ISSN 2504-5687

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Volume 1(25)
2020

SCIENTIFIC JOURNAL

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European Union
Editorial office
«EUREKA: Life Sciences»
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CONTENT

CYTOLOGICAL CHARACTERISTICS OF POSTOPERATIVE METASTASES OF PAPILLARY THYROID CANCER DURING THE DEVELOPMENT OF SECONDARY RADIOIODINE REFRACTORINESS

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Abstract

Radioiodine refractoriness is the main problem in the diagnosis and treatment of papillary thyroid carcinoma. The aim of the study was to investigate the cytological and immunocytochemical changes of thyrocytes in fine-needle aspiration smears of thyroid papillary cancer metastases in the course of the development of secondary radioiodine resistance. A total of 70 postoperative metastases of thyroid papillary cancer (secondary radioiodine refractory metastases, previously responsive to radioiodine, that eventually loses the ability to radioiodine accumulation, radioiodine-avid metastases, primary radioiodine-refractory metastases), immunohistochemical staining of thyroid peroxidase, thyroglobulin, cytokeratin 17 and cytological analysis were performed. Revealing the presence of specific cellular phenotypes and structures in punctuates, a low percentage of thyroid peroxidase and thyroglobulin-positive thyrocytes allows the development of the method of cytological prediction of the radioiodine therapy effectiveness.

Keywords: secondary radioiodine refractory metastases, papillary thyroid carcinoma, fine needle aspiration smears, thyroid peroxidase, thyroglobulin.

DOI: 10.21303/2504-5695.2020.001117

1. Introduction

As a result of the Chernobyl accident, there was a sharp increase in incidence of the thyroid cancer [1, 2]. For 20 years of observation, most cases of differentiated thyroid cancer (DTC) have shown the excellent prognosis for more than 95 % of patients thanks to thyroidectomy and radioiodine (RI) – therapy, based on the unique ability of the thyroid cells to accumulate RI [3, 4]. Despite the mainly auspicious prognosis of papillary thyroid carcinoma (PTC) without relapses in most cases even using the standard therapy (thyroidectomy, RI and suppressive therapy), metastases occur during the postoperative period in 2–29 % of cases [3].

Metastases which occur during the postoperative period can be of two types: radioiodine-avid (RIAM) (able to accumulate RI) and radioiodine refractory metastases (RIRM). RIRM develop in 5–20 % of cases, their cells lose their ability to RI accumulation, and RI therapy becomes ineffective for them [5, 6]. A combination of studies appears to support the notion that survival for patients with RI-refractory DTC distant metastases is around 2.5–3.5 years [7, 8]. Early prediction of RI ability of metastatic DTC can be based on the cytological feature determination of thyrocytes in fine needle aspiration (FNA) smears of the RIRM. There are some ideas about the morphological, immunohistochemical and molecular characteristics of RIRM [9, 10]. However, the cytological

studies of FNA smears in RIRM have not yet been conducted and accordingly no data have been obtained on the cytological characteristics of RIRM.

The data regarding RI-refractoriness, classifies it as primary (the metastatic tissue does not ever concentrate RI), secondary (the metastatic tissue loses the ability to concentrate RI after previous evidence of RI-avid disease), and stable metastatic disease [4]. The study of changes of metastases' thyrocytes' characteristics, correlated with the loss of RI accumulation, presents scientific and practical interest. The results can be the basis for developing new methods for predicting and diagnosing radioiodine refractoriness. A suitable model for investigation of changes may be secondary radioiodine-refractory metastases (SRIRM).

The study of antigens' expression – thyroid peroxidase (TPO) and thyroglobulin (Tg) – which are involved in the process of RI accumulation and its retention with thyrocytes is of particular interest. We have previously shown that cytokeratin No. 17 (Ck17) is a cytological marker of the preoperative prognosis of RI resistance when determining its expression in FNA smears of primary PTC [11]. The thyrocytes that contains Ck17 are characterized by the weak expression of Tg, and TPO, which also makes it relevant to study the expression of Ck17 antigen in FNA smears of postoperative PTC metastases.

The actual purpose of this work is to carry out cytological and immunocytochemical researches of the thyrocyte population in FNA smears of PTC metastases that appear in the postoperative period, and also to identify cytological changes that occur with the development of secondary radioiodine refractoriness in metastases. There is a unique opportunity to conduct a comparative cytological investigation of SRIRM on different stages of its existence (when metastases accumulate RI (STAGE_1) and when they lose this ability (STAGE_2)).

2. Materials and methods of research

2. 1. Patients

Investigated groups included FNA smears of 70 PTC regional metastases in the neck which were found during the sonographic and scintigraphic examination after thyroidectomy and RI – therapy, i. e. in the postoperative period. The specimens were obtained from patients who were examined, diagnosed with the tumor and underwent to thyroid surgery and RI therapy in the Institute of Endocrinology and Metabolism (IEM). PTC metastases were identified by the neck sonography after treating patients with 100 mCi RI. All histopathological diagnoses were established according to the World Health Organisation (WHO) classification at the Laboratory of Morphology of Endocrine System of the IEM [12]. 4 patients had the histological diagnosis – follicular variant of PTC (FVPC) in the group of RIAM. 3 patients had the histological diagnosis – diffuse-sclerosing variant of PTC (1-in group of RIAM, 1-in group of PRIRM, 1-in group of SRIRM). All other patients had the histological diagnosis – classical variant of PTC. The patients were both women (55) and man (15), with their age ranging from 27 to 61 years (average age 39.29±17.13). This study has been approved by the Ethics Committee of IEM (No. 28/1-KE of 16 June, 2014) and all patients have signed the written form consent. All procedures in this study strictly complied with the guidelines and principles of the Declaration of Helsinki, the Council of the Convention Europe on human rights and biomedicine, as well as relevant provisions of the WHO and the laws of Ukraine.

We have analyzed FNA smears of 15 metastases, previously responsive to RI, that eventually loses the ability to RI accumulation (SRIRM), 25 metastases that were successfully treated, using RI therapy (RIAM) and 30 primary RI-refractory PTC metastases, which does not ever concentrate RI (PRIRM). The specimens were obtained from PTC regional metastases in the neck (paratraheal, jugular (cranial, medial, caudal), submandibular, supraclavicular metastatic lymph node), size from 4 to 33 mm. FNA of thyroid and metastases was performed under ultrasound guidance using a 21-gauge needle. Dried FNA smears were fixed for 5 minutes in methanol, followed by staining in Giemsa dye diluted in 0.067M phosphate buffer (pH 6.4) for 30 minutes.

2. 2. Immunohistochemical staining

Immunocytochemistry (ICH) was performed on representative Giemsa-stained smears after they have been analyzed cytomorphologically which helps to unmask antigens [13]. We ap-

plied indirect immunoperoxidase technique to identify certain antigens, using primary monoclonal mouse antibodies against Tg (DAK-Tg6, Dako, Denmark, 1:100 dilution,), TPO (TPO-47, Dako-Cytomation, Denmark, 1:50 dilution), epithelial cell adhesion molecule (epCAM) (Ber-Ep4 Dako, Denmark, 1:100 dilution), Ck17 (E3, Dako, Denmark, 1:50 dilution). Polyclonal rabbit anti-mouse immunoglobulins/HRP (Dako, Denmark, 1:100 dilution) were applied as enzyme-labeled secondary antibodies. 3.3-diaminobenzidine tetrahydrochloride (Sigma, USA) was used as a chromogen. Endogenous peroxidase was inactivated by incubation in 1 % H_2O_2 in phosphate buffer (pH 7.4) at the room temperature for 30 minutes. Appropriate positive and negative controls for ICH were included. The expression of antigens was considered positive in the case cytoplasm of thyrocytes intensive staining. As a result approximately 1000 thyrocytes were counted at high magnification (×400) in each case.

2. 3. Statistical analysis

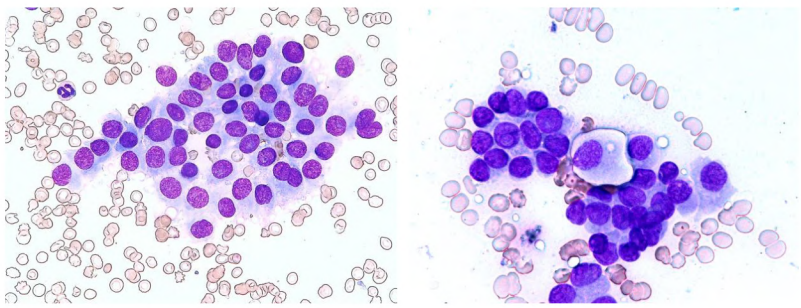
Data were statistically processed using Statistica, version 11.0. When the p-value was <0.05, any differences were considered statistically significant. The Wilcoxon's non-parametric test was applied to compare the expression of TPO, Tg, Ck17 between different stages of the existence of SRIRM (when they accumulate RI (STAGE_1) and when they lose this ability (STAGE_2) in the same patients. The Mann-Whitney U-test was applied to compare the expression of TPO, Tg, Ck17 between PRIRM and RIAM. The chi-square test was used to compare frequencies of cytological signs (specific cellular phenotypes, structures, cystic degeneration) between PRIRM and RIAM and between different stages of the SRIRM.

3. Results

3. 1. Cytological features of PTC postoperative metastases

A comparative cytologic study of thyrocytes' population of postoperative PTC metastases with different iodine accumulating ability was performed. From the point of view of cytology, when the metastases had the ability to accumulate RI (RIAM), they had the regular structure of cellular groups. These cellular groups were represented as homogeneous thyrocytes without signs of atypia (**Fig. 1, *a***). In contrast, in a case of RI accumulation loss (in SRIRM and PRIRM) cellular groups with irregular structure appeared. They are represented as polymorphic cells.

Some cellular phenotype, which differed from other cells of the thyrocyte population with cytomorphological and ICH characteristics in 40 % of STAGE_2 of SRIRM and 30 % PRIRM was found. Their positive antibody reaction to cytokeratins 7 and 8 instantiates an epithelial nature. These thyrocytes don't contain Tg and do not react to antibodies against epCAM. This cellular phenotype looked lighter among the other epithelial cells and had clear-cut edges (**Fig. 1, *b***). Statistically significant difference was observed in the presence of this specific cellular phenotype of thyrocytes between metastases of STAGE_1 and STAGE_2 of SRIRM.



a *b*

Fig. 1. The cellular groups in FNA smears of postoperative PTC metastases:
a – regular structure of cellular groups in RIAM;
b – particular cellular phenotype in STAGE_2 of SRIRM. ×400

Besides, there are specific cellular complexes of psammous bodies and vacuolated cells in 20 % of PRIRM and 46 % of STAGE_2 of SRIRM. These complexes were absent in metastases, when they had an ability to accumulate RI. (**Fig. 2**).

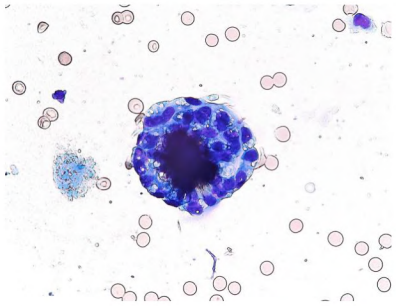


Fig. 2. Specific cellular complexes of psammous bodies and vacuolated cells in FNA smear of STAGE_2 of SRIRM. ×400

Also, in 43 % of PRIRM and 40 % of cases of STAGE_2 of SRIRM there are cytological sign of cystic degeneration, in contrast to metastases, when they had an ability to accumulate RI. The data of the frequency of the studied cytological features in FNA smears of postoperative PTC metastases are given in **Table 1**.

Table 1

The frequency of various cytological signs in FNA smears of postoperative PTC metastases (RIAM, PRIRM and SRIRM)

Cytological features	RIAM (n=25)	PRIRM (n=30)	SRIRM (n=15)	
			Stage of RI accumulation (STAGE_1)	Stage of lost of RI accumulation (STAGE_2)
Special cellular phenotype	0 %#	30 % (9)	0 %*	40 % (6)
Cystic degeneration	4 % (1)#	43 % (13)	6.7 % (1)*	40 % (6)
Complexes of psammous body and thyrocytes	0 %#	20 % (6)	0 %*	46.6 % (7)

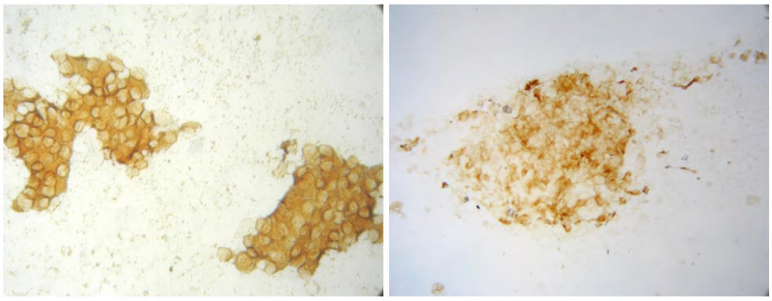
*Note: RIAM – radioiodine-avid metastases, successfully treated using the radioiodine therapy, PRIRM – radioiodine-refractory metastases, which never accumulated radioiodine, SRIRM – which previously were responsive to radioiodine and eventually lose the ability to accumulate it; # – $p<0.05$ in comparison RIAM with PRIRM; * – $p<0.05$ in comparison STAGE_1 with the STAGE_2 of SRIRM*

So, conducted researches demonstrate appearance of the special cellular phenotype, complexes of psammous body and thyrocytes and cystic degeneration in FNA smears of primary radioiodine-refractory metastases and the stage of lost radioiodine accumulation (STAGE_2) of SRIRM, compared to radioiodine-avid metastases and the stage of radioiodine-accumulation (STAGE_1) of SRIRM.

3. 2. Immunocytochemical features of PTC postoperative metastases

The statistically significant reduction of the expression of TPO and Tg at the level of significance $p<0.05$ between RIAM and PRIRM was shown ($p=0$ and $p=0.000028$ respectively). The statistically significant reduction in the expression of TPO and Tg at the level of significance $p<0.05$ between different stages of the existence of SRIRM (STAGE_1 and STAGE_2) was shown ($p=0.003346$ for both antigens) (**Fig. 3**). However, in the smears of RIAM (which were successfully treated by RI), the percentage of TPO-positive thyrocytes reached 100 %. Whereas, in the FNA smears of STAGE_1 of SRIRM the percentage of TPO-positive cells was 15–75 % of thyrocytes. The difference between these groups of metastases in the expression of TPO was statisti-

cally probable at the level of significance $p<0.05$ with the non-parametric Mann-Whitney U-test (p=0,000047). At the same time, after the loss of RI accumulation ability (STAGE_2), the FNA smears of SRIRM had only 0–7 % of TPO-positive cells.



a *b*

Fig. 3. Immunocytochemical reaction with antibody to thyroid peroxidase in FNA smears of postoperative PTC radioiodine accumulating metastases: *a* – intensive expression of thyroid peroxidase in punctate of RIAM; *b* – mosaic expression of thyroid peroxidase in punctate of STAGE_1 of SRIRM, ×200

A statistically significant difference between STAGE_2 and STAGE_1 of SRIRM and as well as between PRIRM and RIAM was not shown with the Ck17-positive cells percentage at the level of significance $p<0.05$ (p=0.108810, p=0.910258).

The data of the frequency of the studied imunocytochemical features in FNA smears of postoperative PTC metastases are given in **Table 2**.

Table 2

The Median values (*Me*, %) of thyrocytes' percentage with antigens' expression (TPO, Tg, cK17) in FNA smears of postoperative PTC metastases (RIAM, PRIRM, SRIRM)

Imunocytochemacal features	RIAM (n=25)	PRIRM (n=30)	SRIRM (n=15)	
			Stage of RI accumulation (STAGE_1)	Stage of lost of RI accumulation (STAGE_2)
TPO-positive cells (*Me*, %)	77.5 %#	0 %	20 %*	0 %
Tg-positive cells (*Me*, %)	92.5 %#	56 %	90 %*	50 %
Ck17-positive cells (*Me*, %)	0 %	0 %	0 %*	10 %

*Note: RIAM – radioiodine-avid metastases, successfully treated using the radioiodine therapy, PRIRM – radioiodine-refractory metastases, which never accumulate radioiodine, SRIRM – which previously were responsive to radioiodine and eventually lose the ability to accumulate it; # – $p<0.05$ in comparison RIAM with RIRM; * – $p<0.05$ in comparison STAGE_1 with STAGE_2 of SRIRM*

So, the statistically significant difference of the expression of thyroid peroxidase and thyroglobulin between radioiodine accumulating metastases and primary radioiodine-refractory metastases, and between different stages of the existence of secondary radioiodine-refractory metastases (STAGE_1 and STAGE_2) was shown. Moreover, the different efficacy of radioiodine-therapy depending on thyroid peroxidase-positive cells percentage in FNA smears of metastases was demonstrated.

4. Discussion

The study of FNA smears of postoperative PTC metastases with different iodine accumulating ability revealed cytological changes and changes of some antigens' expression that occurred in the thyrocyte' population in course of the loss of RI-accumulation ability. The

conducted researches demonstrate the appearance of special cellular phenotypes and complexes in FNA smears of PRIRM and STAGE_2 of SRIRM, compared to RIAM and STAGE_1 of SRIRM. There is an emergence of some specific cellular phenotype that have no expression of Tg (marker of differentiated thyrocytes), which is relevant to the accumulation of RI during the loss of the ability to RI accumulation. The special cellular phenotype does not react with anti-epCAM (Ber EP4 antigen) antibodies. This is somewhat unexpected because epCAM, consisting of two glycoproteins, 34 and 39 kDa, is found on the cell surface and in the cytoplasm of virtually all epithelial cells, with very few exceptions. In particular, epCAM expression is typical of follicular (A-cells), Hurthle (B-cells) and parafollicular (C-cells) cells of the thyroid, both in health and cancer [14]. EpCAM – adhesion molecules of epithelial cells, they also considered to be one of the key factors in the process of epithelial-mesenchymal transition, when epithelial cells lose their polarity and intercellular adhesion and acquire the ability to migration. Probably, these characteristics of specific cellular phenotype in explored metastases are a source of RI refractoriness.

Also, there are specific cellular complexes of psammoma bodies and vacuolated thyrocytes in PRIRM and STAGE_2 of SRIRM that were absent in RI-accumulation metastases. Cytopathologists describe the numerous psammoma bodies in the single tissue fragment in a FNA smears from a diffuse sclerosing variant of PTC [15]. This variant of PTC is recognized as aggressive variants by the WHO. Probably, we can consider these complexes as a cytopathological sign of thyroid carcinoma' aggression and RI-refractoriness. However, this assumption requires further investigation.

The data regarding the tumors' resistance to the commonly used therapy has shown that the clonal tumor heterogeneity may be based on its development [16]. Previously there was a demonstration of the population heterogeneity in follicular epithelium only on the histological sections of the thyroid nodule's tissue [17]. We were the first to conduct the study of the tumor heterogeneity in the FNA smears of PTC metastases.

There is a statistically significant reduction of PRIRM, compared to RIAM and of STAGE_2, compared to STAGE_1 of SRIRM in the expression of TPO and Tg, which is momentous in the accumulation and retention of RI by cells of follicular epithelium. The received results do not contradict the literature data where researcher's ICH investigations of the RIRM showed a significant reduction in their tissue Tg, TPO, and their mRNA [18, 19]. However, studies of these antigens' expression in FNA smears of metastases during the development of secondary radioiodine refractoriness were first conducted in this work. The appearance of special cellular phenotypes and complexes, the loss of antigens which take part in the accumulation and RI retention (TPO, Tg) may be a manifestation of the loss of cytological signs of high differentiation of thyrocytes that cause successful RI treatment. These data do not contradict the previously obtained results in the study of the histological material of PTC and their metastases [20].

TPO-antigen is related to the accumulation of RI [21, 22]. We can see, that the median value of TPO-positive cells percentage for RIAM, successfully treated using the radioiodine therapy (*Me*=80 %), was statistically probably higher than for the group of STAGE_1 that eventually became STAGE_2 of SRIRM (*Me*=20 %). It demonstrated different efficacy of RI therapy, depending on TPO-positive cells percentage in FNA smears of metastases. We can see that the loss of the ability to RI accumulation of metastases happens despite the initial moderate ability during the development of secondary radioiodine refractoriness**.** Therefore, probably the low percentage of TPO-positive cells (up to 15 %), observable in FNA smears of STAGE_1 of SRIRM, may be not enough for the successful RI therapy. Basically, the reason of this phenomenon can be behind the phenotypic heterogeneity of tumors. Apparently, thyrocytes that have TPO and Tg are able to accumulate RI and eventually are destroyed by this radiopharmaceutical means. And the development of secondary radioiodine refractoriness in metastases happens thanks to thyrocytes that do not contain TPO and Tg and are not able to RI accumulation.

5. Conclusions

The postoperative secondary radioiodine-refractory metastases of papillary thyroid carcinomas, which initially accumulated radioiodine (STAGE_1), but eventually lost this ability

(STAGE_2) were chosen as modeling for the study of cytological and immunocytochemical cells' changes that occur in the dynamics of development of radioiodine refractoriness.

The statistically significant reduction of the expression of thyroid peroxidase and thyroglobulin between radioiodine accumulating metastases and primary radioiodine-refractory metastases and between different stages of the existence of secondary radioiodine-refractory metastases (STAGE_1 and STAGE_2) was shown.

The conducted researches demonstrate the appearance of special cellular phenotypes and complexes in FNA smears of primary radioiodine-refractory metastases and the stage of lost radioiodine accumulation (STAGE_2) of secondary radioiodine-refractory metastases, compared to radioiodine-avid metastases, and the stage of radioiodine-accumulation (STAGE_1) of secondary radioiodine-refractory metastases.

The median value of thyroid peroxidase-positive cells percentage for radioiodine-avid metastases, successfully treated, using the radioiodine therapy, was statistically probably higher than for the group of the radioiodine-accumulative stage of postoperative metastases (STAGE_1), which eventually became secondary radioiodine-refractory metastases. It demonstrated different efficacy of the radioiodine-therapy, depending on thyroid peroxidase-positive cells percentage in FNA smears of metastases.

Revealing the phenotypic heterogeneity of thyrocytes (presence of specific cellular phenotypes, structures, cystic degeneration) in FNA smears and a low percentage of thyroid peroxidase and thyroglobulin-positive thyrocytes allows the development of the method of cytological prediction of the effectiveness of the radioiodine therapy of postoperative metastases of papillary thyroid cancer. Cytopathologists can use these results to provide their clinicians and patients with pertinent additional diagnostic information, which could significantly impact patient management and outcome.

Acknowledgments

The authors gratefully acknowledge histological confirmation, provided by the Laboratory of Pathology, Institute of Endocrinology and Metabolism (the head – Tatyana Ivanovna Bogdanova, Doctor of Bioligical Sciences) and Yuri Mikhailovich Bozhok, Doctor of Bioligical Sciences (the head of Laboratory of Cytology)

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Received date 29.11.2019
Accepted date 08.01.2020
Published date 24.01.2020

QUALITY INVESTIGATION OF FROZEN GARDEN STRAWBERRIES AT PARTIAL DEHYDRATION BEFORE FREEZING

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Abstract

Garden strawberry is an important berry culture, consumed fresh and frozen. But a quality of frozen berries is not always at the high level because of changing organoleptic properties, tissues structure and biological active substances losses. It motivates searches for different methods of previous processing of berries before freezing. There was used a production technology of frozen strawberry with partial dehydration before freezing for solving the problem.

Garden strawberries of varieties Rusanivka, Honey and Polka were dried on air before freezing ("control" variant), and another part was partially dehydrated in a drying chamber at temperature 40 °C during 30 min ("partial dehydration" variant) with further freezing to final temperature - 18 °C, with packing in packages of polyethylene film with a mass up to 500 g and storing in a refrigerator at temperature –18 °C during 6 months. There were studied main parameters of the chemical composition of fresh and frozen strawberries: content of dry soluble substances, sugars, organic acids, ascorbic acid and sugar-acidic index. Organoleptic quality parameters of frozen strawberries were assessed by the 5-point scale. The experiment was repeated trice.

It has been established, that frozen strawberries, partially dehydrated before freezing, saved by 0.2–0.3 % more dry soluble substances, by 0.2 % – sugars, by 7.0–7.9 % – ascorbic acid at a practically equal level of organic acids.

The organoleptic mark of frozen partially dehydrated strawberries was by 0.2–0.3 points higher against the control. Among the studied varieties of strawberry, Polka berries got a mark higher by 0.2–0.9 points.

Keywords: strawberries, partial dehydration, freezing of garden strawberry.

DOI: 10.21303/2504-5695.2020.001051

1. Introduction

Garden strawberry is a leading berry culture in the world, which production volumes in 2017, according to data of the Britain analytic company Fresh4cast, reached 9.7 mln tons that was 72 % of the world production of berries, with a prognosis for 2020 as up to 15.4 mln tons [1, 2].

Garden strawberry is highly appreciated by consumers because of the pleasant outlook, harmonic taste and smell, essential amount of sugars, organic acids, vitamins, mineral compounds [3, 4]. Garden strawberry is consumed fresh, frozen and as other processing products.

Fast freezing as a preserving way favors the maximal saving of initial properties of raw materials, but a quality of frozen strawberry not always satisfies consumers' requirements. This fact is conditioned by changing organoleptic parameters and microstructure of berries' tissue as a result of recrystallization. The essential demand for frozen strawberry at world and Ukrainian markets stimulates searching for methods of its preliminary processing before breezing that maximally favor berries' natural properties preservation.

For stabilizing a quality of frozen strawberry, there are recommended solutions with antioxidizing, antiseptic properties that favor preservation of C-vitamin value, among which aqueous extracts from oak bark, birch, tutsan grass and green tea infusion [4], concentrated solutions of saccharose with cryoprotective properties [5]. The positive influence on preservation of the strawberry tissue microstructure is made by solutions of calcium chloride ($CaCl_2$) and pectin methyl esterase, 0.3 % guar gum and 2 % sugar-pectin [6–8]. But at these methods of preliminary processing of strawberries before freezing, there appears a necessity to buy auxiliary materials, not always easily accessible.

This all allows to state that studies, devoted to a quality of frozen garden strawberries at different methods of preliminary processing before freezing, are expedient.

For solving the quality problem of frozen strawberry, we offered partial dehydration of berries before freezing that favors getting more concentrated products, saving the tissue structure, inactivation of oxidizing-renewing components and decreasing storage duration.

The aim of the work was to study a quality of frozen garden strawberry at partial dehydration of berries before freezing by the complex of physical-chemical and organoleptic parameters that allows to improve a quality of frozen strawberry.

The following tasks were solved for attaining this aim:

– to asses an influence of partial dehydration of strawberries before freezing on changes of physical-chemical quality parameters, based on experimental studies;

– to assess organoleptic quality parameters of frozen strawberries at partial dehydration before freezing.

2. Materials and Methods

The studies were conducted in 2015–2016 at the department of storage and processing of fruits and vegetables of the Uman national university of gardening, Uman, Ukraine. Strawberries

Rusanivka, Honey and Polka, cultivated by the traditional technology, were harvested at the consumption ripeness stage and immediately transported to the laboratory. Strawberries were prepared for freezing according to the technological instruction for producing fast-frozen fruits and berries: sorted, cleaned from pedicles and sepals, washed, dried and frozen scattering up to final temperature within berries – 18 °C, packed in packages of polyethylene film for food products with a mass up to 500 g and stored in a refrigerator at temperature -18 °C during 6 months. The experiment was repeated trice.

3. Experimental procedures

A part of strawberries was dried on air ("control" variant), and another part was partially dehydrated in a drying chamber at temperature 40 °C during 30 min ("partial dehydration" variant) that gives a possibility to evaporate an essential amount of moisture, without excessive drying of berries. Control and experimental samples of strawberries wee frozen in the aerial medium to final temperature –18 °C (according to the technological instruction for producing fast-frozen fruits and berries). Frozen strawberry was packed in packages of polyethylene film for food products with a mass up to 500 g and stored in a refrigerator at temperature -18 °C during 6 months (according to the technological instruction for producing fast-frozen fruits and berries). The experiment was repeated trice.

A content of dry soluble substances was determined in fresh and frozen strawberries by the electric refractometer of Pal–1 type (Japan), sugars – by the spectrophotomeric method [9, 10], titrated acids – by alkali titration [10], ascorbic acid – by Tillmans method [11]. Orhanoleptic quality parameters of frozen strawberry were assessed by the 5-point scale. 10 testers assessed them by parameters of outlook, consistence, color, taste, smell and general estimation. Strawberries, frozen without partial dehydration before freezing, were accepted as a control.

The statistical analysis was conducted, using the program StatSoft STATISTICA 6.1.478 Russian, Enterprise Single User (2007).

4. Results and Discussion

The studies have established **(Fig. 1)**, that strawberries of different pomoloogic varieties accumulated in their composition from 9.3 to 9.8 % of dry soluble substances with the essential advantage of Polka ones.

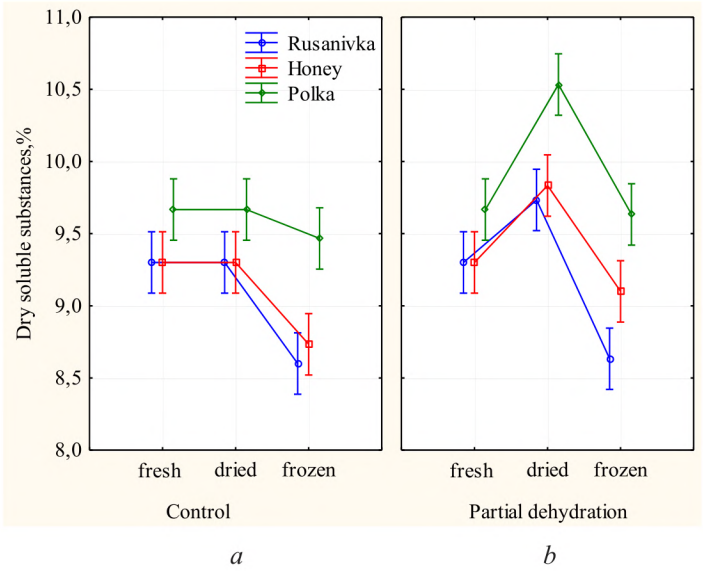
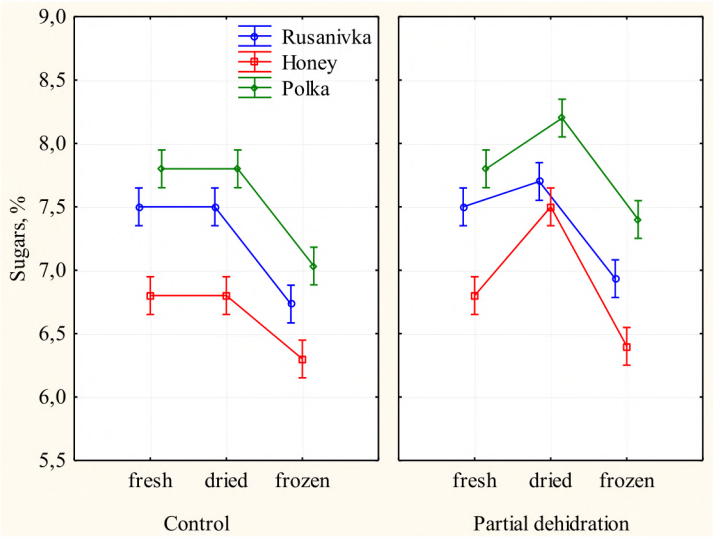


Fig. 1. Content of dry soluble substances in garden strawberries depending on variety, preliminary processing and freezing: *a* – control; *b* – with partial dehydration

Preliminary drying of strawberry on air didn't influence a content of dry soluble substances in them, whereas this index in partially dehydrated berries increased by 0.4–0.6 % depending on variety that is conditioned by partial evaporation of moisture from the product. It must be noted, that the high level of dry soluble substances was saved by Polka berries.

It is known, that just at the stage of freezing main changes of the chemical composition of raw materials take place that is proved by the research results: losses of soluble dry substances were 0.8–1.2 % from their content after preliminary drying. Moreover, in the control they were higher by 0.2–0.3 %. The essential losses of dry soluble substances were revealed in Honey berries, frozen without partial dehydration – 1.2 %.

The content of sugars in fresh strawberries of the studied varieties varied within 6.9 – 7.8 %. By 0.5-0.9 % higher saccharinity was revealed in Polka strawberries (**Fig. 2**), that is testified by variety peculiarities of berries.



a *b*

Fig. 2. Content of sugars in garden strawberries depending on variety, preliminary processing and freezing: *a* – control; *b* – with partial dehydration

Partial dehydration of berries before freezing favored the growth of the sugars content in them by 0.3–0.6 %, and after freezing - vice versa. Their level essentially decreased (by 0.7–1.2 %) with losses, higher by 0.2 % in the control.

The acidity of strawberries was established at level 0.9–1.0 %, moreover their higher level 1 % was established in Honey berries (**Fig. 3**), that is conditioned by variety peculiarities.

As a result of partial dehydration of berries, the content of organic acids in them decreased by 0.2–0.3 % from the initial, whereas no changes were revealed in the control.

On the contrary, during freezing of berries the level of organic acids grew in practically all variants of the experiment – by 0.1–0,. %, that is a special feature of frozen strawberry.

The sugar-acid index of strawberries of the studied varieties was established at level 6.9–8.7, that, according to W. Wozniak [12], allows to consider the taste of berries as sweet. The low sugar-acidic index was inherent to Honey strawberries; this fact is conditioned by the low sugars level (**Fig. 4**).

As a result of partial dehydration, the sugar-acidic index of berries grew by 2.5–4.6 units and reached value 9.4–12.8 due to the change of the ratio between sugars and organic acids in berries. The decrease of the index by 2.1–5.2 units was observed in frozen berries, with the essential one in Rusanivka ones, that is conditioned by essential losses of sugars.

The antioxidant activity of garden strawberries is mainly determined by a content of ascorbic acid in them [13]. At freezing there are observed losses of ascorbic acid at the expanse of its oxidation to dehydroascorbic one [14].

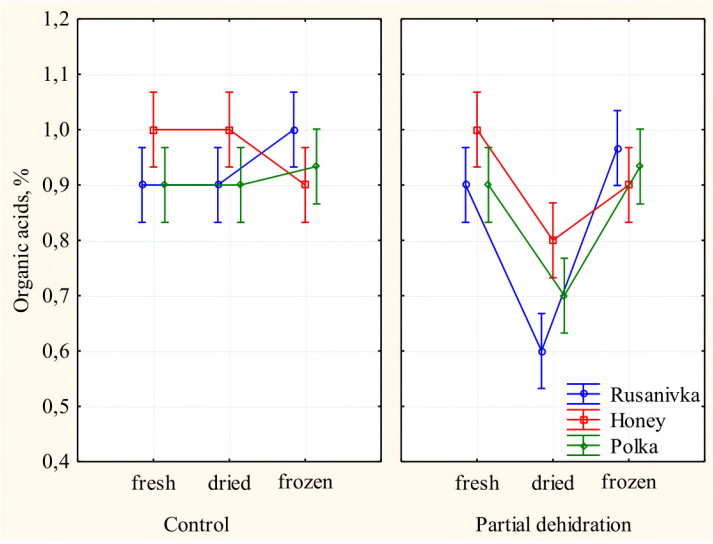


Fig. 3. Content of organic acids in garden strawberries depending on variety, preliminary processing and freezing: *a* – control; *b* – with partial dehydration

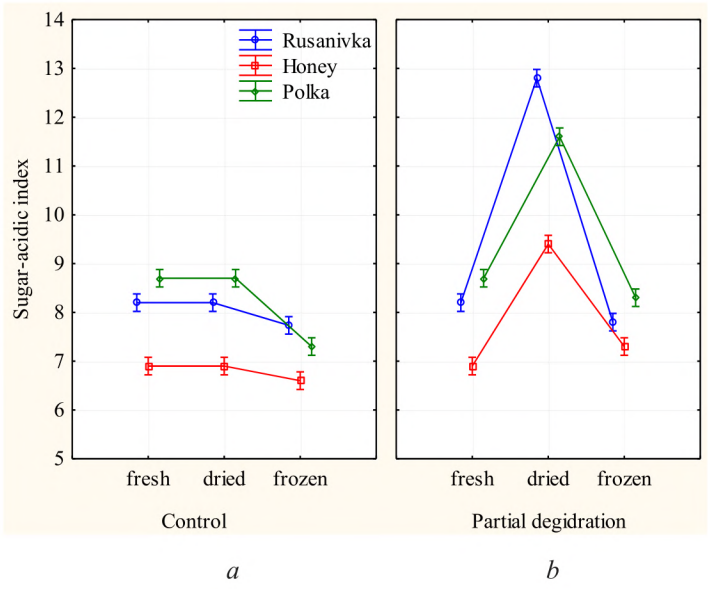


Fig. 4. Sugar-acidic index of garden strawberries depending on variety, preliminary processing and freezing: *a* – control; *b* – with partial dehydration

It has been established, that fresh Honey strawberries differed by the content of ascorbic acid – 105.1 mg/100 g (**Fig. 5**), that is a special feature of this variety. As a result of partial dehydration of berries, the losses of ascorbic acid were 6.8–12.3 % of the initial content, whereas no losses were revealed in the control.

As a result of freezing, the content of ascorbic acid in berries decreased by 4.3–12.6 % more. In the experimental variants without partial dehydration the losses were by 7.0–7.9 % higher. Honey strawberries had the losses at level 5.2–12.6 %.

At freezing, storage of frozen products and as a result of defrost, there are changes of their organoleptic properties, conditioned by the activity of enzymes. Undesirable changes of the consistence, color, taste and smell of defrost vegetable raw materials are connected with their activity [15].

The organoleptic parameters of defrost berries are presented on **Fig. 6**. The outlook of frozen strawberries was estimated as 3.8–4.8 points. Samples of partially dehydrated berries received by 0.2–0.3 points higher mark. The analogous data were obtained also at assessing the consistence of frozen strawberries that testifies to higher water-retaining capacity of partially dehydrated berries at freezing.

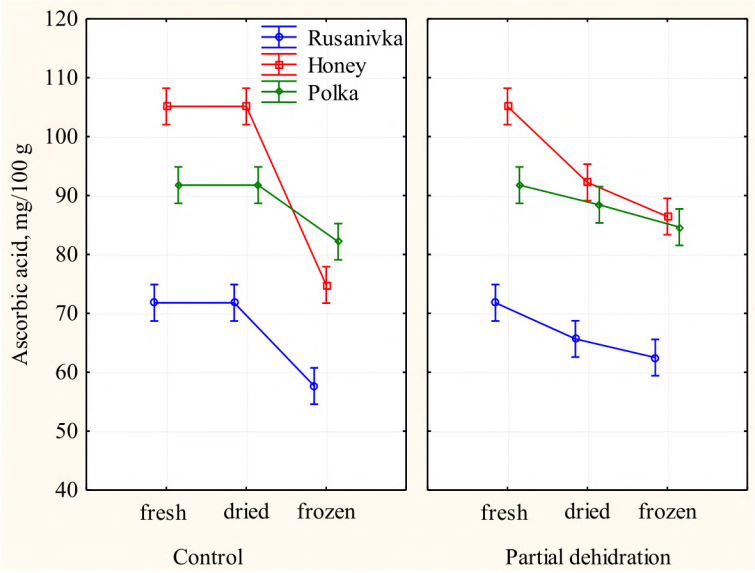


Fig. 5. Content of ascorbic acid in garden strawberries depending on variety, preliminary processing and freezing: *a* – control; *b* – with partial dehydration

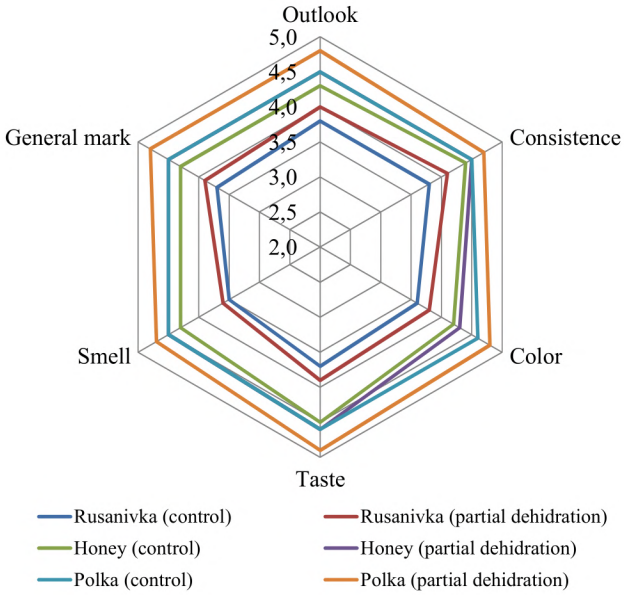


Fig. 6. Organoleptic assessment of frozen garden strawberries

The color and taste of frozen strawberries were assessed by testers as 3.6–4.8 and 3.7–4.9 points, respectively.

It is known, that the process of freezing causes changes of the aromatic profile of strawberries [16]. The worsening of the smell of frozen berries is observed also at storage at the expanse of the decreasing content of esters at the constant influence of carbonyl compounds [16]. The use

of partial dehydration of berries before freezing favored the preservation of their smell. In general the quality of strawberries, partially dehydrated before freezing, is estimated higher. Among the studied varieties, Polka berries received the mark, by 0.2–0.9 points higher.

5. Conclusions

The use of partial dehydration of berries before freezing favors the preservation of main components of the chemical composition, vitamin value and increases the organoleptic mark. Partially dehydrated frozen Polka berries have the higher quality. The further studies will be directed at studying the suitableness of different pomologic garden strawberry varieties for freezing at partial dehydration.

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Received date 25.09.2019
Accepted date 08.11.2019
Published date 24.01.2020

INVESTIGATION OF THE EMULSIFYING CAPACITY OF SNACK PASTE BASED ON FATLESS COTTAGE CHEESE

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Abstract

Technological parameters of the process of refined deodorized sunflower oil emulsification in a protein base – fatless cottage cheese for making a snack paste are presented. The expedience of introducing a melting salt – sodium citrate as a main emulsifier and its concentration are substantiated.

It has been established, that with increasing a content of sodium citrate the emulsifying capacity of a protein base grows, and at its concentration 2.0 %, reaches the maximal value – 50 vol un of oil. At a further increase of the sodium citrate concentration the emulsifying capacity decreases probably as a result of an abrupt pH growth.

It has been proved, that at adding dry skimmed milk in amount 4.0±0.5 % as an additional emulsifier in the protein base of a snack paste at 40 % of fatless cottage cheese in the recipe an increase of its emulsifying capacity by 6 vol un of oil, probably as a result of the growth of surface active substances, takes place.

The temperature influence on the viscosity of the snack paste protein base has been investigated and the rational concentration of refined deodorized sunflower oil has been determined as 25±2 %.

It has been established, that the temperature decrease from 50 to 30 °C and content increase of sunflower oil in the protein base from 25±2 % to 30±2 % result in the essential viscosity increase that may worsen emulsifying conditions.

It has been proved, that emulsion stability that is an important parameter for a snack paste of the emulsion type with a long storage term depends on content of main protein-containing components, sunflower oil and active acidity of the protein base.

The obtained results have a practical importance for determining the rational concentration of refined deodorized oil and sodium citrate that provides more necessary emulsifying capacity of the protein base and emulsion stability at storage in the technology of snack pastes, based on fatless cottage cheese.

Keywords: technology of emulsion products, emulsifying capacity, protein base, inversion point, aggregative and kinetic stability of emulsion.

DOI: 10.21303/2504-5695.2020.001104

1. Introduction

A segment of snack products, based on milk protein, relates to high-competitive ones at the products market by its demand among the population of Ukraine.

It is known, that the main fat component in snack products of the modern product market is milk fat, contained by hard cheeses – traditional protein base, and also as cream or cream butter. Milk fat gives snacks a creamy taste and consistence [1, 2].

But the essential decrease of milk production and its high cost in Ukraine created a deficit of milk fat, used in production of the essential spectrum of milk products [3]. At the same time new economic conditions of the market forced producers to search for less deficit and cheaper

vegetable fat raw materials for its replacement with a synchronous increase of the biological and food value. It resulted in the wide use of different fats and their compositions for partial or complete replacement of milk fat. The key demand of replacing milk fat by vegetable oil is a food value increase and improvement of organoleptic parameters of milk products with a possible decrease of cholesterol content.

It is known, that milk fat contains little amounts of essential oils: linoleic acid is within 1.5…4.4 %, linolenic – 0.2…2.1 %, whereas the content on linoleic acid in sunflower oil reaches up to 60 % [2, 4].

Vegetable fats contain many vitally important essential polyunsaturated fatty acids and also vitamin E (tocopherol), playing an important role in the human organism [4]. Physical-chemical properties of milk fat and several vegetable oils [2, 4], according to the data of native scientists, are presented in **Table 1.**

A taste and smell of vegetable oil, used in the recipe of a snack paste as a fat component, must imitate the typical taste or be neutral and stable at storage of the ready product.

Table 1

Physical-chemical properties of milk fat and several vegetable oils

Name	Temperature, °C		Saponification number of	Iodine number
	melting	congelation		
Milk fat	28...33	18...23	220...234	28…45
Sunflower oil	–	–16...–19	186...194	119…145
Corn oil	–	–10...–20	187...190	111…113

The use of refined deodorized sunflower oil as a fat component allows not only to decrease costs and to raise productivity, but also gives a possibility to widen the assortment, allows to make products with a less cholesterol content or without it, to balance a content of saturated and polyunsaturated fatty acids.

The aim of the study is to substantiate a concentration of the main recipe components – fatless cottage cheese and refined deodorized sunflower oil in the technology of a snack paste of the emulsion type, using a melting salt as sodium citrate as a main emulsifier.

The series of tasks must be solved according to the set aim:

– to study the viscosity of the snack paste protein base;

– to study the dependence of the protein system viscosity on temperature;

– to study the emulsifying capacity of the protein base;

– to determine the emulsion aggregative and kinetic stability.

2. Materials and Methods

The research objects were fatless cottage cheese of cow milk by SSU 4554:2006, obtained by the method of acid-abomasum coagulation of protein, refined deodorized sunflower oil by SS 1129, melting salt – sodium citrate (E331i, 331iii), dry skimmed milk by SSU 4273:2003, made by spraying with the mass share of: moisture 5 %, fat 1.5 %, protein 32 %, lactose 50 %.

Conventional standard research methods were used. Emulsification was realized on a laboratory emulsifier. For this aim a sample of the snack paste protein base as fatless cottage cheese with volume 10 ml was placed in a chemical glass with volume 100 ml, and added with refined deodorized sunflower oil with speed 78...80 drops/min up to the phase inversion moment [5–8].

2. 1. Determination of emulsion type

The emulsion type was determined by the dilution method, which essence is that emulsions as “fat in water” keep stability at water dilution and become non-homogenous at adding fat, emulsions of the reverse type keep stability at adding fat, but become non-homogenous at adding water.

A drop of the studied emulsion was put on an object-plate besides a water drop: drops mixture characterizes the emulsion "fat in water" [5, 6].

The volume of vegetable oil, poured from a funnel, corresponds to the phase inversion point value. The stability (constancy) of emulsions was determined, fixing phase volumes, separated after centrifuging with speed (33.3...35.0) s^{-1} during (10...11)×60 s.

2. 2. Determination of emulsion viscosity

The dynamic viscosity of the snack paste protein base as fatless cottage cheese with adding refined deodorized oil was studied in temperature diapason 30…95 °C, heating and cooling samples with interval 5 °C on Geppler rheo-viscosimeter [9], working by the principle of a displacing glass ball, falling in a liquid, produced by the plant FEB Karl Ceiss Yen with a tolerance for size and form distinctness less 0,001 mm, which falling speed is a viscosity measure. The studies were conducted in two measuring cylinders by turns, one of which characterizes number 1 (normal liquid NF 1000), the other characterizes number 10 (normal liquid NF 10000). The shearing stress was measured by using special weights, included in the device set.

The dynamic viscosity was calculated by formula (1):

$$\eta = P \cdot t \cdot K \cdot 30, \quad (1)$$

where P – load, shearing stress, g/cm^2; t – research time, s; K – measuring cylinder coefficient.

2. 3. Determination of emulsifying capacity

The emulsifying capacity of the snack paste protein base was studied by determining the phase inversion point at emulsification, changing the concentration of one of main components of the protein base by the standard methodology at temperature 35…40 °C, moisture 77,6 %, with mixer frequency 25 s^{-1}. The emulsifying capacity (% of fat) was determined by the inversion point as a maximal amount of fat, emulsified in the studied solution to the inversion point [5–8, 10]. The inversion point was determined by the abrupt decrease of voltage indications of the voltmeter, connected to the emulsification device.

2. 4. Determination of emulsion stability

The total stability of model emulsions was determined by the method of constructing diagrams of emulsion stability that reflect the ratio of volumetric parts (%) of the stable emulsion and phases, separated after centrifuging [5, 11, 12]. According to the data of obtained dependencies, there was estimated the effectiveness of the stabilized effect of the studied systems: the volumetric share of the fat phase was put on the x-axis, and volumetric shares of water and fat phases, separated in the centrifuging regime, were put on the y-axis from the left and right side, respectively. The lines, taken through experimental points, limit the area of separated phases and one of stable emulsion that may be a generalized measure of stability for the system "fat-water solution".

For studying the emulsion stability (constancy) of the emulsion before and after thermal processing, the diagrams were constructed by the standard method, that provides measuring of the volume of the fat and water phases, separated after centrifuging from the total volume as a result of emulsion destruction [5, 7, 8].

2. 5. Statistical analysis

The aggregative (*As*) and kinetic (*Ks*) stability were determined by formulas (2), (3) [5]:

$$As = 100 - \frac{Hf}{He} \times 100, \%, \quad (2)$$

$$Ks = 100 - \frac{Hw}{He} \times 100, \%, \quad (3)$$

where *Hf* – height of the fat phase, separated after centrifuging, $\times 10^{-2}$ m; *He* – height of the initial emulsion, $\times 10^{-2}$ m; *Hw* – Height of the water phase, separated after centrifuging, $\times 10^{-2}$ m.

Each experiment was conducted with no less than 5 iterations. The regularities were reproduced in each equivalent experiment, and for the objective judgment about the reliability degree of the obtained data, the research results were mathematically processed, using the standard package Excel 2016.

3. Results and discussion

According to the data of authors [4], the viscosity difference of various deodorized refined oils is not essential and is in temperature diapason 90…70 °C $(1.2\pm0.2)\times10^3$ Pa·s, and in temperature diapason 50…30 °C – $(2.5\pm0.1)\times10^3$ Pa·s.

For determining the rational concentration of sunflower oil at its emulsification in the protein base of snack pastes, the study of the dynamic viscosity of the emulsion with different contents of sunflower oil (**Fig. 1**) and the one of the protein base emulsifying capacity (**Fig. 2**) were conducted.

The studies of the temperature influence on the viscosity of the snack paste protein system with different contents of refined deodorized sunflower oil: 15; 20; 25 % have established, that the dynamic viscosity in temperature diapason 90…60 °C is practically equal and is near ~$0.5\cdot10^3$ Pa·s.

The temperature decrease in diapason 50…30 °C results in the viscosity growth within 1.0…$4.0\cdot10^3$ Pa·s. The increase of sunflower oil content in the milk base up to 30±2 % results in the essential viscosity growth in temperature diapason 90…60 °C within 0.75…$2.0\cdot10^3$ Pa·s and to the essential growth within 4.8…$13.5\cdot10^3$ Pa·s in temperature diapason 50…30 °C that may worsen emulsification conditions [13].

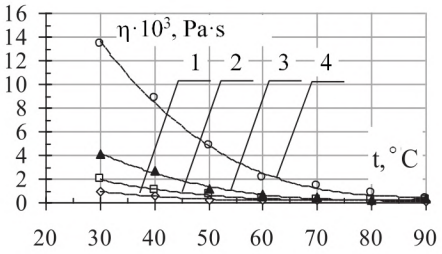

Fig. 1. Dependence of the viscosity of the snack paste protein base on temperature at sunflower oil content: 1 – 15 %, 2 – 20 %, 3 – 25 %, 4 – 30 %

It is known, that emulsification is a process that takes place with essential energy consumption [5–8], so it is expedient to realize it in the zone with the low viscosity, that is why for emulsification we accept oil concentration 25±2 %, rational at temperature 30…40 °C, because it provides the lowest viscosity of the protein base at level 2.8…$4.0\cdot10^3$ Pa·s.

It has been established (**Fig. 2**), that with the increase of sodium citrate concentration, the emulsifying capacity of the protein base E c grows and at concentration 2.0 % reaches its maximal value – 50 vol un of oil. At the further increase of sodium citrate concentration the emulsifying capacity decreases, probably as a result of pH growth (**Fig. 2**).

It has been proved (**Fig. 2**), that with the increase of fatless cottage cheese content from 30 to 40 %, the emulsifying capacity of the protein base intensively grows from 20 to 50 vol un of oil. At the further increase of fatless cottage cheese content in the recipe, the emulsifying capacity doesn't grow, probably as a result of the essential viscosity increase.

The addition of dry skimmed milk in amount 4.0±0.5 % as an additional emulsifier in the protein base at 40 % of fatless cottage cheese favors an increase of its emulsifying capacity from 50 to 56 vol un of oil (**Fig. 2),** probably as a result of the growth of surface active substances [5, 7, 10, 14].

For products of the emulsion type with long storage terms, an important parameter is emulsion stability. It was determined by the content of non-destructed emulsion after twofold centrifuging with intermediate heating up to 90 °C.

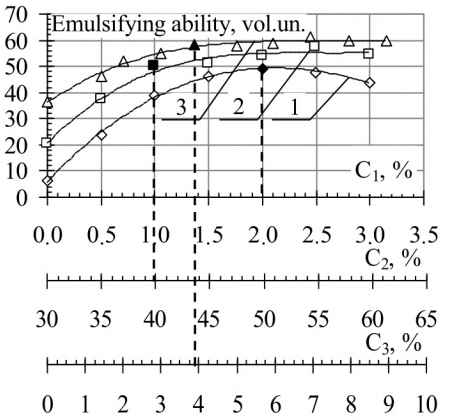

Fig. 2. Dependence of the emulsifying capacity of the snack paste protein base on concentration of main components: 1 – sodium citrate (C1); 2 – fatless cottage cheese (C2); 3 – dry skimmed milk (C3)

It has been established, that the mass share of the non-destructed phase of the snack paste model emulsion before thermal processing (**Table 2**) depends on fat content, concentration of protein-containing components of the protein base and sodium citrate concentration [15, 16].

Table 2

The stability of the snack paste model emulsion before thermal processing

Component name	Concentration, %	Mass share of non-destructed model emulsion, % at fat content (including vegetable oil), %			
		20	**40**	**60**	**80**
Fatless cottage cheese	30	24	66	84	94
	40	60	**83**	86	96
	50	76	88	94	98
	60	78	90	96	98
Dry skimmed milk	0	38	63	76	88
	4	56	**78**	82	92
	6	60	83	86	96
	8	86	94	98	98
Sodium citrate	0	22	31	40	48
	1	42	58	64	81
	2	60	**83**	88	96
	3	62	80	86	94

The analysis of **Table 2** testifies that the stability of the snack paste model emulsion at fat content 20…80 % is characterized by the mass share of the non-destructed structure correspondingly within 24…98 %, that depends on concentration of protein-containing components and also sunflower oil content in the recipe and active acidity of the protein base that also depends on sodium citrate concentration [5, 7, 10].

The analysis of the right part of the diagram **(Fig. 3)** demonstrated that the stability of the model emulsion before thermal processing is high as 96…98 % and almost doesn't depend on concentration of protein-containing components and sunflower oil within the studied concentrations.

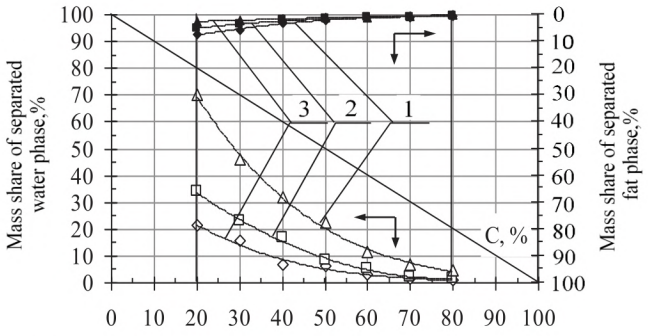

Fig. 3. Dependence of the stability of the model emulsion before thermal processing on sunflower oil concentration at fatless cottage cheese content, %: 1 – 30; 2 – 40; 3 – 50

But the analysis of the left part of the diagram (**Fig. 3**) testifies that the kinetic stability is low and at sunflower oil content in the model emulsion 20±1 %, dry milk 4.0±0.5 % and fatless cottage cheese in amount 30±2 %, 40±2 %, 50±3 % is 30±2 %, 65±2 %, 78±2 %, respectively. The sunflower content increase from 20…80 % at fatless cottage cheese concentration in the protein base 30 % raises the emulsion stability by 70 %, at the further cottage cheese concentration increase up to 40 % by 36 %, up to 50 % by 22 %, and up to 60 % by 20 %.

It has been established, that thermal processing at temperature 80±2 °C favors the stability increase of the snack paste model emulsion in almost 1.5 times (**Fig. 4**).

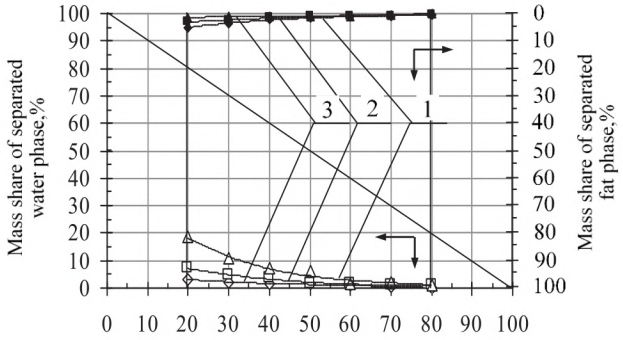

Fig. 4. Dependence of the stability of the model emulsion after thermal processing on sunflower oil concentration at fatless cottage cheese content, %: 1 – 30; 2 – 40; 3 – 50

After thermal processing the stability of the emulsion, containing 20±1 % of sunflower oil, grows at fatless cottage cheese content 30±2 % up to 70 %, at 40±2 % up to 84 %, at 50±2 % up to 94 % probably as a result of the increase of water binding by protein.

4. Conclusions

The studies have proved that the fat content of the snack paste model emulsion may have a wide diapason from 20 to 60 % at keeping the aggregative stability.

It has been established, that the fatless cottage cheese content in amount 40±2 % is a rational concentration in the snack paste model emulsion and provides necessary conditions for emulsification.

It is expedient to introduce dry skimmed milk in amount 4±1 % in the recipe that raises the emulsifying capacity of the protein base by 28±2 vol un of oil.

There has been proved the rational sodium citrate concentration in the protein base as 2±0.2 %, that provides the maximal emulsifying capacity as 50 vol un of oil (**Fig. 2**).

It is also necessary to introduce in the recipe a structure former with a high water-binding capacity for providing the high kinetic stability of the snack paste model emulsion together with thermal processing.

The conducted study allows to determine the rational concentrations of recipe components that may guarantee necessary rheological parameters of products of the emulsion type. It is planned to develop this study at elaborating technologies of fruit and dessert pastes, based on fatless cottage cheese. The obtained research results may be applied at producing melt cheeses, pastes, sauces, mayonnaises and other products of the emulsifying type, using milk-vegetable raw materials.

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Received date 20.11.2019
Accepted date 18.12.2019
Published date 24.01.2020

STUDY OF QUALITY OF SNACK GHERKIN TINNED FOOD

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Abstract

This work considers a problem of raising a marinade quality for producing snack gherkin tinned food. There is offered a new way for raising a marinade food value. The aim of the work is to raise a tinned food quality at the expanse of recipe peculiarities of ingredients. There is offered to produce snack tinned food with adding mustard. The tinned food contains gherkin, sugar refined sunflower oil, kitchen vinegar 9 %, salt, dry mustard, grinded red pepper and chopped garlic. An optimal recipe for diminishing mass consumption of the raw materials is developed in the study. The tinned food recipe was modeled by the simplex method that allowed to get an optimal variant with a maximal complex quality parameter. According to the recipe, a bank of I-82-500 needs: gherkin – 375 g, sugar – 37.5 g, refined sunflower oil – 37.5 g., kitchen vinegar 9 % – 37.75 g, salt – 3.75 g, garlic – 3.75 g, mustard (powder) – 3.75 g, grinded red pepper – 1 g.

It is established, that the new snack tinned food is characterized by high organoleptic properties.

The technological scheme at producing the snack tinned food "Pickled gherkins with mustard" includes the following processes: preparation of the raw materials (cleaning, sorting), soaking in cold water for 5–8 hours; inspection; pouring with marinade; mixing and infusion; packing; closing; sterilization, formation of ready products. Gherkins are processed by the standard technology for pickled vegetables. Physical-chemical parameters in the raw materials and ready products were studied during the work: the content of soluble dry substances – by the refractometric method; the total content of organic acids – by titration; pH-medium – by the potentiometric method; the content of nitrates – by the ionometric method. Mustard was added for raising a food value and quality of the snack tinned food. It is healthy, because it improves the appetite, disintegrates fats and facilitates digestion of protein meals, at that activating metabolism. Main healthy properties of mustard are antimicrobial, antifungal, antioxidant and anti-inflammatory effects. Added spices and garlic give a pleasant taste and add the composition of mineral substances.

The developed recipe is designed for production technological lines and recommended for implementation at processing enterprises. The conducted work testifies to the expedience of producing new types of snack tinned food, which food value is increased and organoleptic parameters are improved at the expanse of ingredients.

Keywords: technological scheme, recipe, vegetable tinned food, marinade, quality, chemical composition, food value, vitamins.

DOI: 10.21303/2504-5695.2020.001118

1. Introduction

Priority directions of the processing industry at the modern stage include the rational use of vegetable raw materials, maximal preservation of biologically active substances, widening of the assortment of products of a raised food and biological value.

A necessary amount of the preservative – acetic acid – is added to vegetables at their preparation for pickling. As a result, microbes cannot develop, and a product becomes tinned. Suppression of different microorganisms is manifested even at small concentrations of acetic acid (0.2–0.3 % of acid of the total mass of pickled products). At small concentration 0.4–0.6 % of acetic acid subacid marinades, not stable at storage, form [1–5]. As a result of the small concentration of vinegar, microorganisms in such marinades are partially suppressed, their essential part can develop and cause spoilage of the product. So, it is necessary to pasteurize subacid marinades. Concentrated acetic acid (essence), obtained at dry wood distillation by the chemical way, is most often used at enterprises. Acetic acid with concentration 80 %

(sometimes 70 %) is for sale. The use of acetic essence negatively influences the condition of the human gastrointestinal tract. The better quality of marinades is attended at using natural vinegar (wine or apple vinegar). Natural vinegar has the consistence of acetic acid from 4 % to 9 %. It has a soft taste and nutritive value, pleasant smell. In contains biologically active substances, including organic acids, some amounts of sugars, phenol substances, aldehydes, ethers and microelements [6–8].

The aim of the study is a way of raising a food value of gherkin tinned food.

2. Problem review

Today different technologies for giving gherkins a crispy texture are used at tinned food enterprises. One of undesirable methods is to add calcium chloride, and cheap synthetic aromatizers and sweeteners, used for eliminating an unpleasant taste and smell. An advantage of such products, made by the "hard" technology, is rather doubtful [9].

One of methods of raising a quality of ready products and eliminating the aforesaid defects is to improve the marinade technology at the expanse of using high-quality vegetable raw materials, determining an optimal recipe with using natural fruit vinegar [10–12]. The analysis of modern studies on the quality improvement of vegetable tinned food testifies to the necessity to optimize a recipe of marinades at preparing snack tinned food for raising a food value of ready products [13–15].

Based on studied consumers' preferences, works [17, 18] demonstrate a method of making new products with given production properties, oriented at the target audience. This method allows to see quality characteristics of a product in their quantitative expression and to compare several products. There appears a possibility to correct undesirable tints and smacks of functional supplements, introduced at the stage of the recipe development, and also to develop a recipe of a maximally competitive product, based on concrete consumption preferences.

Thus, problems of designing new food products are solved at the expanse of multi-ingredient character of a product, under condition of evaluating the complex quality parameter (CQP). The results of the quality evaluation of tinned food are presented on **Fig. 1.**

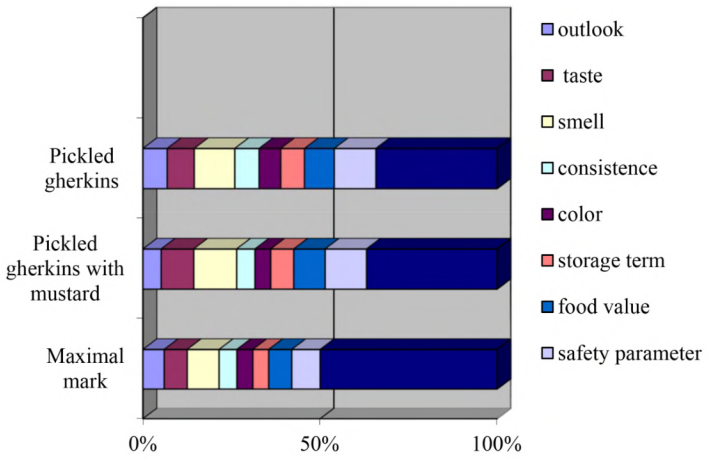

Fig. 1. Quality parameters of the pickled gherkin tinned food

For evaluating a quality of pickled gherkins, the tinned food was estimated by the organoleptic parameters: taste, smell, consistence, color. There were also estimated the physical-chemical parameters: mass share of dry substances, titrated acids, chloride content. The maximal amount of points for each parameter was calculated by the ranking method, based on expert marks. Based on literary data, an unalienable part is studies for determining a quality of the tinned food "Pickled gherkins with mustard", produced by the changed recipe.

3. Materials and methods

The research object is the snack tinned food "Pickled gherkins with mustard".

The research subject is marinade, technological scheme and production processes of vegetable tinned food.

The research methods are theoretical and experimental. Theoretical studies are scientific methods of determining normative quality and safety parameters of food products for improving a quality of pickled products.

The experimental studies were conducted at the department of Food technologies of Kherson national technical university. The commission included 5 testers (professors of the department of Food technologies). The studies were conducted, using the methods of determining organoleptic parameters; existent standard physical, chemical, physical-chemical, biochemical, microbiological methods of analyzing functional-technological and structural-mechanical quality and safety parameters of the ready pickled tinned food.

The chemical composition of gherkins includes vitamins of the groups: A, PP, C, B5, B1, B2, K. At that the vegetables are rich of the microelements and minerals: carotene, Ca (23 mg), Na (8 mg) and K (141 mg), P (42 mg), Fe (0.6 mg), folic acid. The composition of cucumbers includes: water 95 %, proteins (0.8 g), organic acids (0.1 g), carbohydrates (2.5 g), mono- and disaccharides (2.4 g).

4. Experiments

4. 1. The development of the marinade recipe for the tinned food "Pickled gherkins with mustard"

The system approach to creation of innovative products with given consumption properties provides realization of a series of main principles. At solving problems for minimum, a value of the target function must change reversely: from the maximal to the minimal possible one. The maximal value of the function will be initial, and the minimally possible – at the final solution. As far as fictious variants of the recipe are included in the initial plan, reverse CQP values that essentially exceed ones for real variants of the recipe must be accepted for them. For obtaining a mathematic model of the problem, several recipe variants are needed [19]. 5 variants of the recipe of the tinned food "Pickled gherkins with mustard", including the following components: vinegar (9 %), sugar, sunflower oil, salt, garlic, mustard (powder), grinded red pepper with different ratios of ingredients, were designed for the experiment. The optimal recipe of the snack tinned food (taking into account the complex quality parameter (CQP 98.67 %) was selected among the experimental recipe variants.

The component ratio of the optimal recipe of the new type of tinned food "Pickled gherkins with mustard" is presented in **Table 1.**

Table 1

The component ratio of the recipe of the tinned food "Pickled gherkins with mustard"

Raw material	Component ratio, mass %
Gherkins	75
Kitchen vinegar 9 %	7.55
Sugar	7.5
Refined sunflower oil	7.5
Salt	0.75
Garlic	0.75
Mustard (powder)	0.75
Red grinded pepper	0.20

The tinned food "Pickled gherkins with mustard", including gherkins, salt, kitchen vinegar 9 %, differs from the prototype "Pickled gherkins" by the presence of mustard (powder), sugar, refined sunflower, grinded red pepper and garlic.

According to the optimal recipe results, standards of the raw materials for package in a bank of I-82-500: gherkin – 375 g, sugar – 37.5 g, refined sunflower oil – 37.5 g, kitchen vinegar 9 % – 37.75 g, salt – 3.75 g, garlic – 3.75 g, mustard (powder) – 3.75 g, grinded red pepper – 1 g.

4. 2. The Method of titration acidity determination. SSU 4957:2008

The essence of the visual method: potentiometric titration of the testing solution by sodium hydroxide of the molar concentration (NaOH)=0.1 mol/dm^3 with the phenolphthalein indicator. Distilled water, used for the study, must not contain carbonic acid, so it must be freshly boiled and cooled or neutralized by the solution of sodium hydroxide of the molar concentration (NaOH)=0.1 mol/dm^3 to the weakly-pink color by phenolphthalein.

A batch of the product with the mass from 5 g to 50 g, depending on permitted acidity, is transferred through a funnel of 50 cm^3 with hot distilled water in a conic flask of 250 cm^3. Then the flask is poured with distilled water at temperature (80±5) °C up to the half of its volume, accurately mixed, kept during 30 min, periodically shaking, or connected to a dephlegmator, the content is heated on the water bath during 30 min. After cooling the content of the flask is put to a measuring flask of 250 cm^3 and the volume is added with distilled water to the mark. Then it is corked, the solution is accurately mixed and filtered through a filter or wadding. If the product is liquid, the batch of mass 50 g is quantitatively transferred by distilled water of the room temperature in the measuring flask of 250 cm^3 and the volume is added with distilled water to the mark, mixed and filtered.

An aliquot portion. 25 cm^3 – 100 cm^3 of filtrate is taken by a pipette to the conic flask of 250 cm^3. Such amount of taken filtrate allows titration at no less 6 cm^3 of the sodium hydroxide solution. The flask with filtrate is added with three drops of the phenolphthalein solution and titration by the sodium hydroxide solution is realized at continuous mixing to the pink coloration that doesn't disappear during 30 min. The mass share of titrated acidity in percents in recalculation for the dominant acid is calculated by the formula:

$$x = \frac{V \times c \times M \times V_0}{0.1 \times m \times V_1},$$

where V – volume of the titrated acid of nitrate silver, used for titration, cm^3; c – molar concentration of the titrated acid of nitrate silver, mol/dm^3; M – molar mass of sodium chloride M(NaCl)= =58.45 g/mol; m – batch mass, g; V_1 – volume that the water extract of the product batch is added to, cm^3; V_2 – volume of filtrate, taken for the determination, cm^3.

At the organoleptic evaluation (5-point scale) there were assessed an outlook, consistence, filling quality, taste and smell of the ready products. The data of the organoleptic evaluation are presented on **Fig. 2.**

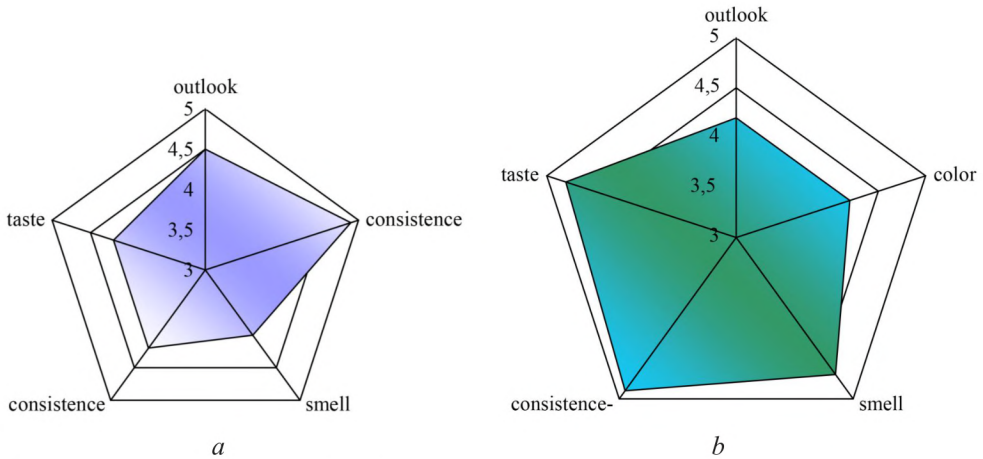

Fig. 2. Comparative evaluation of organoleptic parameters of the snack tinned food: *a* – pickled gherkins; *b* – pickled gherkins with mustard

Based on the results of the conducted testing, a conclusion may be made that pickled gherkins with mustard, developed by the improved technology, differ by the high organoleptic properties.

The snack tinned food "Pickled gherkins with mustard" have the olive color; the smell is pleasant, typical for pickled vegetables. The taste is a bit bitter, a bit sweet, typical for pickled vegetables, brightly expressed taste of cucumbers, mustard is perceived in marinade, and garlic with red pepper give a spicy smack and pleasant fragrance. For improving the filling quality, it is recommended to use mustard in grains instead of dry powder.

4. 3. The technological production scheme of the snack tinned food "Pickled gherkins with mustard"

For producing the snack tinned food "Pickled gherkins with mustard", there are used gherkins of the technical or biological ripeness stage, with the green fruit color. Gherkins are considered a dietetic foodstuff because of the low caloric content (10–15 kcal for 100 g of the product). At that the substances, included in it, improve digestion and help the gastrointestinal tract to digest other products, perfectly help to cope with removal of harmful toxins. For improving the food value and quality of snack tinned food, mustard was added. Its use is in a fact that it improves the appetite, disintegrates fats and facilitates digestion of protein meals, at that activating metabolism. Main healthy properties of mustard are antimicrobial, antifungal, antioxidant and anti-inflammatory effects [3, 20].

Taking into account the aforesaid, these components were purposefully introduced in the recipes of the offered vegetable tinned food.

The authors developed a procedural production scheme of new types of snack tinned food, corresponding to the international quality control system (HACPP). The technological production scheme of the snack tinned food is presented on **Fig. 3.**

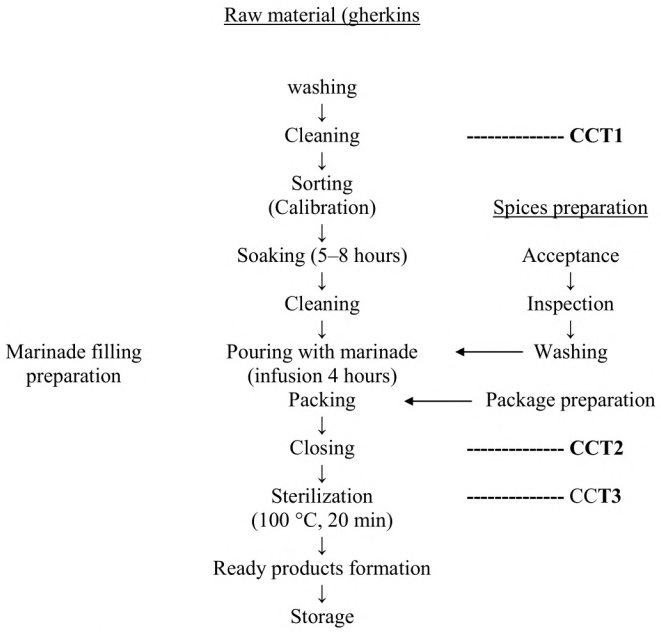

Fig. 3. Technological production scheme of the snack tinned food "Pickled gherkins with mustard"

The technological production scheme of thesnack tinned food "Pickled gherkins with mustard" includes the following processes: preparation of the raw materials (cleaning, inspection), soaking in cold water for 5–8 hours; inspection; pouring with marinade; mixing and infusion; packing; closing; sterilization, formation of ready products. Gherkins are processed by the standard technology for pickled tinned food [16].

6. Results discussion

Mathematical modeling at creating new types of fruit-vegetable products is necessary for determining an optimal recipe and also for choosing ready products with high organoleptic indices.

The methodological base of the conducted studies for forming and evaluating the products, based on the vegetable raw materials is a system approach. It allows to consider different factors, forming a quality of the ready products as a system of independent processes that transform the initial raw materials in the ready product with the determined consumption properties.

Based on the conducted studies, the authors substantiated the production technology of vegetable tinned food by the new recipe. The recipe model was made by using the simplex method that allows to get an optimal variant with the maximal complex quality parameter.

At studying the physical-chemical parameters of pickled vegetables, the special attention was paid to their functional properties. The tinned food "Pickled gherkins with mustard" differs by the high organoleptic indices at the expanse of the favorable combination of sugars and acids and also well-expressed marinade smell and taste.

The comparative characteristic of the organoleptic parameters is presented in **Table 2.**

Table 2

Organoleptic quality parameters

Parameter name	Pickled gherkins (SSU 7989:2015) Sample 1	Pickled gherkins with mustard Sample 2
Outlook	Fruits correspond to standards	Fruits correspond to standards
Taste and smell	Taste is a bit sour, vinegar smell is felt, without side admixtures	Natural without side smacks and admixtures
Consistence	Fruits are a bit hard, not enough crispy	Cucumbers are hard, crispy, flesh is dense
Marinade quality	Typical color with a weak yellow tint	Color is green-olive

The studied pickled cucumbers have perfect taste characteristics and don't deviate from requirements of the correspondent standard (SSU 7989:2015 Pickled cucumbers. Technical conditions) by the physical-chemical parameters.

7. Conclusions

The addition of mustard powder in marinade raised the food value of the snack gherkin tinned food. Its quality by taste and smell had better parameters, comparing with the traditional recipe, the consistence of gherkins remained dense and crispy. The complex quality parameter allowed to evaluate the organoleptic properties of the ready tinned food.

The use of the simplex method at developing the marinade recipe allowed to choose the optimal ratio of ingredients.

The technological processing scheme of the raw materials (gherkins) doesn't include the process of blanching by water that allows to decrease production costs.

The studies have the practical importance for implementing at processing tinned food enterprises.

Development prospects of the study are:

1. The change of mustard powder for grains in the marinade recipe for eliminating turbidity.

2. The improvement of the instrument-technological scheme for determining control critical points, corresponding to international standards.

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Received date 26.11.2019
Accepted date 27.12.2019
Published date 24.01.2020

USE OF NON-TRADITIONAL VEGETABLE RAW MATERIALS IN THE TECHNOLOGY OF FLOURY CONFECTIONARY PRODUCTS FOR RESTAURANT ECONOMY ENTERPRISES

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Abstract

Products of biscuit dough are ones of most popular among floury confectionary products that is conditioned by their taste advantages, and ones of constant elements of food rations. Biscuit semi-products are a base of such confectionary products as tarts, fancy cakes, cookies.

It is expedient to use supplements of non-traditional raw materials that can not only influence the technological process and quality of ready products, but also enrich them with biologically active substances as additional components of floury confectionary products. The most promising raw material for enriching products of this group is vegetable powders, because fresh products are seasonal and don't regularly provide the food ration of the population with biologically active substances.

The article considers a possibility of using snowball, ashberry and buckthorn powders for making biscuit semi-products. The aim of the work was to study the expedience and technological possibility of using vegetable raw materials in the biscuit semi-product technology.

The chemical composition of chosen powders was studied. The influence of vegetable powder on the quality and quantity of cellulose, structural-mechanical and physical properties of dough was established. The expedience of using surface-active substances in the biscuit semi-product technology for improving the quality of ready products was substantiated.

Keywords: floury confectionary products, biscuit semi-product, vegetable powders, improvers, non-traditional vegetable raw materials.

DOI: 10.21303/2504-5695.2020.001113

1. Introduction

Under modern conditions of economic activity an essential part of restaurant economy enterprises (REE) offer visitors floury confectionary products (FCP), produced by themselves. FCP are of the wide demand among the population and REE visitors. At that their chemical composition is unbalanced by main nutrients and characterized by the high content of easily assimilated carbohydrates and fats. Determining the chemical composition of FCP purposefully, we can effectively influence the food ration of a person, his/her health status, labor activity and so on.

Near 25 % in the total volume of produced FCP belong to ones of biscuit dough. Biscuit products are remarkable for easy assimilability, pleasant taste and smell, pleasant outlook. Well baked biscuit is suitable for processing, has a thin even surface crust; porous elastic crumble struc-

ture – is easily compressed at pressing, renews an initial form after removing an effort. A wide assortment of tarts, fancy cakes, rolls is produced, based on biscuit semi-products.

Main tasks, set for own production, are connected with a necessity to widen the assortment of FCP, prolongation of their storage term, increase of their food value at the expanse of using new non-traditional raw materials. Non-traditional vegetable raw materials have a wide spectrum of functional properties that allow to influence ones of products, course of the technological process, to regulate properties of structural components of raw materials in the given direction, to improve physical-chemical and organoleptic characteristics of semi-products and ready products, to improve their quality indices, food value and to correct their chemical composition.

2. Literature review

Powders of non-traditional vegetable raw materials are promising for enriching FCP. Fresh products are seasonal and don't regularly supply the food ration of the population with biologically active substances. At drying moisture is released from vegetable objects, concentration of substances in cellular juice and its osmotic pressure increase that prevents the development of microorganisms. The chemical concentration of dried berries is concentrated and high-energetic, rich in carbohydrates, pectin and mineral substances, vitamins and organic acids [1].

Apple powder became widely used in food technologies. Its food value is in the content of vitamins and microelements, able to be stored for up to two years.

Studies as to the possibility of using apple powder in the caramel technology are conducted. It has been established, that adding apple powder at producing caramel allows to increase the food value of a ready product at the expanse of pectin and mineral substances, to exclude synthetic aromatic, flavoring and coloring substances from the recipe [2]. Technologies of using apple powder for producing fruit biscuits, gingerbread and decorating semi-products are substantiated and developed. The authors have established that adding apple powder to biscuits, cookies and gingerbread in amount 10…15 % allows to get high-quality ready products, to prolong storage terms of products, to increase their biological value [3–5].

There is substantiated a possibility of using 10 % of persimmon powder instead of wheat flour in the technology of sandy products that improves structural parameters of sandy cookies, increases their biological value and at the same time results in decreasing the energetic value of the product [6].

The introduction of pumpkin powder to the recipe of biscuits in amount 5…15 % of the flour mass favors the improvement of their food value due to the pumpkin biochemical composition. The great amount of easily assimilated sugars, pectin, iron, cooper, cobalt, zinc, fluorine actively influence the blood circulation, increases the immunity, remove hard metals and radionuclides from the organism [7].

The addition of blackberry powder in the technology of biscuit semi-products allows to get products with an increased content of biologically active substances, especially antioxidants, fatty acids and minerals [8].

A possibility of getting waffle leaves, enriched with girasol powder, is studied [9]. It has been established, that girasol powder decreases the dough viscosity and increase the waffle brittleness.

Analyzing the literary data, a conclusion may be made that vegetable powders are promising raw materials for using in the FCP technology.

3. Aim and tasks

The aim of the work was to study the possibility of using vegetable raw materials of snowball, ashberry and sea buckthorn in the biscuit semi-product technology.

The following tasks were set for attaining this aim:

– to study the chemical composition of snowball, ashberry and sea buckthorn powders;

– to establish an influence of adding the selected vegetable powders on the quality and quantity of dough cellulose;

– to determine an influence of the vegetable powders on firm-elastic properties of dough.

4. Materials and methods

The content of total protein in vegetable powders was determined by the standard Kjeldahl method. The determination of the amino acid composition of vegetable powders was conducted by the method of ion-exchanging liquid-column chromatography, using the automatic amino acid analyzer T 339 (Czechia) [10].

The content of ash in the vegetable powders was determined by burning a batch of a studied sample with burning a mineral through in the muffle stove at temperature 450…500 °C. The content of separate mineral elements was established by the method of X-ray fluorescent analysis (RFA), using the spectrometer of X-raying energy ElvaX. RFA method is based on measuring energy (wave length in spectrometers with wave dispersion) and intensity of spectral lines, imitated at secondary x-ray emission. The initial flow of quanta from the x-ray tube irradiates a sample, in such a way making each element of this sample to emit secondary x-ray quanta. They have a set of energies (base for the quality determination of the composition), inherent to this element only, and flow intensity of the secondary emission, depending on the content of this element in a sample (base for quantity analysis). Spectrums of x-ray fluorescence are connected with electronic passages in internal levels of an atom that makes them insensitive to chemical connections.

The content of cellulose in flour and its quality was determined by the standard method according to SS 27839-88, elasticity of cellulose – on the device IDC-1 by the standard method.

Physical characteristics of dough samples were determined by the alveographing method on the alveograph Chopin (SSU 4111.4-2002). Rheological properties of dough of wheat flour were determined by the analysis of farinograms, obtained on Brabender farinograph (SSU 4111.1-2002).

Rheological properties of the experimental samples were studied on «RHEOMETER AX-2000». The rheometer allows to determine the main rheological parameter – effective viscosity of an experimental sample that is a non-Newtonian liquid. The measurements were conducted immediately after dough mixing at the room temperature.

The porosity of ready products was determined on the device by Zhuravlev by the standard method.

5. Results

It is offered to use fruit powders (TC U 15.3-23913766-002:2005), namely ashberry (PA), snowball (PS) and sea buckthorn (PB) as non-traditional vegetable raw materials in the technology of biscuit semi-products. Based on analytic reviews [11–13] and obtained experimental data, there was studied the chemical composition of vegetable powders. A control was chosen as wheat flour of the highest sort, the main recipe component of floury confectionary products. The chemical composition is presented in **Table 1**.

Table 1

Chemical composition of powders of ashberry, snowball, sea buckthorn and wheat flour of the highest sort

Main components, g/100 g	Studied raw material			
	Wheat flour h/s	PA	PS	PB
Proteins	10.3	5.9	4.7	6.8
Fats	1.1	2.9	0.3	4.1
Carbohydrates	73.6	81.2	86	79.1
– Mono and disaccharides	1.6	16.7	16.9	19.1
– Starch	68.5	0.4	0.2	0.3
– Dietary fiber	3.5	23.2	21.3	25.0
– Ash	0.5	3.2	1.9	2.5
Organic acids	–	5.6	11.8	9.7

The research results (**Table 1**) demonstrate that the chosen powders are inferior to wheat flour by the protein content in 1.5…2.2 times. By the fat content PA exceeds wheat flour in 2.6 times, PB – in 3.7 times. At that PS contains only traces of fats. At the same time the content of mono- and disaccharides in PA, PS and PB exceeds their content in wheat flour in 10.4, 10.6 and 11.9 times respectively. The content of dietary fiber – in 6.6, 6,1 and 7.1 times respectively that allows to use them as a source of essential ingredients.

As far as vegetable powders contain the essential content of proteins, a decision was made to conduct a research for determining their amino acid composition and comparing analysis with one of wheat flour. The results are presented in **Table 2**.

Table 2

The amino acid composition of proteins of powders of ashberry, snowball, sea buckthorn and ones of wheat flour of the highest sort

Amino acids, mg/g	Wheat flour h/s	PA	PS	PB
Alanine	0.077	1.77	2.70	9.69
Arginine	0.075	1.79	3.18	18.85
Aminosuccinic acid	0.171	5.13	6.57	19.66
Valine	0.04	1.96	3.14	5.01
Histidine	0.009	0.31	0.24	3.38
Glycine	0.024	2.94	3.62	14.29
Glutamic acid	0.098	8.62	11.19	36.75
Isoleucine	0.028	0.45	0.61	3.54
Leucine	0.083	2.13	3.19	9.46
Lysine	0.023	1.14	1.98	8.52
Methionine	0.017	0.28	0.57	1.81
Proline	–	5.40	7.21	11.50
Serine	0.203	1.44	3.08	9.84
Tyrosine	0.032	0.79	1.34	4.88
Threonine	0.138	1.00	1.95	5.38
Phenylalanine	0.067	0.93	1.67	5.71
Cystine	0.019	0.81	0.87	1.73

Analyzing the data of **Table 2**, a conclusion may be made that proteins of vegetable raw material powders exceed ones of wheat flour of the highest sort by the content of amino acids in 30…400 times. At that the part of irreplaceable and conditionally irreplaceable amino acids in PA is more than 27 %, PS – 31 %, PB – 36 %, that indicates their high biological value. Proteins of the studied powders contain the essential amount of such amino acids as glycine, aminosuccinic and glutamic acids. Thus, PA, PS and PB contain in 123, 151 and 595 times more glycine than proteins of wheat flour, aminosuccinic acid – in 30, 38 115 times, glutamic acid – in 88, 114 and 375 times respectively. Proteins of PA, PS and PB contain the essential amount of proline that is absent at all in ones of wheat flour of the highest sort and arginine that is an irreplaceable amino acid for children.

For confirming the expedience and possibility of using powders of dried berries of wild raw materials as supplements, enriching floury confectionary products with vitally important nutrients, there was determined a mass share of vitamins and mineral substances of powders, comparing with the composition of wheat flour of the highest sort. The obtained data are presented in **Table 3**.

Table 3

The content of vitamins and mineral substances in the studied vegetable powders and wheat flour of the highest sort

Main components, mg/100g	Wheat flour h/s	PA	PS	PB
Vitamins				
Ascorbic acid (vitamin C)	–	66.1	34.7	68.6
β-carotene	–	16.6	4.5	8.2
Tocopherol (vitamin E)	2.45	11.6	2	90.6
P-active:				
Flavonols	–	88.1	95.2	111.9
Catechins	–	48.7	447.9	53.0
Anthocyans	–	103.2	947.0	250.0
Macroelements				
Calcium	18.0	390	167.2	107
Potassium	122.0	625.3	921.3	1341
Magnesium	16.0	114.4	62.9	102.6
Phosphorus	86.0	183	96.7	46.1
Sodium	3.0	12.8	21.5	17.5
Microelements				
Iron	1.2	8.0	4.72	10.4
Manganese	0.57	11.5	0.2	0.93

Having analyzed the chemical composition of PA, PS and PB and wheat flour, a conclusion may be made that these vegetable raw materials can be an effective improver of FCP with biologically active substances (BAS), especially ß-carotene, vitamins E, C, P mineral substances and micro/macroelements (Ca, Mg, K, P, Na, Fe, Mn).

PA, PS and PB have the improved vitamin composition, comparing with wheat flour. At that PA exceeds wheat flour in almost 5 times by the content of vitamin E, and PB – in 36 times by the content of vitamin C and P. Thus, analyzing the obtained data, a conclusion may be made that the studied vegetable powders have the rather high content of polyphenol substances and beta-carotene, tocopherol that give them antioxidant properties.

Comparing with wheat four of the highest sort, the studied raw materials contain more calcium in 6…22 times, potassium in 5…11 times, magnesium in 4…7 times, sodium in 4…7 times, iron in 4…8 times. PA contains 2 times more phosphorus than wheat flour and 20 times more magnesium.

Thus, PA, PS and PB contain much more micro and macroelements, comparing with wheat flour of the highest sort. It allows to enrich FCP, especially biscuit semi-products, with essential nutrients.

At the research there was determined an influence of PA, PS and PB on the quality and quantity of cellulose, namely elasticity, extensibility and ability to hydration. Quality parameters of cellulose directly depend on the content and properties of dough recipe components. As far as vegetable powders are able to intermolecular connections with other biscuit dough ingredients, their influence on wheat flour cellulose was studied. At studying the influence on cellulose, wheat flour was added with 3, 6 and 9 % of the studied supplements to the flour mass. The influence of the vegetable powders on the cellulose quantity (**Fig. 1**) and its quality was determined for each dosage. Wheat flour without supplements was used as a control.

As it can be seen from the obtained data, a tendency to the cellulose content decrease was established in the whole diapason of concentrations of the introduced powders. The amount decrease of wet cellulose with the mass share increase of powders may be explained by the fact that vegetable

raw materials bind recipe moisture and prevent proteins swelling. In its turn, it favors their washing out from a flour sample together with starch and other components. It has been established, that cellulose with adding vegetable powders is characterized with higher elasticity parameters. Thus, the extensibility decreases (with PA by 9.7…16 %, PS – 16…26 %, PB – by 16…35 % with dosage increase) and correspondingly elasticity (with PA by 2…4.4 %, PS – 11.5…18 %, PB – 8.6…31.5 % with dosage increase) and hydration capacity (with PA by 12.4…16 %, PS – 8.2…18.4 %, PA – 7…15.7 % with dosage increase). The strengthening of the structural-mechanical properties is probably conditioned by creation of complex compounds of flour proteins with carbohydrates and lipids of the introduced supplements. At that there takes place compression of a "package" of protein molecules as a result of creation of additional ion, sorption, hydrogen and other connections.

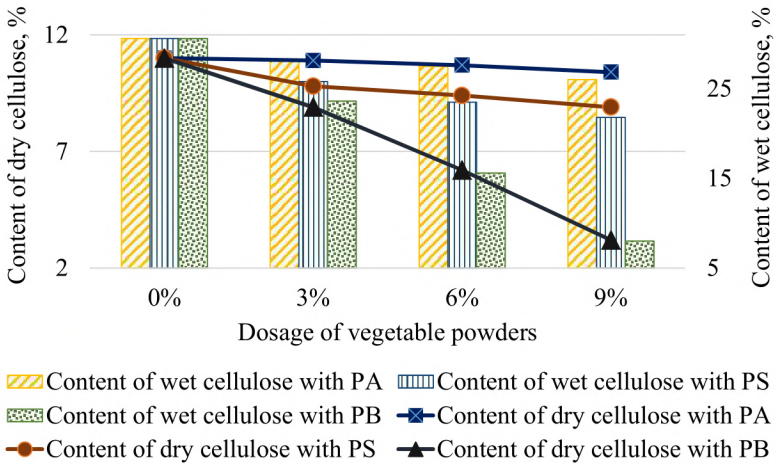

Fig. 1. Influence of vegetable powders on the amount of dry and wet cellulose

The addition of PA, PS and PB decreases the time of dough creation by 0.5 min. It is probably explained by the amount decrease of cellulose in the mixture and so, its hydration capacity. It has been established, that the addition of the studied powders results in the essential increase of dough dilution, comparing with the control (with PA by 233…283 %, PS – 233…333 %, PB – 233…340 % with dosage increase) that is a positive precondition for improving the porosity of ready biscuit semi-products.

The research results of the influence of vegetable powders on the rheological properties of dough have demonstrated that at introducing the supplements the dough elasticity increased (with PA by 29…59 %, PS – 42…130 %, PB – 95…163 % with dosage increase) and extensibility essentially decreased (with PA by 29.5…60 %, PS – 31…74 %, PB –45…80 % with dosage increase).

For verifying the obtained regularities, the experimental baking of biscuit semi-products with the chosen powders in amounts 3…9 % was realized. Analyzing the quality of the ready products, the special attention was paid to their porosity that influences the organoleptic, structural-mechanical and rheological properties of biscuits. The total porosity index was considered as a quantity characteristic of sumptuousness of the products, because the increase of this index testifies to the fact that the volume of products grows and their hardness decreases. At adding 3 % of the fruit powders, the porosity of the ready biscuit semi-products a bit increases by 3–4 %. At the dosage increase of PA, PS and PB the porosity decreases correspondingly by 5…6 %, 5.5…6.4 %, 5.7…6.6 %. It may be explained by more dispersion of fruit powders than wheat flour. Taking into account the obtained data, the desired dosage of PA, PS and PB must be 3 % of the flour mass. But this dosage doesn't provide the needed increase of the products' food value. That is why it is expedient to offer to use SAS for improving the ready products' quality and their food value.

Such SAS of the non-ionogenic effect as propylene glycol monostearate, esters of saccharose, sorbite, polyglycerine and fatty acids and so on are widely used in the confectionary industry. The use of improvers of this group allows to change the rheological properties of dough and favors

prolongation of the storage term of fresh ready products. SAS are presented at the Ukrainian market by rather wide assortment.

Almost all known producers of SAS for products of biscuit dough offer to introduce them at the stage of shaking mélange with sugar. Such introduction of SAS allows to increase FFC (foam-forming capacity) and foam stability. The system resistance to the mechanical influence makes it possible to introduce additional raw materials, especial ones, containing fat, and as a result, to get products with fluffy crumble and increased specific volume.

We studied the influence of improvers for floury confectionary products, most widespread in Ukraine – Grindsted PGE 55 (Danisco, Denmark), Grindsted cake 100 (Danisco, Denmark) and Ester M03 (EGH ingredients, Ukraine) on the main foam parameter – FFC.

There was determined the FFC of mélange foam, mélange with sugar and mélange with sugar and chosen SAS in the amount according to recommendations of the producers (Grindsted PGE 55 in amount 0.4 %, Grindsted cake 100 – 1 %, Ester M03 – 1.5 %), at temperature 20 °C (**Fig. 2**).

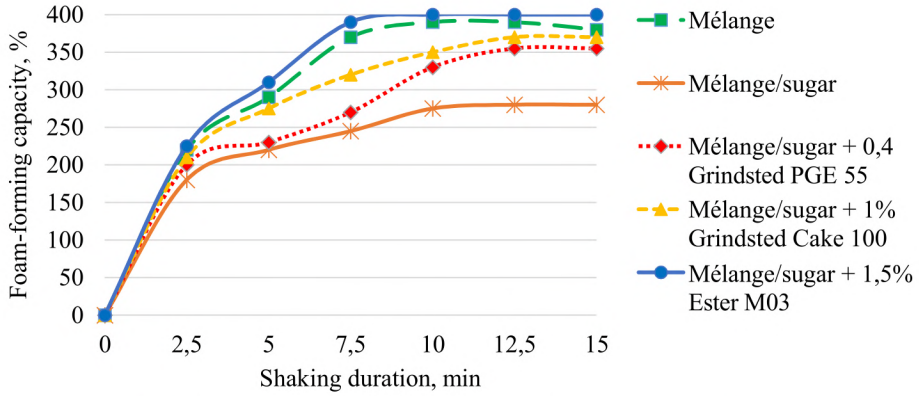

Fig. 2. Kinetics of foam formation of the studied samples

The obtained data have demonstrated that the most value of FFC is inherent to mélange. A sample of mélange with adding sugar has the lowest FFC indices that may be explained by the increase of the surface tension of the liquid phase that complicates its foam formation. At that the increase of the FFC index may be explained by more stable protein structure in sugar solutions, due to which protein molecules are worse untwisted at adsorption at the limit of phase distribution.

Fig. 2. has established that the studied SAS increase the FFC of mélange with adding sugar by 27…43 % and decrease the time of mixture shaking in 1.5 times. Especially, the improver Ester M03 has the highest FFC value among the studied samples, namely 400 %. That is why it was chosen for further studies in the technology of biscuit semi-products.

The dependence of the shift speed on the tangent tension in biscuit dough is presented on **Fig. 3.**

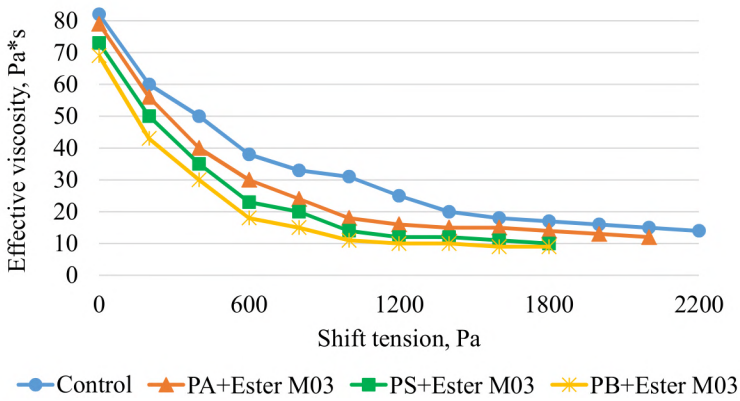

Fig. 3. Rheological curves of viscosity of biscuit dough with vegetable powders and SAS

The analysis of the presented results has demonstrated that the biscuit dough viscosity decreases with the shift speed increase in both control samples and ones with adding the vegetable powders and SAS. The vegetable powders for the model experiment were added in amount 6 %, Ester M03 in amount 1.5 %. It has been established, that introduction of the selected powders and SAS results in decreasing the effective viscosity of biscuit dough, comparing with the control sample. The dough viscosity decrease in this case may be noted as a positive effect. As a result of less dough viscosity, air bubbles, included to the dispersed phase, widen more at baking, but a film frame of eggs, sugar, wheat flour and dietary fiber, stronger, comparing with dough without supplements and with ashberry powder, prevents air removal from bubbles outside. A biscuit semi-product at baking settles down less and is characterized by more values of specific volume and porosity that is confirmed by epy physical-chemical parameters of baked products.

The porosity of ready biscuit semi-products with PA, PS and PB and improver Ester M03 increases, comparing with ones with vegetable powders and without SAS correspondingly by 6…10 %.

6. Conclusions

It has been established**,** that the dosage increase of vegetable powders results in strengthening cellulose, it becomes more elastic and has better extensibility. The strengthening of structural-mechanical properties of cellulose is, probably, conditioned by creation of complex compounds of flour proteins with carbohydrates and lipids of the introduced supplements and the effect of organic acids of the chosen powders.

The introduction of PA, Ps and PB in amount 3…9 % of the flour mass increases the dough elasticity in 1.2…2.5 times and decreases extensibility in 1.5…3 times, comparing with the control. The obtained data may be explained by the essential amount of polysaccharides in the studied raw materials that don't allow to form an elastic cellulose frame and they increase the dough viscosity.

It has been established, that the dosage increase of PA, PS and PB decreases the porosity of ready biscuit semi-products. That is why for raising the quality of ready products, it is expedient to offer to use quality improvers of biscuit semi-products.

It has been demonstrated, that the use of the improver Ester M03 in amount 1.5 % in semi-products with vegetable powders in the technology of biscuit products decreases the biscuit dough viscosity. At the same time there is observed the positive influence of SAS on the FFC of the egg-sugar mixture, main component of biscuit dough.

The use of powders of non-traditional raw materials in the FCP technology results in increasing the food and biological value of ready products. The use of the studied powders at restaurant economy enterprises is a precondition for widening the FCP assortment in a menu.

In further studies it is expedient to determine an influence of vegetable powders on a freshness preservation degree in products with their addition.

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Received date 27.11.2019
Accepted date 03.01.2020
Published date 24.01.2020

STUDY OF THE INFLUENCE OF MEALS OF WHEAT AND OAT GERMS AND WILD ROSE FRUITS ON THE FERMENTING MICROFLORA ACTIVITY OF RYE-WHEAT DOUGH

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Abstract

The aim of the research was to study an influence of meals of wheat germs (WGM) and oat germs (OGM) in amount 10…20 %, and also ones of wild rose fruits (WRFM) in amount 2…6 % of the total mass of flour on the fermenting microflora of rye-wheat dough; and also to establish an influence of the experimental supplements on main microbiological processes in it.

It has been established, that adding experimental meals favors the activation of bakery yeast. At introducing WGM, OGM and WRFM, its lifting force grows by 16.0–54.0, 6.0–18.0, 10.0–44.0 % respectively, and zymase and maltase activity – by 16.0–53.3, 6.0–17.7 and 11.1–44.0 % and 18.8–55.0, 6.3 31.3 and 7.5–25.0 % respectively. It has been established, that there also takes place the activity increase of lactate bacteria in rye-wheat dough with adding meals of wheat, oat germs and wild rose fruits. It is possible at the expanse of adding an additional nutritive medium with the supplements.

Such action of enriching raw materials on the microflora favors intensification of alcoholic and lactate fermentation that is established by data of acid accumulation and gas formation in rye-wheat dough. The counted indices at introducing WGM, OGM, WRFM increase by 39.0, 27.8, 33.9 % and 18.2, 13.6, 16.7 % respectively.

Keywords: rye-wheat dough, wheat germ meal, oat germ meal, wild rose fruit meal, lactate bacteria, lifting force, fermenting activity, microbiological processes.

DOI: 10.21303/2504-5695.2020.001114

1. Introduction

An important problem, faced by mankind last years, is the abrupt spread of "civilization diseases" with an alimentary character. In this connection an urgent direction of the food industry is the development of technologies of healthy products with an increased content of functional-physiological elements, based on fruit-berry, vegetable grain raw materials and so on [1–4]. In many European countries, including Ukraine, bread of the mixture of rye and wheat flour is very popular that makes it a promising object for enriching with essential substances.

For increasing the food and biological value of bakery products, there are successfully used non-traditional types of vegetable raw materials with essential contents of biologically active substances. Introduction of such raw materials to dough recipes may influence the vital activity of its fermenting microflora, namely lactate bacteria and yeast that play an important role in the formation of the rye-wheat dough quality. Products of lactate fermentation that are mainly organic acids favor the improvement of dough rheological characteristics and formation of a taste and smell of bread. The dough fluffiness, porosity status and volume of ready products are mainly conditioned by the intensity of alcoholic fermentation, which agent is yeast [5].

At adding processing products of raw materials, easily assimilated sugars and also mineral and other biologically active substances are additionally introduced in dough. It results in improving technological characteristics of yeast, favors the activation of lactate bacteria. Thus, it has been established, that introduction of potato and beetroot paste in dough favors intensification of acid accumulation in rye-wheat dough and increase of the yeast lifting force [6]. There are also known data about a positive influence of potato powder [7], carrot juice [8], honeysuckle puree [9], powder of pumpkin pressed skins [10] on the activity of bakery yeast that results in intensification of alcoholic fermentation in wheat and rye-wheat dough.

Introduction of chicory root powder in small dosages (less 1 %) favors the increase of zymase and maltase activity of yeast, and the increase of its dosage results in inhibition of yeast cells at the expanse of coumarin that inhibits the development of yeast cells at high concentrations [11].

There is information about a positive influence of pea-anisic decoction on reproduction of yeast cells and lactate bacteria in dough in wheat leaven. Such effect is observed at the expanse of introducing vitamins and mineral substances of an enriching raw material that is an additional nutritive medium for the fermenting microflora [12]. But adding cultures, containing mucus, for example, comminuted golden flax seeds, dry or wet, results in the intensity decrease of gas formation in dough. It is connected with the decrease of yeast microflora activity at the expanse of its covering by flax mucus. It is offered to solve this problem by preparing bread on oat leaven [13].

From the scientific and practical point of view, meals of wheat and oat germs – secondary products at making germ and oat oils – are interesting for enriching rye-wheat bread. The experience of using these supplements in the technology of wheat sorts of bread testifies that their introduction in amount 10–20 % of the flour mass favors intensification of gas formation and acid accumulation in wheat dough [14–16]. Thus, at adding wheat germ meal, an amount of CO_2, emitted at dough fermentation increases by 7.5–15.7 %, and titrated acidity – by 26.0–50.0 % respectively [14]. At using oat germ meal, these indices also increase by 7.1–16.5 % and 13.3–40.0 %, comparing with a sample of wheat dough without supplements [15, 16]. The authors explain it by the possible activation of lactate bacteria in wheat dough at the expanse of introducing additional amino acids, mineral and other biologically active substances together with meals. But in these works the influence of oat and wheat germ meals on the status and activity of the fermenting microflora is insufficiently studied.

The expedience of using wild rose fruits and their processing products for activating the fermenting microfora activity and intensifying dough maturation processes is also proved in bakery [17–19]. It is possible because of the essential content of vitamins in them that are mainly presented by ascorbic acid, and mineral substances. Carbohydrates of such raw materials mainly consist of mono- and disaccharides that are also positive for the microflora activity. Work [20] proves that the use of syrup or juice of wild rose fruits as a nutritive medium has a stimulating influence on the yeast activity. According to the authors' data, adding vitamins that are growth factors for yeast cells with syrup or juice of wild rose fruits favors intensification of yeast cells reproduction. The intensity of CO_2 synthesis in experimental samples increased in 1.6 (with syrup) and 2.1 (with juice) times, comparing with the control.

As a research result of the influence of water and serum extracts of wild rose fruits in amount 30 and 15 % of the liquid fraction mass in wheat dough, it has been established, that their introduction favors the improvement of conditions for anabolic and catabolic processes in yeast cells. There has been established the positive influence of extracts on technological properties and generative functions of yeast. Such changes result in intensification of biochemical and microbiological processes in wheat dough [17].

It is also known, that it is effective for getting high-quality wheat bread to use wild rose fruit powder in amount 5 % of the four mass [18] or wild rose fruit and ashberry powders together in amount 1–3 % of the flour mass [19]. These supplements favor intensification of maturation processes and getting products with high quality indices. But the influence of powders on technological characteristics of yeast and lactate bacteria is not established in these studies.

A promising raw material for the bakery branch is wild rose fruit meal – secondary product in the technology of the correspondent oil. It includes the essential amount of dietary fiber (near 50 %), and also mineral substances and vitamins, especially ascorbic acid (46.6 mg/100 g) [21]. Scientific information about using wild rose fruit meal for influencing the status of the fermenting microflora of rye-wheat dough has not been found.

The aim of the research was to study an influence of meals of wheat and oat germs and ones of wild rose fruits on the fermenting microflora of rye-wheat dough.

The following tasks were set for attaining this aim:

– to study an influence of meals of wheat germs (WGM), oat germs (OGM), wild rose fruits (WRFM) on technological characteristics of bakery yeast and activity of lactate bacteria;

– to study an influence of the experimental meals on microbiological maturation processes in rye-wheat dough.

2. Materials and methods

Peeled rye flour, wheat flour of the first sort, pressed bakery yeast, dry rye leaven, kitchen salt, wheat germ meal, oat germ meal, wild rose fruit germ meal were used in the studies. The mass share of moisture of the experimental meals was 12.4, 11.4 and 7.1 % respectively. WGM acidity was 6.0 degrees, OGM – 5.9 degrees, WRFM – 53.0 degrees [14–16, 21].

The chemical composition of rye, wheat flour and experimental meals is presented in **Table 1.**

Table 1

The content of nutritive, ballast and biologically active substances in the experimental meals [5, 15, 16]

Name of nutritive and biologically active substances	Mass share of substance in the raw material				
	Peeled rye four	Wheat flour of 1 sort	Wheat germ meal	Oat germ meal	Wild rose meal
Protein, %	8.9	10.6	45.0	23.0	5.7
Fat, %	1.7	1.3		traces	
Carbohydrates, %:	73.2	72.0	44.8	58.4	15.5
Including mono-, disaccharides	4.5	1.8	18.0	5.1	15.9
starch	59.3	69.1	traces	30.0	0.4
Non-starch polysaccharides, %	13.2	4.0	26.0	23.3	43.4
Mineral substances (mg/100 g):					
Sodium	17.0	12.0	7.3	24.8	11.7
Potassium	350.0	176.0	2190.0	812.50	3543.0
Calcium	34.0	24.0	115.0	57.0	336.8
Magnesium	60.0	44.0	220.0	280.0	813.3
Cooper	–	–	1.8	1.5	3.9
Iron	3.5	2.1	7.1	15.0	4.40
Zinc	–	–	21.9	10.5	3.5
Manganese	–	–	36.0	15.0	15.0

The lifting force of yeast was determined by the arbitral method according to SSU 4812:2007, measuring time that dough lifts by 70 mm in.

The zymase and maltase yeast activity was determined, using a device with a manometer and fixed corks. 0.5 g of yeast and 10 cm^3 of water with temperature 35 °C, were placed in it and accurately mixed. Yeast suspension was added with 10 cm^3 of 10 % solution of one of sugars (glucose or maltose). The device was closed, a tap was open for equating an internal pressure with the atmospheric one, and the device was placed in a thermostat at temperature 30 °C. In 5 min the tap was closed, and a liquid level in a graded tube was fixed. The device was left in the thermostat. The determination was considered as finished, when a saline solution in the tube rose by 10 cm^3 [22].

For determining the activity of lactate bacteria, there were taken 20 g of rye-wheat dough and 40 cm^3 of distilled water with temperature 39±1 °C, rubbed in a mortar to the homogenous consistence and taken in two test-tubes, 10 cm^3 of the obtained suspension in each one. One of test-tubes was added with 1 cm^3 0.05 % of the blue methylene water solution, and the other one was a control for comparing a color. The tubes were covered by rubber corks, shaken and placed in the thermostat with temperature 40 °C. The time, in which blue methylene became colorless in them, was fixed [23].

The gas-forming capacity of rye-wheat dough was determined by the amount of CO_2, emitted at maturation [23]. The titrated acidity – by the conventional method, presented in [23].

Fisher-Student method was used for processing the experimental data at reliability level 0.95. The research results were calculated as a mean of no less five iterations.

3. Experiments

One of main normative characteristics of bakery yeast that allows to judge about the lifting speed of dough, prepared of it, is a lifting force index. But this method allows to estimate only the activity of the zymase complex of yeast, whereas the intensity and duration of dough fermentation are determined mainly by the speed maltose supply to a cell and disintegration. In this connection the influence of the experimental meals on the bakery yeast activity was determined by the complex of parameters, namely by the lifting force and indices of the activity of zymase complex enzymes and maltose activity.

There was studied the activity of lactate bacteria at presence of meals of wheat and oat germs and wild rose fruits by preparing rye-wheat dough with them. The analogous index in dough without supplements was determined for comparing.

For establishing the influence of the fermenting microflora of rye-wheat dough with the experimental meals on processes that take place at maturation, the gas-forming capacity of dough was studied. The influence of the supplements on the acid accumulation intensity in rye-wheat dough was also studied.

After conducting these studies, a control sample was prepared of the mixture of peeled rye and wheat flour of 1 sort in ratio 1:1, 2.5 % of dry rye leaven, 2 % of bakery pressed yeast, 1.5 % of kitchen salt. Maturation was conducted during 90 min at temperature 30±2 °C.

The experimental sample were added with WGM or OGM in amount 10–20 % of the total four mass, and WRFM – in amount 2–6 % of the total flour mass. Experimental intervals of dosages of WGM and OGM were chosen, based on the research results as to their use in the wheat bread technology [14–16], and wild rose fruit meal amount – based on the data, presented in work [21].

It is demonstrated, that adding wheat and oat germ meals and also wild rose fruit meal to model systems of yeast and rye-wheat dough favors the fermenting microflora activity increase (**Tables 2, 3**, **Fig. 1**).

According to the data, presented in **Table 2**, introduction of WGM, OGM and WRFM favors the increase of the lifting force index of bakery yeast that testifies to its activity increase. At that the most influence on this index is made by wheat germ and wild rose fruit meals – at their addition it decreases by 16.0–540 and 10.0–44.0 %. At adding oat germ meal the lifting force of yeast rises by 6.0–18.0 %.

The positive influence of meals of wheat and oat germs and wild rose fruits on the fermenting activity of bakery yeast was proved also at determining its enzymic activity (**Table 3**).

Table 2

The influence of meals of wheat and oat germs and wild rose fruits on the lifting force of bakery yeast

Quality parameters of yeast	Experimental samples								
	Without supplements (control)	With the experimental meals, % of the total flour mass								
		WGM			OGM			WRFM		
		10	15	20	10	15	20	2	4	6
Lifting force, min	50	42	31	23	47	44	41	45	37	28

Table 3

The influence of meals of wheat and oat germs and wild rose fruits on the enzymic activity of bakery yeast

Quality parameters of yeast	Experimental samples								
	Without supplements (control)	With the experimental meals, % of the total flour mass								
		WGM			OGM			WRFM		
		10	15	20	10	15	20	2	4	6
Zymase activity, min	45.0	37.8	27.9	21.0	42.3	39.6	37.0	40.0	33.3	25.2
Maltase activity, min	80.0	65.0	50.0	36.0	75.0	67.0	55.0	74.0	68.0	60.0

It is testified by the decrease of the yeast zymase activity index at adding WGM – by 16.0–53.3 %, at adding OGM – by 6.0–17.7 % and at using WRFM – by 11.1–44.0 %. The maltase activity at introducing WGM and OGM increases by 16.0–53.3 and 6.0–17.7 %, and at adding WRFM – by 11.1–44.0 %.

It has been also established, that the experimental meals favor the activity increase of lactate bacteria (**Fig. 1**).

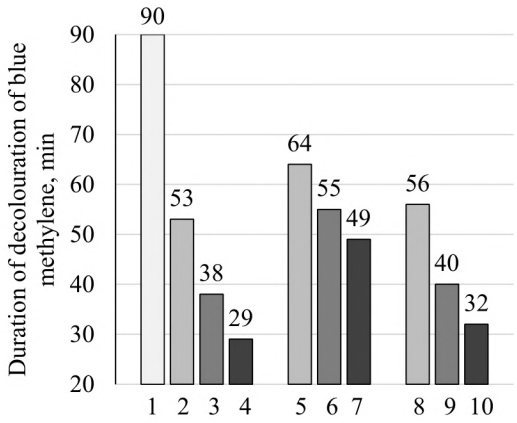

Fig. 1. Activity of lactate bacteria in dough: 1 – without addition (control); without addition: 2 – 10 % WGM, 3 – 15 % WGM, 4 – 20 % WGM, 5 – 10 % OGM, 6 – 15 % OGM, 7 – 20 % OGM, 8 – 2 % WRFM, 9 – 4 % WRFM, 10 – 6 % WRFM

Moreover like in the studies of the meals' influence on the yeast activity, the positive influence of WGM and WRFM is more expressed, comparing цшер oat germ meal. Thus, it is established, that at adding WGM, WRFM and OGM in rye-wheat dough in the experimental intervals of dosages, the decolouration duration of blue methylene shortens by 41.1–67.8 %, 37.8–64.4 % and 28.9–45.5 % respectively, comparing with this index in a sample without supplements.

So, adding 10…20 % of wheat and oat germ meals and 2…6 % of wild rose fruit meal favors the activity increase of bakery yeast and lactate bacteria. It was also proved by the data about gas

formation and acid accumulation in rye-wheat dough at their adding in amount 15 % for WGM and OGM and 4 % – for WRFM of the flour mass (**Fig. 2, 3**).

Thus, it is established (**Fig. 2**) that introduction of the experimental supplements results in intensification of fermentation in dough that is testified by the higher amount of emitted CO_2 at all fermentation stages. At the end of maturation its amount in dough samples with meals of wheat and oat germs and wild rose fruits was by 39.0 %, 27.8 % and 33.9 % higher than in the control sample.

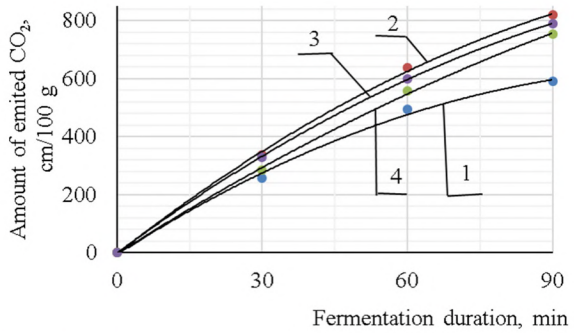

Fig. 2. Influence of the supplements on the amount of emitted CO_2 in rye-wheat dough: 1 – control (without supplements); with adding: 2 – 15 % of WGM, 3 – 15 % of OGM, 4 – 4 % of WRFM

The analysis of the data, presented on **Fig. 3,** testifies that adding the experimental meals results in both the increase of initial titrated acidity of rye-wheat dough and its more intense change at maturation.

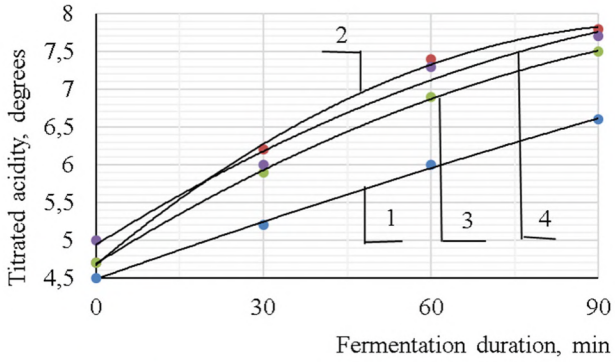

Fig. 3. Influence of the supplements on the titrated acidity change in rye-wheat dough: 1 – control (without supplements); with adding: 2 – 15 % of WGM, 3 – 15 % of OGM, 4 – 4 % of WRFM

Thus, at the end of the experiment the value of this parameter of dough at adding WGM, OGM and WRFM was higher than the one of the control sample by 18.2 **%**, 13.6 **%** and 16.7 **%** respectively.

4. Results

The results of the complex of conducted studies allowed to establish the positive influence of meals of wheat, oat germs and wild rose fruits in the experimental interval of dosages on the activity of bakery yeast and one of lactate bacteria.

The essential improvement of its lifting force (**Table 2**) and fermenting activity (**Table 3**) indices at presence of supplements is, probably, conditioned by the additional introduction of easily accessible sugars, mineral substances, proteins and other components, nutritive for yeast cells, contained more in the experimental meals than in wheat and rye flour, together with meals (**Table 1**). The best indices of lifting force, maltase and zymase activity are observed at introducing

wheat germ meal that may be connected with the higher content of mono- and disaccharides in this supplement, comparing with the other experimental meals.

In samples with adding wild rose fruit meal with high titrated acidity (53.0 degrees) the activation effect may be conditioned also by decreasing dough pH to the values, favorable for the yeast vital activity. These causes may also explain the activity increase of lactate bacteria in rye-wheat dough with the meals.

The activity increase of the dough fermenting microflora at presence of the meals in the experimental dosages became a precondition for intensifying microbiological processes in dough, especially alcoholic and lactate fermentation, resulting in acceleration of gas formation (**Fig. 2**) and acid accumulation (**Fig. 3**).

The acceleration of microbiological processes influences the acidity of baked products, their porosity and specific volume and may be a precondition for shortening the maturation duration of dough semi-products. Such problems need special studying. So, further studies will be directed on determining the influence of meals of wheat, oat germs and wild rose fruits on structural-mechanical properties of rye-wheat dough and quality of ready products.

5. Conclusions

It has been proved, that at presence of wheat and oat germ meals in amount 10…20 % of the flour mass and ones of wild rose fruits in amount 2…6 % of the flour mass the bakery yeast activity increases. At introducing WGM and OGM, its lifting force grows by 16.0–54.0 and 6.0–18.0 % respectively, and at adding WRFM – by 10.0–44.0 %, that is caused by its zymase and maltase activity improvement. The activity of lactate bacteria also increases at adding WGM and OGM by 41.1–67.8 % and 28.9–45.5 % respectively and at presence of WRFM – by 37.8–64.4 %.

2. It has been established, that adding wheat and oat germ meals in amount 10…20 % and ones of wild rose fruits in amount 2…6 % of the total flour mass favors intensification of maturation processes in rye-wheat dough. It is testified by its titrated acidity indices, higher than ones of the control samples by 18.2 **%**, 13.6 **%** and 16.7 **%**, and also by ones of emitted carbon dioxide, higher by 39.0, 27.8, 33.9 % respectively.

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Received date 29.11.2019
Accepted date 08.01.2019
Published date 24.01.2020

INVESTIGATION OF THE INFLUENCE OF GLYCERIN ON RHEOLOGICAL CHARACTERISTICS OF MARZIPAN PASTES WITH DRY MINERALIZED WHEY

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Abstract

There is studied the influence of glycerin on rheological characteristics of marzipan pastes with dry demineralized whey (DDW) for determining its rational concentration in the composition of decorative semi-products PKV and MFV. PKV – marzipan pastes with DDW, used for covering confectionary products and as an interlayer; MFV – marzipan pastes with DDW, used for making candies and modeling figured products.

According to research results, it has been established, that an increase of a glycerin concentration in the composition of model mixtures of marzipan pastes PKV (20 % of DDW) and MFV (30 % of DDW) results in decreasing deformation characteristics of a reversible type. Irreversible deformation is constant and doesn't depend on glycerin concentration.

According to results of the analysis of main rheological constants by a diapason of glycerin concentrations, there has been established a gradual decrease of indices of a highly elastic and conventionally instant resilience module of model compositions of marzipan pastes PKV (20 % of DDW) and MFV (30 % of DDW). Viscosity indices of a resilient aftereffect and pliability gradually grow with an increase of a glycerin concentration in the composition of model marzipan pastes PKV (20 % of DDW) and MFV (30 % of DDW).

Research results testify that the use of glycerin in the composition of marzipan pastes PKV (20 % of DDW) and MFV (30 % of DDW) gives a possibility to increase their elasticity and softness, at that keeping high forming properties.

The conducted studies have proved the availability of producing marzipan pastes with DDW and glycerin. There has been substantiated the rational content of glycerin in the composition of marzipan pastes with DDW that allows to provide given (desirable) rheological characteristics. The rational concentration of glycerin in the composition of marzipan pastes PKV (20 % of DDW), used for covering floury and confectionary products and as an interlayer is 5 % of the total mass of recipe components. The rational concentration of glycerin in the composition of marzipan pastes MFV (30 % of DDW), used for making candies, modeling figured products is 5 % of the total mass of recipe components.

An improved technological solution doesn't complicate the general technological process and doesn't need the additional technical equipment. Rheological characteristics of the developed marzipan pastes correspond to directions of the technological destination and allow to decorate floury confectionary products with different levels of technological complication, providing the maximal beauty of ready products.

Keywords: marzipan paste, dry demineralized whey, glycerin, rheological characteristics.

DOI: 10.21303/2504-5695.2020.001120

1. Introduction

Modern decorative semi-products for confectionary products are presented by the wide assortment of diverse creams, pomades, glaze masses, plastic masses of chocolate, marzipan, sugar, painting masses, powders, molten decoration of caramel, chocolate and so on [1–3]. The special place among decorative semi-products is occupied by marzipan [4, 5].

Marzipan belongs to high-caloric semi-products, produced of expensive raw materials, because it contains 80 % of almond kernel. Results of previous studies proved the perspective of using dry demineralized whey (DDW) in the recipe composition of marzipan pastes.

The use of DDW essentially improves the biological value of marzipan pastes at the expanse of 1.4 times protein increase and addition with such limiting amino acids as lysine and threonine. In which result consumption of 100 g of almond paste with DDW concentration 20–30 % provides the human daily need by 45–64 % in lysine, 65–91 % in threonine [6]. DDW also gives a possibility to decrease the energetic value of marzipan pastes by 29–35 % in first turn as a result of changing the qualitative carbohydrate composition, presented by lactose [6]. Lactose is an energy source for a human and also: participates in such important process as calcium metabolism; stimulates processes of nervous regulation. Its sweetness is 5 times lower, comparing with sucrose. Lactose may be consumed by patients with diabetes mellitus, because its glycemic index is 1.5 times less than one of sucrose [7, 8].

There is also established the positive influence of DDW on sensor and rheological characteristics of model compositions of marzipan pastes. Results of complex studies have proved a possibility of a partial replacement of import-depending raw materials in the composition of marzipan pastes, so decrease of the prime cost of ready products.

As a result of the study of surface characteristics of marzipan pastes with DDW, there has been established an increase of their adhesive-cohesive properties. Adhesion is an indirect parameter that characterizes a consistence of a food system and influences its consumption properties. Taking into account the research object, an increase of adhesive-cohesive properties not only regulates a consistence of marzipan pastes, but positively influences the technological process of producing decorative semi-products of it. But at the industrial production of marzipan pastes, especially, formation of candies, an adhesion increase has negative results. Adhesion negatively influences the effectiveness of using the equipment, results in an increase of losses of raw materials and energetic resources. The stickiness of marzipan masses is demonstrated at its contact with construction materials during the whole technological process of making a food product. These properties mainly determine the choice of a construction material, working mode of machines or their working bodies. Taking it into account, the expedience of using glycerin in the composition of marzipan pastes with DDW for regulating their adhesive-cohesive interaction has been proved. It has been experimentally established, that introduction of 4…5 % of glycerin in the composition

of marzipan pastes with DDW allows to decrease the strength of adhesion and to approximate it to ones, produced by the traditional technology. But for determining the rational concentration of glycerin in the composition of marzipan pastes with DDW, it is expedient to consider its influence on rheological characteristics.

2. Materials and methods

Resilient-elastic and plastic-viscous properties of model compositions of marzipan pastes, based on determining a shift deformation, related to the thickness of a sample, were studied on the Tolstoy flat-parallel elastoplastometer, **Fig. 1** [9, 10].

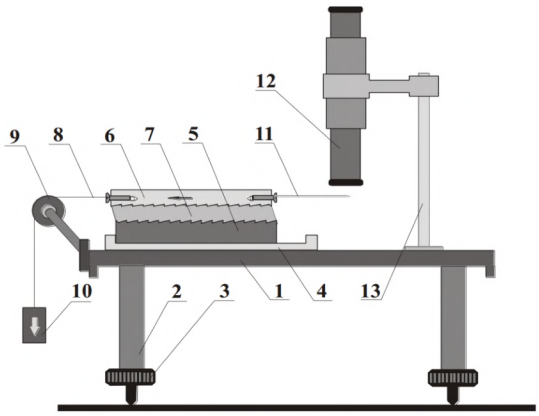

Fig. 1. Setting scheme of the Tolstoy flat-parallel elastoplastometer: 1 – table; 2 – supporting leg; 3 – regulating screw; 4 – metal stand; 5 – metal plate; 6 – plate of plaxiglass; 7 – experimental sample; 8 – silk thread; 9 – block; 10 – load; 11 – observing needle; 12 – microscope; 13 – tripod

The first value of absolute deformation was obtained by the microscope instantly, as soon as the load became to affect the upper plate. After that the value of absolute deformation was fixed with 1 min periodicity during 10 min. Further observations were conducted with 5 min periodicity. After removing the load, the instant deformation was fixed, then device indications were fixed with 1 min periodicity during 10 min. At studying rheological characteristics of model compositions of marzipan pastes, the fixed load was selected for all systems as 65 g. At the same time equal temperature (+6 °C) and height of samples (7 mm) were provided.

For determining rheological parameters, the dependence of relative deformation on time of the tension effect was constructed, **Fig**. **2**. The following segments were separated on it:

– γ_0, ε_0 (segment OA) – resilient conventionally instant deformation that instantly (in a very short time interval) appears under the effect of the applied tension and instantly disappear after removing it;

– γ_m, ε_m (segment OC) – maximally reached deformation under the effect of the applied tension;

– γ_{rev}, ε_{rev} (segment OB1) – highly elastic deformation – completely reversible relative deformation;

– $\gamma_{rev}=\gamma_0+\gamma_{rev}$ ($\varepsilon_{rev}=\varepsilon_0+\varepsilon_{he}$); ε_{he} (segment AB1) – highly elastic deformation – relative deformation, gradually disappearing after removing the load:

– $\gamma_{he}=\gamma_{rev}-\gamma_0$ ($\varepsilon_{he}=\varepsilon_{rev}-\varepsilon_0$);

– γ_{res}, ε_{res} (segment EO1) – residual (plastic) deformation that doesn't disappear after removing the applied tension during infinitely long time: $\gamma_{res}=\gamma_{pl}$(ε_{res}=pl).

Separation of the total deformation in reversible and irreversible ones is realized by the simplified method of extrapolation of the deformation linear segment to the cross with the Y-axis $\gamma=f(t)$ (offered by Rebinder). It is supposed, that the growing speed of irreversible deformation is stable and doesn't depend on elastic deformation value. If extrapolate the linear segment to null and transfer it to the beginning of coordinates, the growing speed of irreversible deformation is obtained [9].

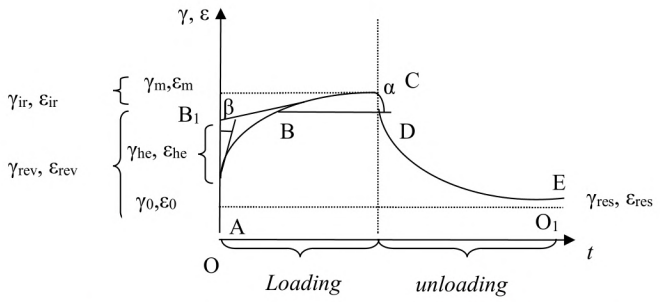

Fig. 2. Creeping curve of a studied sample under the effect of the applied shift tension (at loading and unloading)

The relative deformation is determined by the formula:

$$\gamma=kxn/d, \quad (1)$$

where k – division value of the microscope, m; n – number of divisions on the microscope scale; d – sample thickness, m.

The ratio coefficient of reversible deformation to the total one was determined by the formula:

$$K\gamma=\gamma_{rev}/\gamma m, \quad (2)$$

where γ_{rev} – value of reversible deformation; γm – value of maximal deformation.

The shift tension was determined by the formula:

$$\tau=mxg/S, \quad (3)$$

where τ – shift tension, Pa; m – load mass, kg; g – free fall acceleration (9.81 m/s²); S – plate area, m².

The pliability that characterizes the ability of the studied samples to deformation under the effect of the applied tension is determined by the formula:

$$I=\gamma m/\tau, \quad (4)$$

where I – pliability of the system, Pa^{-1}; γm – relative maximal deformation.

The module of instant resilience that characterizes the ability of the studied samples to resist proportionally to its deformation was determined by the formula:

$$G_{resl}=\tau/\gamma_0, \quad (5)$$

where G_{resl} – module of instant resilience, Pa; γ_0 – relative conventionally instant deformation.

The module of elasticity that characterizes the ability to decrease deformation of the studied samples with time after removing the tension was determined by the formula:

$$G_{el}=\tau/\gamma_{he} \quad (6)$$

where G_{el} – module of elasticity, Pa; γ_{he} – relative highly elastic deformation.

The plastic viscosity that characterizes the ability of the structured condition to flow without destruction under the effect of the constant tension was determined by the formula:

$$\acute{\eta}*0=\tau/tg\alpha, \quad (7)$$

where $\acute{\eta}*0$ – plastic viscosity, Pa·s; $tg\alpha$ – tilt angle of the final linear segment of the curve to X-axis.

The viscosity of the resilient aftereffect was determined by the formula:

$$\acute{\eta}_{den}=\tau/tg\beta, \quad (8)$$

where $\acute{\eta}_{den}$ – viscosity of the resilient aftereffect, Pa·s; tgβ – tilt angle of the initial linear segment of the curve to X-axis.

3. Results

For determining the rational concentration of glycerin in the recipe composition of marzipan pastes with DDW, it was added in amount 1…6 % of the total mass of dry components (**Table 1**).

Table 1

The recipe components of model systems of marzipan pastes with DDW, for 100 g

Raw material name	Samples with adding glycerin, %					
	1	2	3	4	5	6
DDW 20 %						
Almond kernel	32.5	32.0	31.5	31.0	30.5	30.0
Sugar powder	32.5	32.0	31.5	31.0	30.5	30.0
Syrup	14.0	14.0	14.0	14.0	14.0	14.0
DDW	20.0	20.0	20.0	20.0	20.0	20.0
Glycerin	1.0	2.0	3.0	4.0	5.0	6.0
DDW 30 %						
Almond kernel	27.5	27.0	26.5	26.0	25.5	25.0
Sugar powder	27.5	27.0	26.5	26.0	25.5	25.0
Syrup	14.0	14.0	14.0	14.0	14.0	14.0
DDW	30.0	30.0	30.0	30.0	30.0	30.0
Glycerin	1.0	2.0	3.0	4.0	5.0	6.0

The influence of the glycerin concentration on deformation characteristics of model compositions of marzipan pastes with DDW: total, reversible, irreversible, relative deformation was determined (**Table 2**).

Table 2

The influence of glycerin on deformation characteristics of model compositions of marzipan pastes with DDW (n=5; $P\leq0.05$)

Parameter name	Symbol		Control	Samples of marzipan pastes with DDW with adding glycerin, %					
				1	2	3	4	5	6
Reversible deformation, 10^{-3}	γ_{rev}	PKV	317.00	322.86	350.00	365.71	380.00	401.43	420.15
		MFV	335.71	360.00	377.14	380.00	387.71	393.71	421.15
Irreversible deformation, 10^{-3}	γ_{ir}	PKV	12.86	12.86	12.86	12.86	12.86	12.86	12.86
		MFV	12.86	12.86	12.86	12.86	12.86	12.86	12.86
Total deformation, 10^{-3}	γ_{tot}	PKV	330.00	335.71	362.86	378.57	392.86	414.29	424.22
		MFV	348.57	372.86	390.00	392.86	408.29	414.29	424.22
Shift tension, Pa	τ	PKV	425.10	425.10	425.10	425.10	425.10	425.10	425.10
		MFV	425.10	425.10	425.10	425.10	425.10	425.10	425.10
Ratio of Rel. deformation to the tot. one	K	PKV	0.96	0.96	0.96	0.97	0.97	0.97	0.97
		MFV	0.96	0.97	0.97	0.97	0.97	0.97	0.97

Indices of total deformation grow with the glycerin concentration increase not directly proportionally and depend on the mass share of DDW in the composition of marzipan pastes. So, at DDW concentration 20 % total deformation indices grow depending on glycerin content up to 1.3 times and are 335.71–4224.22, at DDW concentration 30 % grow up to 1.2 times and are 372.86–424.22 respectively.

The irreversible deformation is constant and doesn't depend on glycerin concentration. The reversible deformation in its turn grows directly proportionally to the total deformation.

According to the results of deformation characteristics of model compositions of marzipan pastes PKV and MFV there were determined main rheological constants by the glycerin concentration diapason (3)–(7).

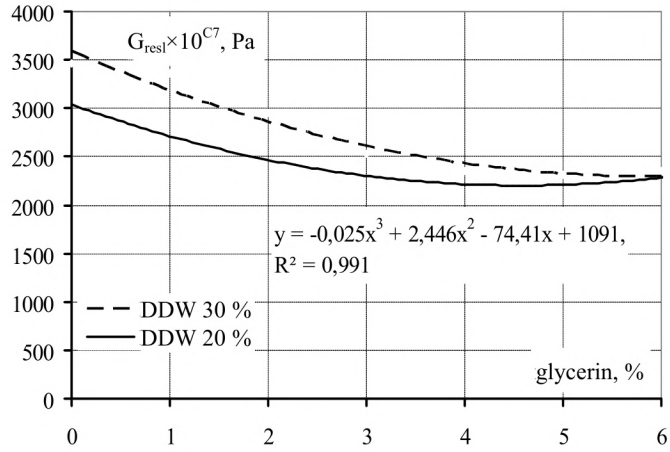

Fig. 3. Influence of glycerin on the conventionally instant resilience module of marzipan pastes PKV (DDW 20 %) and MFV (DDW 30 %)

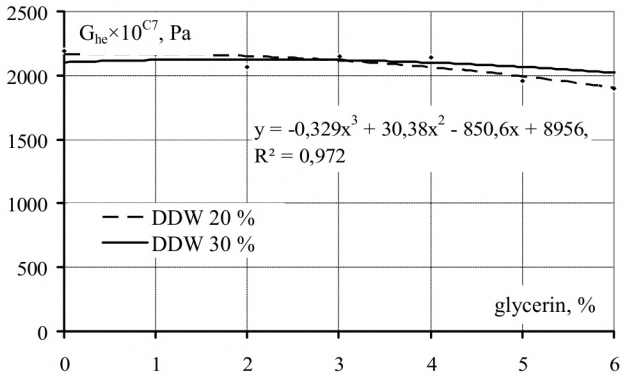

Fig. 4. Influence of glycerin on the highly elastic module of marzipan pastes PKV (DDW 20 %) and MFV (DDW 30 %)

The dependence of indices of the resilience conventionally constant module (Gresl) of marzipan pastes with DDW on glycerin concentration characterizes the ability of the studied samples to resist proportionally to their deformation (**Fig. 3**). The indices of the resilience conventionally constant module in the control samples at DDW concentration 20 % are 346.1 Pa, at DDW 30 % – 315.9 Pa. Introduction of glycerin in the recipe composition of marzipan pastes with DDW results in the decrease of the resilience conventionally constant module indices that abruptly lower at glycerin content 2 %, then decrease gradually and are 335.5 – 235.2 Pa at DDW concentration 20 %, 253.3–222.4 Pa at DDW concentration 30 %.

The dependence of indices of the highly elastic module (Gel) of marzipan pastes with DDW on glycerin concentration characterizes the ability to the deformation disappearance in the studied

samples with time after tension elimination (**Fig. 4**). The indices of the highly elastic module in the control samples at DDW concentration 20 % are 218.0 Pa, at DDW 30 % – 211.4 Pa. A glycerin concentration has no essential effect on highly elastic module indices, results in their gradual decrease from 216.7 to 211.0 Pa at DWW concentration 20 %, from 221.0 to 200.8 Pa at DDW concentration 30 % respectively.

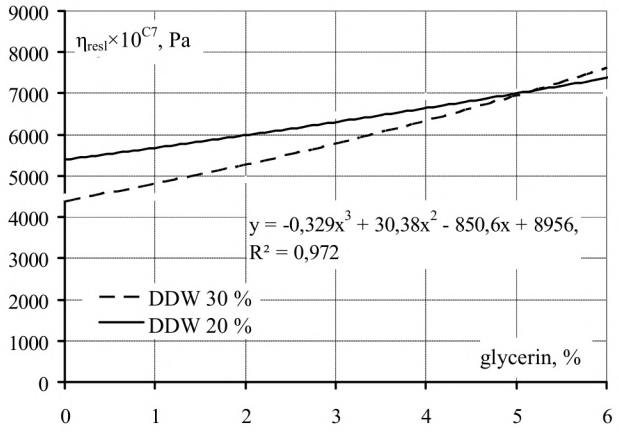

Fig.5. Influence of glycerin on the plastic viscosity of marzipan pastes PKV (DDW 20 %) and MFV (DDW 30 %)

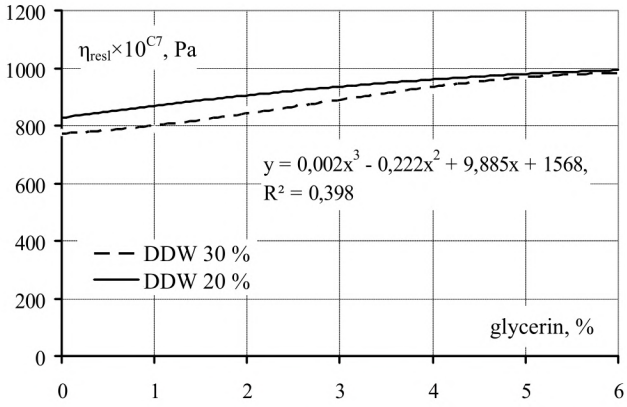

Fig. 6. Influence of glycerin on the resilient aftereffect viscosity of marzipan pastes PKV (DDW 20 %) and MFV (DDW 30 %)

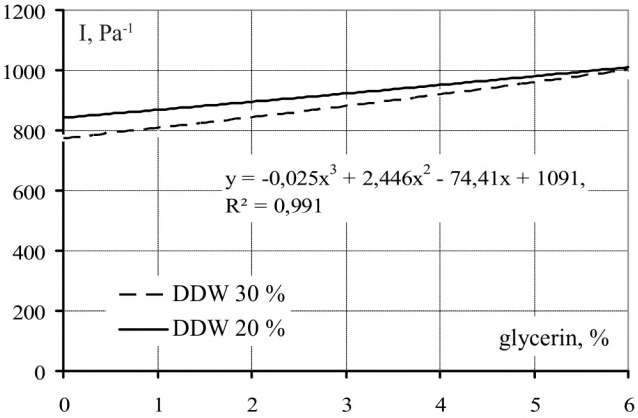

Fig. 7. Influence of glycerin on the pliability of marzipan pastes PKV (DDW 20 %) and MFV (DDW 30 %)

The decrease of indices of the rheological modules with the reversible deformation character favors the plasticity increase. It is testified by the growth of plastic viscosity indices (ή) that characterizes the ability of the structured condition to flow without destruction under the effect of constant tension in 1.5 times comparing with the correspondent control samples, **Fig. 5**. At the expanse of it the formation ability of model compositions of marzipan pastes with DDW improves that is the main criterion of characterizing the consistence of pastes, used for decorating confectionary products.

The glycerin concentration increase results in the growth of viscosity indices of the resilient aftereffect (**Fig. 6**). At DDW concentration 20 % this index grows up to 1.5 times that is 4485–7001 Pa·s. At DDW concentration 30 % this index grows in 1.2–1.4 times and is 6121–7012 Pa·s.

Glycerin introduction in the composition of marzipan pastes PKV and MFV results in their softening that makes them more pliable in the process of making decorative semi-products. It is testified by the growth of pliability indices (I) of the food system of marzipan pastes by 40 % (**Fig. 7**) that characterizes the ability of the studied samples to deformation under the effect of the applied tension.

The growth of viscosity characteristics and pliability of marzipan pastes with DDW is explained by the mobility increase of adsorption layers and weakening of the spatial frame. The further glycerin concentration increase results in destruction of the paste-like structure and loss of the forming ability. So, it is not expedient to increase the glycerin concentration in the composition of marzipan pastes with DDW over 5 %.

4. Conclusions

The experimental studies of the rheological parameters have established the rational glycerin concentration of marzipan pastes PKV and MFV.

The increase of the glycerin concentration in the composition of model mixtures of marzipan pastes with DDW results in gradually decreasing deformation characteristics of a reversible type. It favors the plasticity increase. As a result the forming ability of marzipan pastes improves. It is testified by the decrease of such rheological constants as conventionally instant module of resilience by 25–30 %, highly elastic module by 25–30 %, and correspondingly plastic viscosity indices up to 45 %.

According to the results of the rheological studies, it is not recommended to increase the glycerin concentration over 5 % of the total mass of dry components of marzipan pastes PKV and MFV, because it results in losing the forming ability.

The obtained research results constructively describe the influence of glycerin on the rheological characteristics of marzipan pastes with DDW that allows to elaborate a technology of new types of them with an increased food and biological value, providing the given rheological characteristics. Depending on technological destination, marzipan pastes have the given consistence parameters, determined by the mass share of used glycerin and DDW. New types of marzipan pastes have rather high quality indices and may be recommended for production in the industry and restaurant economy enterprises for nutrition of different population layers.

But in further it may be expedient to consider the influence of other surface active substances on rheological characteristics of marzipan pastes for a comparative analysis.

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Received date 10.01.2020
Accepted date 17.10.2020
Published date 24.01.2020