial pressures in the gaseous and liquid phases; τ – the process duration.

From equation (1) it can be seen that the speed of the mass transfer process is directly proportional to the absorption coefficient, the contact surface of the phases and the difference of the partial pressures. The absorption coefficient depends on the temperature. The dissolution of gases in liquids is almost always accompanied by the heat release. Therefore, the solubility of gases with increasing temperature, in accordance with the principle of Le Chatelier, is reduced. The absorption coefficient decreases with increasing temperature. There is a concentration of gas at which the equilibrium between its gaseous and dissolved forms is established. When dissolving gas in water there is a significant decrease in the system volume. Therefore, increasing the pressure, in accordance with the principle of Le Chatelier, should lead to a shift of equilibrium to the right, that is, to increase the solubility of gas. If the gas is slightly soluble in the liquid and the pressure is small, then the solubility of the gas is proportional to its pressure. This dependence is expressed by Henry's law (1803): the amount of gas dissolved at a given temperature in a certain volume of a liquid, at equilibrium is directly proportional to gas pressure. Henry's law can only be used for relatively dilute solutions, with low pressures and the absence of chemical interaction between soluble gas molecules and solvent.

Saturation is carried out to the carbon dioxide content in a solution of 0.5 - 0.6% by mass. The saturation limit depends on the temperature and pressure at which the gas is dissolved. Such, at 2 ° C and an excess pressure of 490 kPa, the gas solubility is 19.234 g/l. However, obtaining an extremely saturated solution is not expedient, since the bulk of carbon dioxide is absorbed in the initial period of saturation at a significant difference in partial pressure. In the next period, as the system approaches the conditions of the phase equilibrium, mass exchange becomes ineffective and a long time is required to achieve the boundary saturation. When choosing the optimal saturation regime, it should be kept in mind that too high a difference of partial pressures in the solution and gas environment causes the formation of a supersaturated solution. In such a solution, carbon dioxide is not tightly bound to water, quickly desorbed and does not provide high quality beverages.

Therefore, an intensive mass transfer can be achieved at high gas pressure, a large contact surface of the phases and low temperature of the aqueous solution. The rational conditions of carbonation are: pressure of CO_2 0,49 – 1,18 MPa, water temperature 1 – 2 °C. Salt content in water also changes the solubility. The contact surface can be increased by vigorous mixing of water in the atmosphere of CO_2, fine water sputtering, water drainage on a nozzle with a large surface in the form of a film in CO_2 atmosphere. To change the absorption coefficient, water activation methods are used which involve the use of shock waves, ultrasound, magnetic field, microwave radiation.

Taking into account this information, in the industry, water is pretreated before saturation - cooled to 2 – 6 ° C and deerated (dissolved air and other gases remove from the water). These processes are a requirement of technology aimed at both improving the quality of beverages and increasing the efficiency of carbonation.

In addition to external factors - pressure and temperature - the carbon dioxide solubility also depends on the nature of the gas and its properties to enter into chemical reactions with water.

In terms of chemical kinetics, the process of carbon dioxide dissolving in water is quite complex. When CO_2 dissolved in water, then the equilibrium between the carbonic acid H_2CO_3, bicarbonate HCO_3^- and carbonate CO_3^{2-} is established:

$$H_2O + CO_2 \leftrightarrow^{*} H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-}.$$

The equilibrium of this system is strongly shifted to the left, because carbon dioxide - the compound is unstable and easily decomposes into carbon dioxide and water. The ionization constant of the pKa process at the same time is $2{,}46 \times 10^{-17}$.

However, only 1% of CO_2, which is in an aqueous solution, is present in it in the form H_2CO_3. Many researchers have drawn attention to this discrepancy, therefore, for the convenience of calculations of chemical equations, pKa and pH it is assumed that everything CO_2 reacts with water.

The balance between carbon dioxide, bicarbonate and carbonate depends on pH. Here the principle of Le Chatelier's affects: a presence in the solution of hydrogen ions displaces the alkaline reaction of the medium to the acid side (pH up to 5.5). Conversely, removing protons from the system displaces the reaction equilibrium to the left when carbon dioxide is rehabilitated oneself from carbonate and bicarbonate (Homen, 1992). Thus, at a low pH value, carbon dioxide prevails in the system, and in fact no bicarbonate or carbonate is formed, whereas at a neutral pH value, bicarbonate dominates. And only at high pH carbonate predominates (Fig. 1).

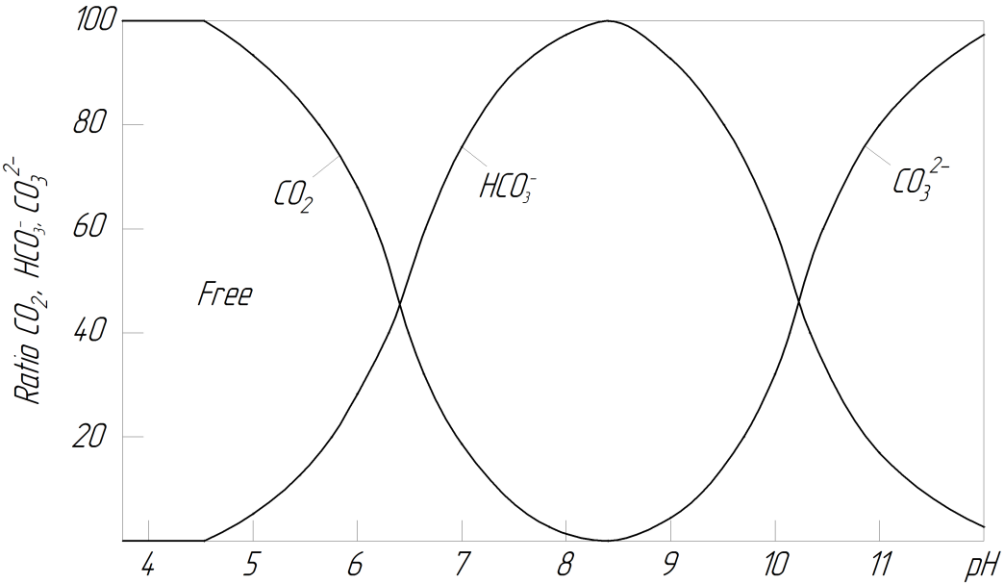

Fig.1. Relationship between Carbon species and pH

Therefore, we consider the possibility of changing the pH value of water, which determines the course of many chemical, technological and biological processes (Dolinskiy, A. A., SHurchkova, YU.A., (2013), before carbonization. pH value and oxidative-reducing potential (ORP) many scientists associate with the peculiarities of the structural water organization and its subsequent influence on living organisms. It's possible to determine pH and ORP by potentiometric method on the device pH-meter I-160 MP.

Numerous studies are devoted to the process of water activating under the influence of various factors - temperature, electric current, ultrasound, magnetic field, etc. It was decided to focus on the electrochemical treatment of water, in which water passes into a metastable state, which is characterized by abnormal values of the electrons activity and other physical and chemical parameters. When electrolysis occurs on a cathode and an anode, a series of chemical reactions takes place. As a result, the system of intermolecular interactions, the composition of water, including the water structure as a solution, changes (Tsarenko, YU.YU., 2014).

Various variants of electrolysers, which are conventionally divided into three types: static, immersed and continuous-flow (Fig.2), are produces for the electrochemical conversion of water and aqueous solutions of electrolytes (Kurchenko, N.YU., Kovko, V.A., 2012). But they are unsuitable for carbonization of beverages.

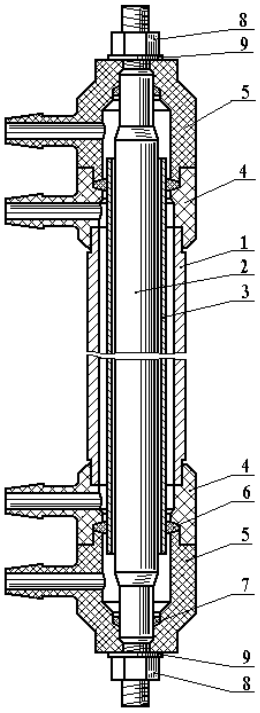

Fig.2. Continuous-flow electrolyser:
1 – cathode; 2 – anode; 3 – diaphragm; 4 – sleeve; 5 – head; 6, 7 – seals; 8 – nut; 9 – washer

The process of electrochemical activation of water and aqueous solutions is influenced by the distance between the electrodes, the voltage of the direct current supplied to the electrodes, the current strength, which is fed to the electrodes, the activation time, the degree of the solution mineralization (Amcheslavskiy, O.V., 2011).

Under the Ohm law, the current strength is a voltage function, but in experiments it also depends on the distance between electrode and a time. At a certain value of the distance L between the electrodes, the current value reaches its maximum, then begins to decrease. This is due to the counteraction of the chaotic heat motion to the electric directional charged particles movement due to rising temperature of the solution as a result of electrochemical treatment. It is also important to take into account the influence of the equipment material, including the electrodes, on the metal content of the finished product (Mareci, D., Trinca, L., Cotea, V., Souto, R., 2017). Electrodes in the operation process should not undergo electrochemical destruction. In published studies using mass-spectrometric studies of the chemical elemental composition of water before and after its electrochemical activation, it was found that the anode should be manufactured from titanium, a cathode from corrosion-resistant steel AISI 321.

As a result of electrochemical treatment the products must meet the established requirements. It is also advisable to control the size of carbon dioxide bubbles, because carbonated beverages containing smaller bubbles have the advantage in taste (Barker, G., Jefferson, B., Judd, S., 2002).

CONCLUSION

It is advisable to realize the saturation process simultaneously with the electrochemical treatment of pre-prepared (cooled and deaerated) water. Parameters that influence the efficiency of electrochemical treatment and the quality of finished products are the magnitude of the voltage, the voltage-ampere characteristic, the relative position and the electrodes material. They will be considered as controlled parameters in further research.

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SAT–LB-P-2-BFT(R)-15

RESIDUES OF ORGANOPHOSPHORUS PESTICIDES IN APPLES

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Abstract: *Apples have a significant positive impact on human health. In the market, the apple supply lasts all year round and this is made possible by cultivating different types of apples. In the Republic of Macedonia, apples are mostly cultivated in the Prespa Region. During the process of cultivation there are used pesticides which belong to different chemical groups, such as organophosphate, organochlorine, pyrethroids, carbamates, dithiocarbamates etc. The purpose of this research was to determine the residue analysis of organophosphorus insecticides in apples: chlorpyrifos, dimethoate and omethoat. There were taken samples of apples from two different locations, Drmeni and Jankovec from Prespa Refion. The processes of extraction/separation and purification were done using acetonitrile and dispersive SPE-QuEChERS method and for their analysis were applied UPLC-TQ/MS. The concentration of residues of insecticides in apples from Jankovec was in the range of 0.01-0.03 mg/kg while in apples from Drmeni the value was between 0.02-0.05 mg/kg. The results show that parts of the analyzed apples containin insecticides with a higher concentration than the maximum residue limit (MRL), therefore the apples are not safe for consumption. Contamination of fruits with pesticides residues in general is one of the most important aspects of the food quality assurance. In order to provide consumers with food that does not contain residues of pesticides above the MRL, it is necessary to reduce the use of pesticides and to increase the application of integrated protection of crops, as well as to monitor and control products from authorized institutions.*

Keywords: *insecticides, apples, QuEChERS, UPLC-TQ/MS*

INTRODUCTION

Apples are one of the most important deciduous fruits belong to the family *Roseceae* and the *Pomoideae* subfamily (Phipps, J. B., 1990). In the market, the apple supply lasts all year round and this is made possible by cultivating different types of apples. Their cultivation depends on the region, the climatic and geographical conditions, the amount of solar radiation, the dry summers and sharp winters, the rainy regions, etc., followed by the different resistance of varieties of apples to pests and diseases. The apple is a delicious fruit, easy to process, and is low on calories. It is a source of vitamins and minerals, including: vitamin A and C, calcium, phosphorus, iron, potassium, soluble and insoluble dietary fiber (Chen, M., Tao, L., McLean, J., & Lu., Ch., 2014). Apples have a significant positive impact on human health (Łozowicka, B., 2015).

Chemical measures for the protection of apples (use of pesticides) are the most effective in the eradication of pests and diseases (Balaž, J., Grahovac, M., Radunović, D., Iličić, R., & Krstić,

M., 2013). During the process of cultivation pesticides are used which belong to different chemical groups and have different mechanisms of action, such as organophosphates, organochlorines, pyrethroids, carbamates, dithiocarbamates, etc. (Jankuloska, V., Karov, I., Pavlovska, G., & Kalevska, T., 2017). Numerous countries are currently initiating programs to reduce pesticide usage in conventional agriculture (Sinha, N. S., Vasudev, K., & Rao, V. V. M., 2012). Organophosphorus pesticides (OPs) used mainly as insecticides, are esters of phosphoric acid with different substituents (Pagliuca, G., Gazzotti, T., Zironi, E., & Sticca, P., 2005). This substances act trough inhibition of acetyl-cholinesterase and represent a risk to human health (Wesseling, C., Keifer, M., Ahlbom, A., Micconnell, R., Moon, J. D., Rosenstock, L., & Hogstedt, C., 2002).

Chlorpyrifos is an organophosphorus pesticide (insecticide) used to protect apples from insects that can cause significant harm in the production of apples (Jankuloska, V., Karov, I., Pavlovska, G., & Buzlevski, I., 2017). Dimethoate is a contact and systemic organophosphorus insecticide (acaricide) and its main toxicological endpoint in animals and humans is the inhibition of acetylcholinesterase (AChE) activity. Omethoate is an oxygen analogue metabolite of dimethoate and plays a dominant role in the toxicity of dimethoate for insects and mammals, i.e. it is a toxic metabolite of dimethoate. In acute exposures, this insecticide is considered highly toxic after oral intake and moderately toxic if it enters the body through the skin or is inhaled (Hayes, W. J., & Laws, E. R., 1990).

Pesticides that are allowed to be used as means of protection in the Republic of Macedonia are presented in the list of allowed active substances (Official Gazette of the Republic Macedonia., 105, 2013) and MRL for residue of pesticides are given on Rulebook on general requirements for food safety (Official Gazette of the Republic Macedonia., 156, 2013). A plant product or food should be destroyed or banned from use if it contains pesticides residue with a higher concentration than MRL (maximum residue limit). Pesticide residue in agricultural products and foods above the MRL that is legally tolerated is the result of inadequate application and application of pesticides in agricultural practice and storage (Bursić, V., Vukovic, G., Spirovic, B., Lazić, S., Pucarevic, M., & Zeremski, T., 2013). Therefore it is necessary to pay attention to withdrawal periods for each pesticide (Sadło, S., Szpyrka, E., Jaźwa, A., & Zawiślak, A., 2007). Although the application of pesticides is high, in the last years the integral protection of apples has gained significance. This type of protection involves the use of natural agents for suppression and use of selective insecticides, which preserve the environment, while simultaneously contributing to the production of health food safety food (Miletić, N., & Tamaš, N., 2009; Fenik, J., Tankiewicz, M., & Biziuk, M., 2011).

EXPOSITION

Sampling and analysis methods

Samples of apples were taken from two different locations, Drmeni and Jankovec from the Prespa Region. Apples of the Golden Delicious variety were analyzed.

In order to analyze pesticide residue it is necessary to prepare the sample and extract the residue, and then to analyse it by using separation techniques. Today, the most commonly used method for extracting pesticide residues is QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe). QuEChERS involves several simple analytical steps, which are easy to perform and are slightly sensitive to errors. Thus, a high yield of extraction of a number of analytes is ensured, and the final extract can be directly analyzed by gas or liquid chromatography (Stocska, J., & Biziuk, M., 2015). Following the new trends in the extraction of pesticide residues, the QuEChERS method was applied in this study (Anastassiades, M., Lehotay, S. J., Stajnbaher, D., & Schenck, F. J., 2003), according to the МКС EN 15662:2011 standard (Jankuloska, V., Karov, I., & Pavlovska, G., 2018).

Pesticides were analyzed with ultra-high-performance liquid chromatography, a consequence of HPLC whose basic principle is that, as the size of the particles (2 μm) in the column decreases, efficiency and resolution increase (Patil, V. P., Tathe, R. D., Devdhe, S. J., Angadi, S. S., & Kale, S. H., 2011; Kumar, P., Singh, S. P., Shrikant, K., & Madhukar, D., 2011). For the analysis of pesticide residues by UPLC-TQ/MS was used Agilent UPLC 1290, detector DAD VL Agilent 1260 G1315D (Waldbronn, Germany), Agilent triple quadropul LC/MS detector 6420 (Agilent

Technologies, Santa Clara, California, USA). The temperature of the column was 35°C and the flow was 0.4 ml/min. The volume of injection is 0,7µl.

The name of the chemical, the withholding period (WHP) and retention time of the analyzed organophosphorus pesticides is given in Table 1.

Table 1. Chemical name and withholding period (WHP) of a group of pesticides

Pesticide	Chemical name	WHP (days)	Retention time (min)
chlorpyrifos	O, O-diethyl O-3, 5, 6-trichloro-2-pyridyl phosphorothioate	28	13,622
dimetoate	2-dimethoxyphosphinothioylthio-N-methylacetamide	7	4,310
ometoate	2-dimethoxyphosphinoylthio-N-methylacetamide	21	2,70

RESULTS AND DISCUSSION

The results for the analyzed residues of pesticides in Golden Delicious apples, grown at the location of Drmeni and Jankovec are presented in Figure 1.

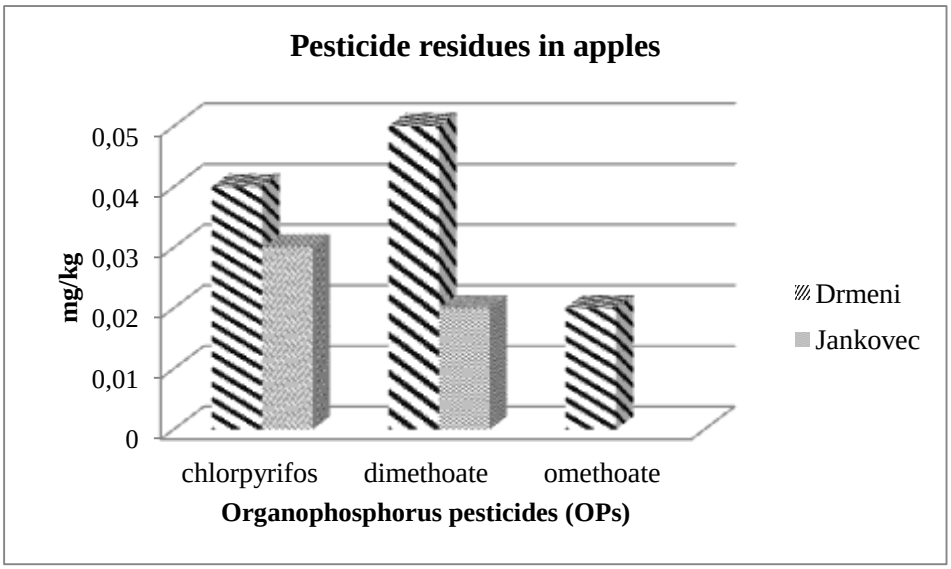

Fig. 1. Residues of organophosphorus pesticides (OP_s) in Golden delicious from Drmeni and Jankovec

The concentration of residues of insecticides in apples from Jankovec was in the range of 0.02-0.03 mg/kg, while in apples from Drmeni the value was between 0.02-0.05 mg/kg. It is noticeable that chlorpyrifos and dimethoate are present in the apples from both locations while the omethoate is detected only in the apples from the Drmeni location (Fig.1).

A side by side comparison of the pesticide residue in apples from Jankovec and their MRL is given in Figure 2.

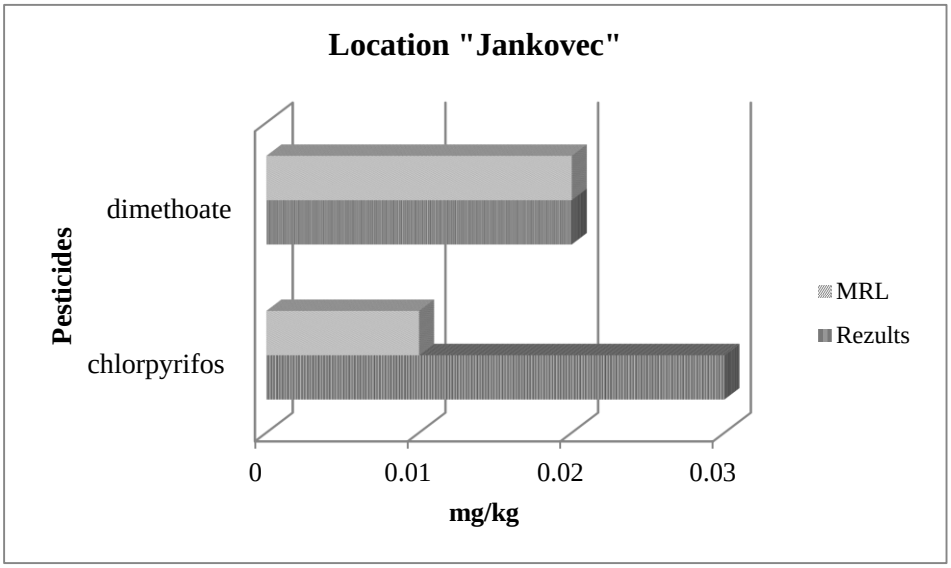

Fig. 2. Comparison of the pesticide residues in apples from the location of Jankovec with MRL

As can be seen from the results shown, chlorpyrifos residues were measured at 0.03 mg/kg, and its MRL is 0.01 mg/kg. It can be concluded that chlorpyrifos residue is three times higher than the MRL, while the insecticide dimethoate residue (0.02 mg/kg) is equal to the MRL (0.02 mg/kg). From the obtained results, it can be concluded that in relation to the insecticide chlorpyrifos, apples of the Golden Delicious variety from Jankovec, are not safe to eat.

A comparison of the concentration of detected pesticide residues in the apple from the location of Drmeni and MRL is given in Figure 3.

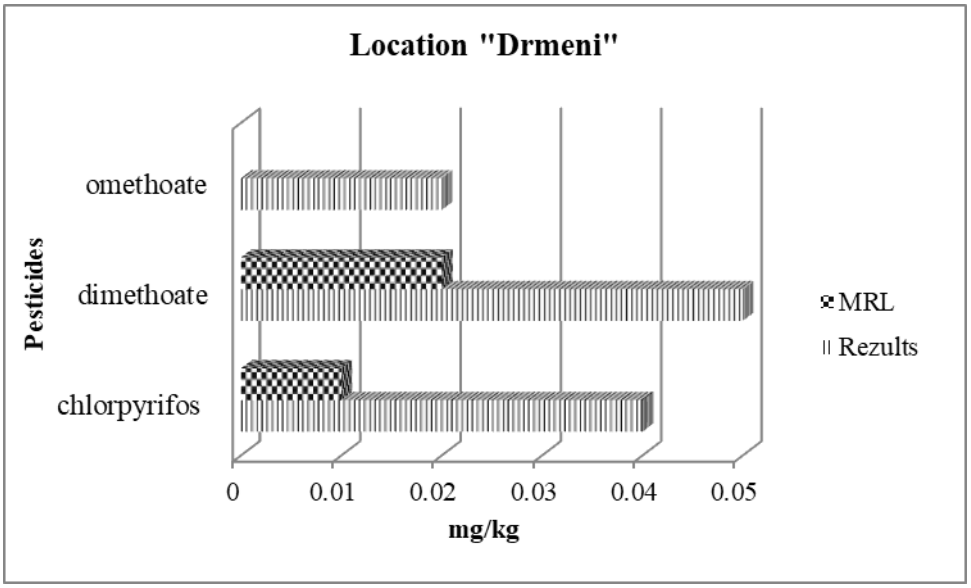

Fig. 3. Comparison of the pesticide residues in apples from the location of Drmeni with MRL

In apples from the location of Drmeni, the residue of insecticides chlorpyrifos, dimethoate and omethoate is higher than the tolerable MRL. The chlorpyrifos residue level is 0.04 mg/kg and the MRL is 0.01 mg/kg, a level four times higher than the MRL. Dimethoate residue level was detected with 0.05 mg/kg and its MRL is 0.02 mg/kg, which means that its level is 2.5 times higher than the MRL. No residue limit for omethoate is provided in the Rulebook for Maximum Residue Limit. But the apples from this location have been shown to contain a residue of 0.02 mg/kg. As a result of the above, it can be concluded that the Golden Delicious variety of apples from the Drmeni location are not safe for consumption, having been found to contain chlorpyrifos, dimethoate and omethoate residue above the MRL.

CONCLUSION

The results show that parts of the analyzed apples contain insecticides residue higher than the maximum residue limit (MRL), and therefore the apples are not safe for consumption. Contamination of fruits with pesticides residues in general is one of the most important aspects of the food quality assurance. In order to provide consumers with food that does not contain residues of pesticides above the MRL, it is necessary to reduce the use of pesticides and to increase the application of integrated protection of crops, as well as to monitor and control products from authorized institutions.

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SAT–LB-P-2-BFT(R)-16

INVESTIGATION OF THE UNIFORMITY OF DISTRIBUTION OF DIFFERENT DOUGH COMPONENTS AFTER FOLLOWING DISCHARGE

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Abstract: *One of the indicators for assessing the effectiveness of mixing the yeast dough is the homogeneity of the resulting mixture. The studies on mixing the yeast dough with the working elements of different configurations and their effect on the homogeneity of the distribution have been carried out. Using a high-precision microscope, homogeneity of distribution of yeast dough was investigated. The conducted studies allowed to obtain a fixed image of the distribution of components of the yeast dough after mixing with the working elements of different configurations. The uniform distribution of components is observed in the cam and finger working elements, in the screw working elements there is no part of mixing and adhesion of the components into large clumps. The research revealed a number of homogeneous particles that formed after mixing the yeast dough. Distribution coefficient after kneading by cam operating elements is 84%, there is even distribution of components in the structure of yeast dough. After mixing by the "finger" kneading elements, the distribution factor is 67%, therefore the uniform distribution of components in the structure of the dough is achieved. During the mixing with auger working elements, the distribution factor reaches 58%, for these values uniform distribution of components in the structure of the test cannot be reached, there contains traces of non-conductivity in the structure. A comparative analysis on the distribution and homogeneity of the yeast dough after mixing was carried out.*

Keywords: *Mixing, Yeast Dough, Working Elements, Distribution, Homogeneity.*

INTRODUCTION

The studies were carried out as follows, the prepared recipe components were kneaded by a dough machine of continuous action. After mixing, samples of yeast dough were investigated using an optical microscope Biorex-3, recorded the obtained image of the structure of the yeast dough. Using the ImageJ software complex, the obtained image was processed and the distribution factor was calculated.

The yeast dough was mixed by working elements of various configurations: screw, finger and cam working elements in a dough machine of continuous action.

At the beginning of mixing, an inelastic mass is formed. During further mechanical treatment of the dough, depolymerization of gluten proteins occurs as a result of the rupture of disulfide bonds between the peptide chains and splitting of non-covalent bonds occurs as well: hydrogen, hydrophobic and salt bridges. The structure of the gluten-free frame is rearranged, it becomes plastic.

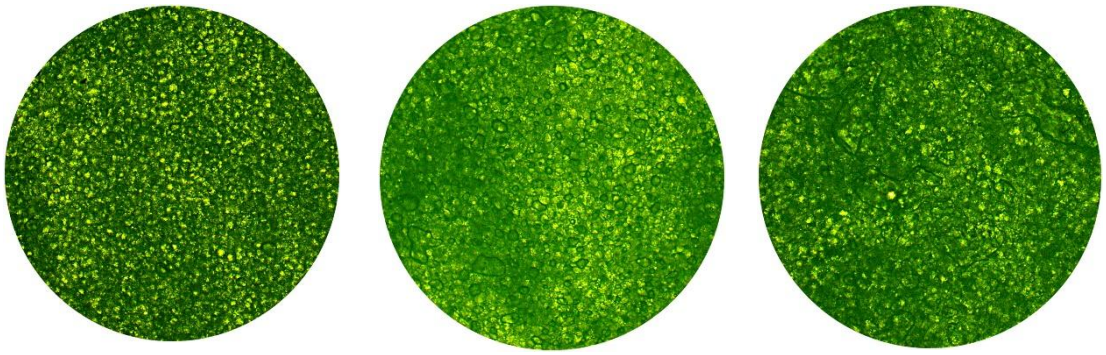
It is believed that the mechanism of plasticization consists in the fact that the spiral polypeptides of the loose protein molecule are cleaved, stretched into protein films and arranged in the form of plates, which include starch grains. As a result of the dissolution of the protein

molecule, the weakening of the strength of the micellar framework intensifies osmotic processes, swelling proteins more fully, increasing the amount of bound water, which makes the dough become dry to the touch, elastic, gluten films acquire the ability to retain carbon dioxide.

For the formation of a dough with an elastic structure, it is required that the gluten proteins are elastic and envelop all grains of starch with a thin film. If the number of protein is not enough or the gluten is not elastic, the dough will have low gas retention capacity.

EXPOSITION

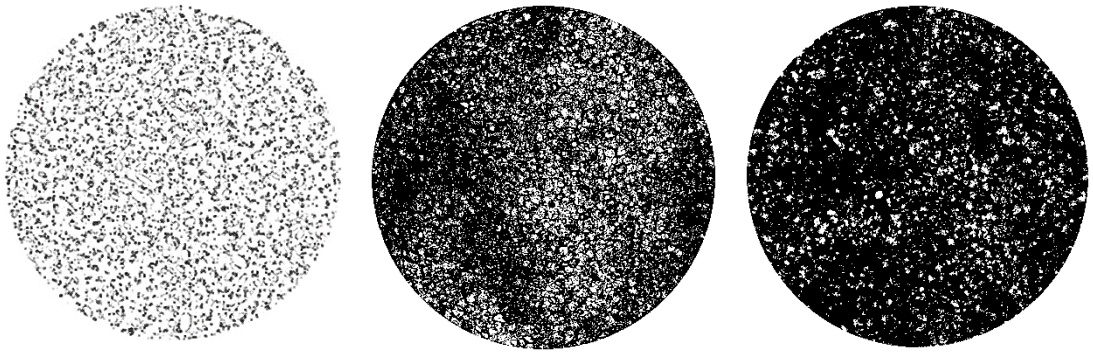
One of the indicators for assessing the effectiveness of mixing the yeast dough is the homogeneity of the resulting mixture., The homogeneity of distribution of yeast dough was investigated by using a high-precision microscope (Fig. 1.).



a.) Cam working element b.)Finger working element c.) Screw working element

Fig. 1. Homogeneity of distribution of components of yeast dough after mixing by working elements of different configurations

The conducted studies allowed to obtain a fixed image of the distribution of components of the yeast dough after mixing with the working elements of different configurations. The equable distribution of components is observed in the cam and finger working elemets, in the screw working elements there is no part of mixing and adhesion of the components into large clumps.



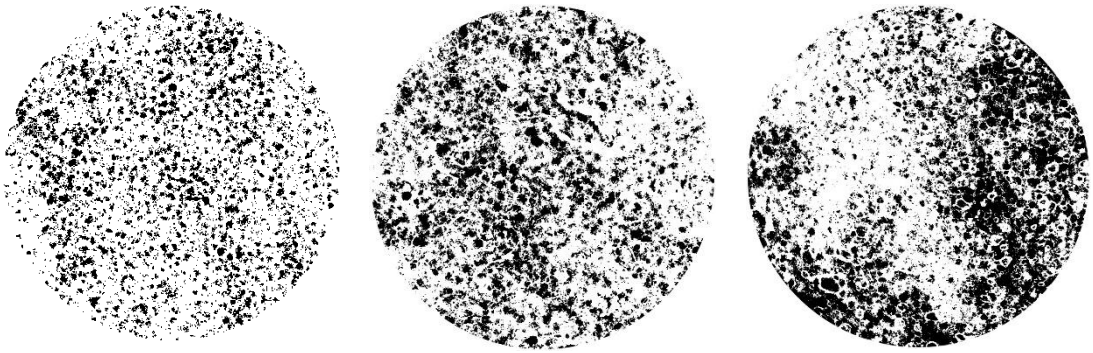
a.) Cam working element b.)Finger working element c.)Screw working element

Fig. 2. Uniformity of distribution of dough components after the processing by complex software ImageJ

The research revealed a number of homogeneous particles that formed after mixing the yeast dough. In cam kneading elements, these indices are the highest (Fig. 2a) and make 2421 pieces of homogeneous particles in the area under examination under a microscope (282600 microns), in fingertips 1439 pcs, in sconces 801 pcs. The average size of parts after kneading by the cam kneading elements is 116.7 microns, the finger working element 196.3 microns, screw working element 352.4 microns. Distribution coefficient after kneading by cam operating elements is 84%, there is even distribution of components in the structure of yeast dough. After mixing with the fingers, the distribution factor is 67% and the equable distribution of components in the structure of the dough is achieved. When mixing by screw working elements, the distribution factor reaches

58%, for these values it is not achieved the equable distribution of components in the structure of the dough, it is contained traces of non-conductivity.

At the beginning of the mixing, an inelastic mass is formed, during the subsequent mechanical processing of the dough the structure of the gluten-free frame is rearranged and becomes plastic. As a result of mechanical processing, during the kneading of yeast dough, volumetric gluten proteins extending beyond the interstitial cracks stick together and form a gluten-free carcass, which provides the dough with the elasticity starch grains impregnated in the gluten-free frame.



a.) Cam working element b.)Finger working element c.)Screw working element

Fig. 3. Formation of the structure of the yeast dough after mixing by the working elements of various configurations (white mesh-gluten-free frame; black inclusions-starch grains)

During the kneading by cam operating elements (Fig. 3a), the dough is formed with an elastic structure, gluten-free proteins acquire elasticity and evenly cover all the starch grains with a thin film, the yeast dough thus has a high gas-retaining ability and subsequently even fine-grained porosity of the finished product. The equable distribution of the dough structure is observed after mixing by the finger working elements (Fig. 3b), but due to its structural parameters, the gluten-free frame is broken down and starch grains are damaged, which absorbs a significant amount of moisture from the gluten-free proteins, thus gluten does not have time to recover, deterioration of the gas-retaining ability and as a result, the porosity of the finished product is deteriorating. After mixing by screw working elements, the dough is poorly mixed and the components are not distributed equally, there is not equable distribution of the structure of the yeast dough (Fig. 3c), large particles of starch grains start to bind water more quickly than the protein, so water is not enough to swell the proteins and the dough does not become elastic.

CONCLUSION

After kneading by the cam operating elements, a high quality yeast dough is achieved, and an equale, fine, thin-walled structure with no cavities is observed. In the dough there are no foreign inclusions in the form of non-stirred flour bundles. During the kneading the yeast dough by the cam operating elements, the gaseous components are evenly distributed in the dough preparation, which further improves the structure of the porosity of the products.

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SAT–LB-P-2-BFT(R)-17

JUSTIFICATION OF THE PRODUCTION LINES ARRANGEMENT BASED ON QUANTITATIVE AND GRAPHIC METHODS FOR ASSESSING THE LEVEL OF EQUIPMENT EXCELLENCE

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Abstract: *On the example of the estimation of technical and economic indicators of machines for the production of burger products, the task of multicriterial choice of equipment for the production lines arrangement by methods of spectral analysis, Pareto and distance to the goal was solved.*

The method of spectral analysis is based on the apparatus of dead-end tests, involves comparing all the definite combinations of features which describe the object, has advantages over Pareto and motion to the goal methods, because it provides a generalized mathematical evaluation of the specimens which are considered.

After analyzing five indicators (productivity, capacity, capacity of the feeding bin, weight, overall dimensions) of eight samples of equipment for the burger products production from different manufacturers, it has been established that according to the chosen parameters, the preference should be given to the machine Laminerva C/E 653 1ph.

The correctness of a decision primarily depends on the correct choice of indicators to be compared. In their composition, in the future it is necessary to include indicators of reliability and durability, as well as quality indicators of finished products.

Keywords: *Multicriterial choice, Method of spectral analysis, Pareto front, Equipment.*

INTRODUCTION

The production lines arrangement for the food industry is associated with certain difficulties, caused by the need to choose the appropriate equipment reasonably. The methods of the justified choice of equipment were actively developed at the end of the 20th century, but were not widely used. The situation has not changed significantly in recent years, although some publications related to the assessment of the equipment technical level in various industries, particularly food industry (Orlov, V., Petrunina, E., 2013), mining industry (Skotnicka-Zasadzień, B., Biały, W., 2011) and energy sector (Hennen, M., Voll, P. Bardow, A., 2014) appear.

The technical level of equipment is a relative characteristic of its quality and is based on the comparison of the indicators that characterize its technical perfection, in comparison with the basic values. When evaluating alternative equipment variants, each of which is characterized by a set of parameters, we have a multicriteria task. The most common are two types of tasks - optimization and choice, which differ, first of all, in decision rules.

Deterministic methods of functions optimization with many variables are used if single criteria, for each of which the weight is determined, can be reduced to one generalized (integral) one (Belton, V., & Stewart, T., 2002). In the case of the assessment of the equipment technical level, it is not possible to develop such a generalized criterion, taking into account various technical and economic aspects, and to ensure the sensitivity of the multifactorial model. Therefore, it is advisable to pay attention to the methods of multicriterial choice of the best variant from the set of those that are considered. Despite the presence of a large number of developed methods, in the mathematical theory of choice and decision making, currently there is no common strategy for solving practical engineering problems and clear criteria for comparing the choices methods themselves.

EXPOSITION

Possibilities of using three methods of multicriteria choise - methods of spectral analysis, Pareto and distance to the goal - were demonstrated by the example of the choice of the best variant of the machine for the burger products forming. For eight variants of equipment a complex assessment of technical characteristics was fulfilled (Table 1).

Table 1. Technical characteristics of machines for burger products forming

Characteristics of machines	Machine brand							
	ABM F-2000	La Minerva C/E 653 1ph	Planus	Formatic R3000	AK2M-40	IPKS - 123	Gaser A-2000	GPM AK-MR 400
Variant number	1 S_1	2 S_2	3 S_3	4 S_4	5 S_5	6 S_6	7 S_7	8 S_8
k_1 Productivity, pcs/h	2000	3900	2100	3000	3900	1680	1900	2100
k_2 Power, kW	0,75	0,7	0,37	0,75	0,55	0,55	0,75	0,37
k_3 Feed pan capacity, l	20	23	32	15	20	50	20	32
k_4 Volume occupied by the machine, m^3	0,189	0,166	0,297	0,29	0,373	0,312	0,183	0,6
k_5 Net weight, kg	67	50	75	95	90	90	66	100

The spectral analysis method

The degree of objects convergence by the method of spectral analysis is calculated not by the sequential comparison of individual features, but by the comparison of all possible (or definite) combinations of features included in the object description. Let's consider a number of design fulfillment variants of equipment in the form of a making decision matrix:

$$M_{md}(S) = \begin{array}{c} \\ S_1 \\ S_2 \\ \\ S_j \end{array} \begin{Vmatrix} k_1 & k_2 & k_n \\ k_{11} & k_{12} & k_{1n} \\ k_{21} & k_{22} & k_{2n} \\ \\ k_{j1} & k_{j2} & k_{jn} \end{Vmatrix}, \quad (1)$$

S_1, S_2, ..., S_j – alternative design fulfillments that are compared; k_1, k_2, ..., k_n – characteristics of alternative variants; k_{im} – the value of the characteristic k_m for the variant S_i (i = 1..j, m = 1..n).

For the transition to the dimensionless characteristics of alternative variants, it's need to carry out the normalization:

$$\overline{k_{im}} = \begin{cases} \dfrac{k_{im}}{k_{im}^{/}}, \text{ if an increase in the characteristics improves the quality of the alternative variant} \\ 1 - \dfrac{k_{im}}{k_{im}^{/}}, \text{ if an increase in the characteristics worsens the quality of the alternative variant} \end{cases}, \quad (2)$$

$k_{im}^{/} = \max(k_{im})$ by the column m of the matrix (1).

Using expressions (2), the transition from the making decision matrix $M_{md}(S)$ to the decision matrix $M_d(S)$ is carried out. Then the degree of severity of the characteristic **g** is determined: if the characteristic exceeds a given level, then it is considered $g_{im} = 1$, otherwise $g_{im} = 0$ (i = 1..j, m = 1..n). The critical level is chosen so that in the received spectral matrix (Mc)

there are no rows and columns that consist only of zeros. $g_{im} = 1$ at $k_{im} \geq k_m^{kp}$, $g_{im} = 0$ at $k_{im} < k_m^{kp}$ ($i = 1..j$, $m = 1..n$).

$$M_d(S) = \begin{Vmatrix} \overline{k_{11}} & \overline{k_{12}} & \overline{k_{1n}} \\ \overline{k_{21}} & \overline{k_{22}} & \overline{k_{2n}} \\ \overline{k_{j1}} & \overline{k_{j2}} & \overline{k_{jn}} \end{Vmatrix}, \quad (3) \qquad M_c(S) = \begin{Vmatrix} g_{11} & g_{12} & g_{1n} \\ g_{21} & g_{22} & g_{2n} \\ g_{j1} & g_{j2} & g_{jn} \end{Vmatrix}, \quad (4)$$

$\overline{k_{11}}, \overline{k_{12}}, .., \overline{k_{jn}}$ – dimensionless characteristics of alternative variants.

The influence of characteristics on the functioning efficiency and the quality of the investigated design fulfillments of equipment is determined based on the load of the rows (the object significance) and the columns (the significance of the object characteristics) of the spectral matrix $M_c(S)$. According to the theory of the blind alley tests, the load of rows (π) is determined by taking into account the load of the columns (ω), and the load of the columns – by taking into account the load of the rows. For the row: $\pi(\omega)_i^l = \sum_{m=1}^{n} G_{\omega m}^{l-1} \cdot g_{im}$, $i = 1...j$; for the column: $\omega(\pi)_m^l = \sum_{i=1}^{j} G_{\pi i}^{l-1} \cdot g_{im}$, $m = 1...n$, were l – the iteration number; G_ω, G_π – normalized column and rows weights respectively.

The initial weights of rows and columns are determined:

$$G_{\pi i}^0 = \sum_{m=1}^{n} g_{im}, \quad i = 1...j; \; G_{\omega m}^0 = \sum_{i=1}^{j} g_{im}, \quad m = 1...n \quad (5)$$

Calculations are stopped when a given convergence of the iterative process is obtained.

In the course of the work, a making decision matrix $M_{md}(S)$, a decision matrix $M_d(S)$ and a spectral matrix $M_c(S)$ are constructed, in which the rows represent the equipment brands under consideration, and the columns – their technical characteristics. The matrix of decisions $M_d(S)$ is obtained by normalizing the characteristics using formulas (2). From the listed characteristics an increase of characteristics k_1 (productivity) and k_3 (capacity of a loading bunker) improves the quality of the alternative variant, while an increase of parameters k_2 (power), k_4 (dimensions), k_5 (weight) worsens them.

Based on the analysis of the characteristics of machines for the burger products forming, given in Table 1, we adopt the following critical levels of characteristics:

$$k_1^{kr} = 0{,}6; \; k_2^{kr} = 0{,}5; \; k_3^{kr} = 0{,}7; \; k_4^{kr} = 0{,}7; \; k_5^{kr} = 0{,}1. \quad (6)$$

Given the loads on rows and columns, weightedness of the objects characteristics is determined. In the solution, two iterations are carried out (Fig. 1, figures in circles denote the sequence of calculation steps), the iterative process converges to the values of the boundary loads. It has been established that the best integrated estimate of 1 is characteristic of the machine Laminerva C/E 653 1ph.

$$M_{dm}(S) = \begin{array}{c} \\ S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \\ S_7 \\ S_8 \end{array} \begin{array}{c} \begin{array}{ccccc} k_1 & k_2 & k_3 & k_4 & k_5 \end{array} \\ \begin{Vmatrix} 2000 & 0.75 & 20 & 0.189 & 67 \\ 3900 & 0.70 & 23 & 0.166 & 50 \\ 2100 & 0.37 & 32 & 0.297 & 75 \\ 3000 & 0.75 & 15 & 0.29 & 95 \\ 3900 & 0.55 & 20 & 0.373 & 90 \\ 1680 & 0.55 & 50 & 0.312 & 90 \\ 1900 & 0.75 & 20 & 0.183 & 66 \\ 2100 & 0.37 & 32 & 0.600 & 100 \end{Vmatrix} \end{array}$$

$$M_d(S) = \begin{Vmatrix} 0{,}51 & 0 & 0{,}4 & 0{,}69 & 0{,}33 \\ 1 & 0{,}07 & 0{,}46 & 0{,}72 & 0{,}5 \\ 0{,}54 & 0{,}51 & 0{,}64 & 0{,}51 & 0{,}25 \\ 0{,}77 & 0 & 0{,}3 & 0{,}52 & 0{,}05 \\ 1 & 0{,}27 & 0{,}4 & 0{,}38 & 0{,}1 \\ 0{,}43 & 0{,}27 & 1 & 0{,}48 & 0{,}1 \\ 0{,}49 & 0 & 0{,}4 & 0{,}7 & 0{,}34 \\ 0{,}54 & 0{,}51 & 0{,}64 & 0 & 0 \end{Vmatrix} \qquad M_c(S) = \begin{Vmatrix} 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 & 1 \\ 0 & 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 \end{Vmatrix}$$

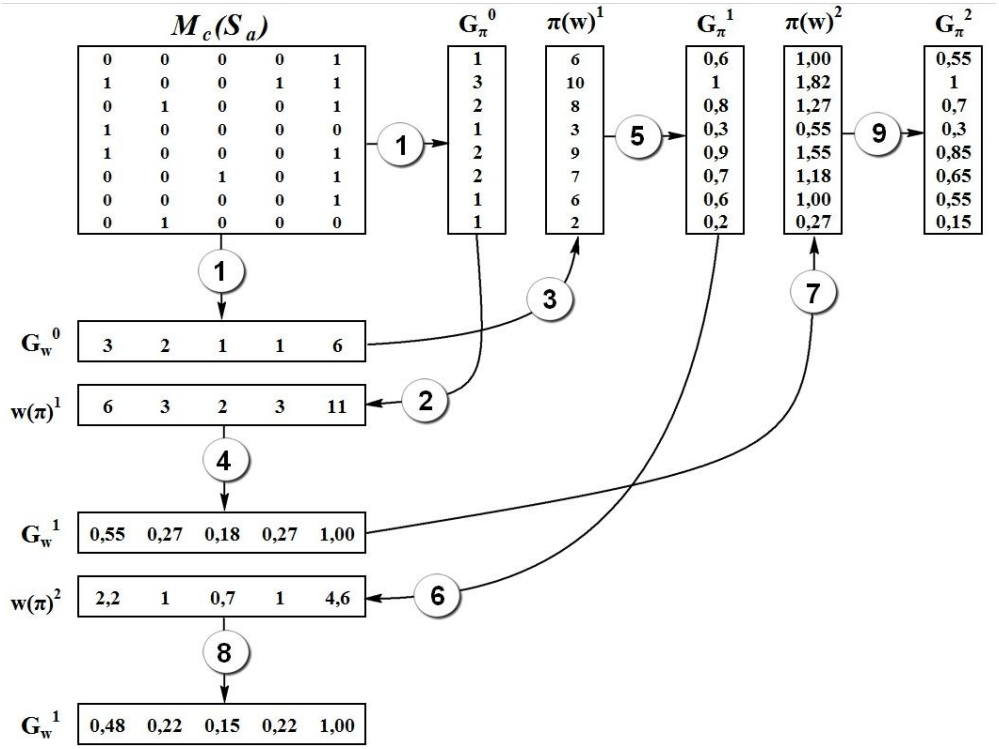


Fig.1 The calculation scheme of the choice of the optimal variant in accordance with the spectral approach to determining the importance of the object characteristics

The Pareto analysis method

Pareto optimality is intended to determine if the proposed change improves the overall level of the object. The principle of dominance is used to find effective (Pareto-optimal) variants. Assume that the variants that are compared are estimated by the vector of criteria: $\mathbf{k} = \{k_1, k_2, .., .k_n\}$, $k_i \in \mathbf{K}$, $i = 1...n$.. Then variant A dominates variant B, if each criterion k_i^A prevails or is equivalent to the corresponding criteria k_i^B, at least for one of them there is a strict preference k_i^A over k_i^B. It convenient to use the Pareto analysis method in graphical interpretation on a plane, alternately comparing two criteria. It gives the opportunity to go out an effective boundary that combines options that dominate others and do not have domination over them. Variants that lie on the effective boundary are called Pareto optimum.

For a visual representation of the solution for a number of alternatives, two criteria were considered alternately (Fig.2). First of all, for the eight design fulfillments of the equipment, we considered the indicators that have the highest weight - productivity, pcs./h and power consumtion, kW (Fig. 2a). The direction of the abscissa (power) axis is inversed, since optimization by the power criterion is associated with its minimization. Points 1 to 8 depict the variants of machines for burger products forming. In this case, the variants of the dominant machines are La Minerva C/E 653 1ph (point 2), Planus (point 3) and GPM AK-MR 400 (point 8), becouse above and right of them there are no variants for improvement by two characteristics at once. Since there are three variants of equipment on the effective border, the following characteristics should be considered. Leaving the most significant indicator – productivity, we take into account the feed pan capacity, which, if the forming process is periodicity, affects the duration of auxiliary operations and hygienic process. In this case, the variants of machines that are on the effective border - La Minerva C/E 653 1ph (point 2) and IPKS-123 (point 6). To obtain a more objective solution, the following characteristic is considered: the overall dimensions of the equipment, which are represented in generalized form by the volume occupied by the machine (Fig. 2 c).

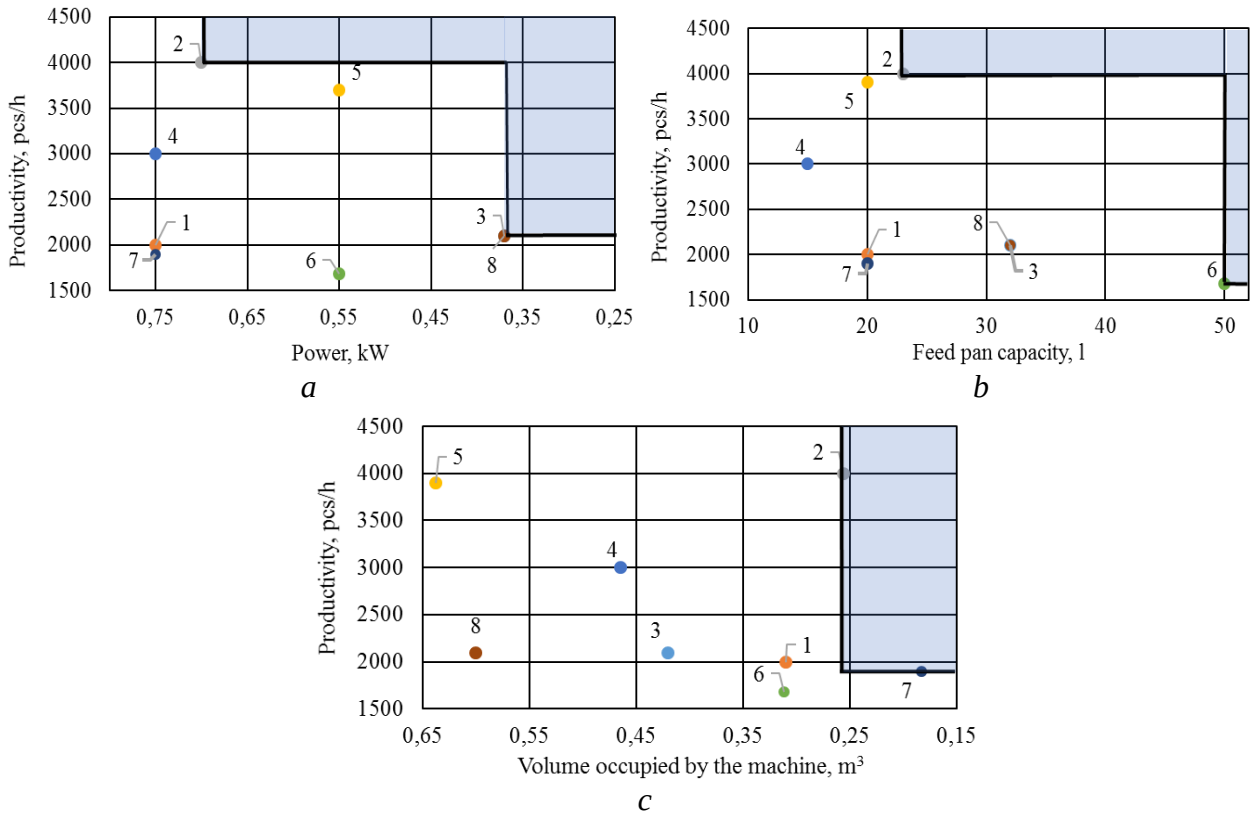
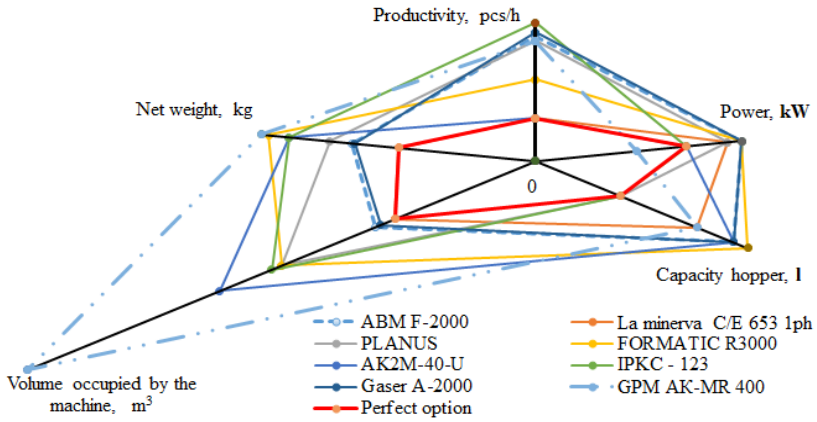


Fig. 2. Choosing the best variant of the machine for burger products forming based on the Pareto principle at the parameters that are considered:
a - productivity - power, *b* - productivity - feed pan capacity, *c* - productivity - volume occupied by the machine

Variants of equipment, which dominate over others, are the machine La Minerva C/E 653 1ph (point 2) and Gaser A-2000 (point 7). The La Minerva C/E 653 1ph there is at an effective boundary for all of the considered combinations of parameters. Consequently, it is appropriate to choose it as one that has the largest productivity among the considered at moderate power consumption and small overall dimensions.

The method of distance to a goal

Another simple method for solving the problem of multicriteria choice is to apply an integral criterion of distance to a goal. The method essence is to justify the ideal and evaluate the degree of approach to it each of the variants of the original set. The ideal variant characterizes such a system, for which each criterion reaches its potentially possible best value, which can be theoretically substantiated or correspond to the best actually achieved value. The practical application of the method is presented on a graphical model (Fig. 3). For variants of the initial set of alternatives, criteria k_i are determined and put on a radially located scales. The scale is constructed so that the improvement of the criterion goes to the center (point 0). By connecting points on the scales for the *j*-th option, a polygon is obtained. At the best values of the criteria, a polygon of an idealized variant is constructed. A generalized criterion of distance to the goal μ is defined as the ratio of the area of *j*-th variant to the idealized area.



Variant	μ
S_1	2,86
S_2	1,51
S_3	2,61
S_4	3,63
S_5	3,20
S_6	2,94
S_7	2,86
S_8	4,98

Fig. 3. Multi-criteria assessment of machines technical level by a distance to the goal method

CONCLUSION

In order to assess the technical level of equipment it is expedient to use methods of multicriteria choice. The results obtained by the three methods of multicriteria choise (spectral analysis, Pareto and distance to the goal) are the same. After analyzing five characteristics of eight variants of equipment for the burger products forming by different manufacturers has been established, that according to the chosen parameters the advantage should be given to the machine La Minerva C/E 653 1ph.

In our opinion, the most expedient is the application of the spectral analysis method because it enables to take into account in a complex way all the criteria that characterize the technical level of equipment and the efficiency of its work. The method does not require special skills in working with graphic information and is the most formalized. The correctness of a decision primarily depends on the correct choice of indicators to be compared. In their composition, in the future it is necessary to include indicators of reliability and durability, as well as quality indicators of finished products.

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