Для виробництва житньо-пшеничного хліба на міні підприємствах та в закладах ресторанного господарства запропоновано прискорену технологію його виготовлення шляхом використання підкислювачів. Розроблено полікомпонентні підкислювачі «Оптимальний 1» та «Оптимальний 2». Їх оптимальне дозування, 2 % до маси борошна, сприяє скороченню технологічного процесу у 2,5…3 рази та забезпечує збереження свіжості готових виробів

Ключові слова: підкислювач, житньо-пшеничний хліб, черствіння, ретроградація крохмалю, харчові добавки, органічні кислоти

Для производства ржано-пшеничного хлеба на мини предприятиях и в заведениях ресторанного хозяйства предложена ускоренная технология его приготовления путем применения подкислителей. Разработаны поликомпонентные подкислители «Оптимальный 1» и «Оптимальный 2». Их оптимальная дозировка, 2 % к массе муки, способствует сокращению технологического процесса в 2,5…3 раза и обеспечивает сохранение свежести готовых изделий

Ключевые слова: подкислители, ржано-пшеничный хлеб, черствение, ретроградация крахмала, пищевые добавки, органические кислоты

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INVESTIGATION OF THE EFFECT OF MULTICOMPONENT ACIDULANTS ON THE PRESERVATION OF FRESHNESS AND AROMA OF RYE-WHEAT BREAD

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1. Introduction

The modern concept of development of mini enterprises and restaurant facilities requires an improvement of methods for producing daily-use products [1] from technologists. Except for a general simplification and cheapening of the technology, a producer seeks to obtain products that meet the principles of rational nutrition and products that have specialized or dietary properties. One of such products is the rye-wheat bread [2]. According to the latest marketing research, it was found that about 30 % of consumers prefer rye-wheat bread types. This fact confirms the expediency of improvement of technology of the given product [3].

Traditional technologies of rye-wheat bread are long-lasting and involve the use of dense or liquid rye ferments [4]. The improvement of production of such bread for small businesses and restaurants involves a reduction in the technological process through the use of multicomponent acidulants [5]. Shortening of bread technology with the use of existing acidulants leads to a rapid staling of the finished products [6].

A relevant direction to solve the task of preservation of freshness of rye-wheat bread, which is made by the accelerated technology, is the development of new multicomponent acidulants (MCA). It is expedient to produce such acidulants using organic acids, enzymatic preparations, and nutritional supplements.

2. Literature review and problem statement

Bread staleness is a result of complex physical, chemical, colloidal, and biochemical processes. Freshly baked products have a distinct taste and flavor, crunchy crust, elastic crumb [7]. During storage, products lose their flavor, crust – its friability, and crumb – its elasticity [8].

It is known that bread staleness is associated with the aging of pasteurized starch and denatured proteins, as well as a change in the forms of moisture bonding in crumb. In the process of dough baking, under the influence of temperature, the microstructure of swollen starch and protein changes with the formation of micropores, which play a role of micro-reservoirs for water. Part of water molecules is thermodynamically bound while the other part is distributed in the intermolecular space of the denatured protein and swollen gelatinized starch and forms the osmotically-bound water. Thermodynamically-bound water comprises 25 % of the total amount of the bound water. It has a density equal to the density of solids and does not affect the process of bakery products staling [9]. The water that fills the intermolecular space of starch is osmotically bound. Scientists believe that slowing down the loss of the osmotically-bound water contributes to a decrease in the speed of bakery products staling [10].

Bakery products based on rye flour are characterized by higher nutritional and biological value, due to the higher content of essential amino acids (lysine, arginine, valine, threonine), vitamins of B group, they contain 30 % more iron and twice as large of magnesium and potassium. Products based on rye flour are recommended for diseases such as diabetes, obesity, disorders of a gastrointestinal tract, liver, kidneys, as well as atherosclerosis [11].

Rye-wheat bread has a number of technological features that complicate its production [12]. This is predetermined by peculiarities of carbohydrate-amylase and protein-proteinase complexes of rye flour, by the features of a structure of dough made from it, and also due to characteristics of the main raw material – rye flour whose baking properties are different from wheat [13]. Rye flour contains 10...15 % less proteins, which under normal conditions do not form gluten. It also contains more water and soluble fractions, 50...52 % of whose total weight may swell. Much of protein of rye flour is susceptible to unlimited swelling. It is peptized and passes into the state of a viscous colloidal solution, which forms a base of the liquid phase of dough. It is necessary to provide a decrease in the activity of α-amylase, rather deep swelling and peptization of proteins and pentosanes to ensure a normal course of the dough formation process. This requires creation of significant acidity of dough during dough formation [14].

The traditional technology of rye-wheat bread implies the use of dense and liquid rye ferments that complicate its production. This leads to the impossibility of introducing this technology to the restaurant facilities (RF) and mini-bakeries.

Modern approaches to the improvement of the technology of rye-wheat bread imply the use of acidulants and improvers aimed at providing high acidity of dough. The use of such improvers makes it possible to simplify technology of the rye-wheat bread. Most of acidulants and improvers are of foreign origin, which is reflected in the cost of finished products [15].

It is known that a reduction in the length of technological process of bread production influences the course of basic biochemical and microbiological processes in dough, which leads to an intensification of the loss of freshness and flavor of finished products during storage [7].

Considering the prospects and effectiveness of the use of accelerated technologies of rye-wheat bread, development of acidulants is an important task [8]. The acidulants should reduce length of the technological process of production of rye-wheat bread [9], avoid traditional shortcomings that arise while using existing improvers and acidulants [10], as well as contribute to the preservation of freshness of finished products [11].

The multicomponent acidulants “Optimum 1” [16] and “Optimum 2” [17] were developed at the National University of Food Technologies (Kyiv, Ukraine). They are based on organic acids, enzyme preparations and nutritional supplements. It is necessary to investigate an effect of new acidulants on the organoleptic, physical-chemical quality parameters of rye-wheat bread and the duration of their preservation of freshness and flavor.

3. The aim and objectives of the study

The aim of present study was to substantiate the feasibility of using the multicomponent acidulants “Optimum 1” and “Optimum 2” to preserve freshness of rye-wheat bread made by the accelerated technology.

The following tasks were set to achieve the objective:

– determination of influence of the multicomponent acidulants “Optimum 1” and “Optimum 2” on the quality of rye-wheat bread and the duration of preservation of its freshness;

– investigation of effect of acidulants on maintaining the rye-wheat bread flavor.

4. Materials and methods for studying effect of multicomponent acidulants on the quality of rye-wheat bread

4. 1. Investigated objects and materials used in the experiment

The composition of “Optimum 1” MCA [16] included Glusim 10000 Mono (glucose oxidase) enzyme preparation (EP), which contributed to the improvement of structural and mechanical properties of dough, Pentopan 500 BG EF (a mixture of pentosanase and hemicellulase), which promoted the modification of non-cerebellar polysaccharides and provided elasticity of products. Citric acid and dry whey (DLS) were added to ensure the proper acidity of dough under the conditions of reducing the length of the process and intensifying the process of its fermentation. In order to improve organoleptic parameters, wheat fermented malt (WFM) was used. Guar gum was added to increase the water absorption capacity of dough and to preserve freshness of the products during storage.

The composition of “Optimum 2” MCA [17] included PhungamilSuper EP (fungal α-amylase and pentosanase) in combination with ascorbic acid in addition to citric acid, DLS, WFM and guar gum.

Rye-wheat bread was prepared according to traditional technology on a dense rye ferment and employing the accelerated technology. The developed MCA and the acidulant “Ibis” (Lesaffre, France), which was selected as the most common among the existing acidulants on the market, were used [4] for the case of applying the accelerated technology.

Bread was prepared from a flour mixture of peeled rye and first grade wheat at a ratio of 50:50, with the addition of salt (1.5 % by weight of flour), sugar (3 % by weight of flour). In order to control traditional technology, the amount of yeast was 1 %, and for the samples with the introduction of additives – 3 % according to the accelerated method of bread production.

Methods of research into quality of rye-wheat bread were described in detail in paper [18].

5. Results of studies of rye-wheat bread quality with multicomponent acidulants

The developed acidulants "Optimum 1" and "Optimum 2" consist of organic acids and enzyme preparations of complex action. The introduction of MCA in the amount of 2.0 % by weight of flour makes it possible to reduce length of the production process by 2.5...3 times and ensures improvement of basic structural and mechanical properties of dough and bread. A detailed analysis of these properties is given in publications [4, 16, 17, 19].

It is known that bread, especially that made by the accelerated technology, stales during storage. Staleness is a result of complex physical-chemical, colloidal and biochemical processes in carbohydrates and proteins and a decrease in mass due to a reduction in the content of moisture and volatile substances [13].

The influence of MCA "Optimum 1" and "Optimum 2" on the rate of rye-wheat bread staling was analyzed in the studies conducted. Freshness was characterized by a change in such indicators as elasticity, crustiness and swelling of bread crumb, the content of bisulfite binding compounds, the amount of free and bound water.

It is known that the more elastic and plastic the bread crumb, the fresher the product. This principle underlies research into structural and mechanical properties of finished products. Determining the elasticity of crumb was carried out over 72 hours after bread baking using the penetrometer AP-4/1 (Table 1).

It was established that bread samples made by the accelerated technology have higher values of parameters of elastic and plastic deformation of bread crumb throughout the whole storage period. The highest degree of deformation, and hence the lower degree of staleness, is characteristic for products with the addition of "Optimum 1" MCA. This is probably due to the effect of the glucose oxidase enzyme, the principle of which is to increase water absorption capacity of dough, which ensures redistribution of free and bound moisture. The degree of deformation of the sample with the addition of "Optimum 2" MCA is inferior to control after 72 hours of storage by 10.1 %, and the sample with the addition of "Ibis" acidulant by 16.8 %. That is, the samples of bread with the addition of the developed acidulants exhibit less susceptibility to staling than the controls prepared by accelerated technology.

A change in the hydrophilic properties of bread crumb, namely, its crustiness and ability to swell, was investigated over 72 hours of storing in order to carry out a more detailed determination of structural and mechanical properties of bread in the process of storage (Table 2).

Bread products with the addition of the acidulant "Ibis" exhibit a greater tendency to produce crumbs compared to the control and the developed MCA, by 2.6 and 2 times, respectively. Crustiness increases evenly over the storage period, which is explained by gradual evaporation of free moisture of the product. For the products with MCA "Optimum 1", the value of crustiness was 12 % higher after 3 days, for those with MCA "Optimum 2" – 48 % higher compared with the control prepared by traditional technology. This is probably due to the deeper hydrolysis of starch under the action of enzymes in the composition of MCA.

Table 1

Changes in the deformation of crumb of rye-wheat bread during storage $n=3$, $p\leq 0.95$

Deformation types	Control 1 (dense ferment)		Control 2 (addition of the acidulant «Ibis»)		Addition of «Optimum 1»		Addition of «Optimum 2»	
	Units of the device	Freshness, %	Units of the device	Freshness, %	Units of the device	Freshness, %	Units of the device	Freshness, %
4 hours,								
general	56	100	76	100	81	100	89	100
plastic	40		50		60		60	
elastic	16		26		21		29	
24 hours,								
general	46	82	48	63.2	51	68.5	49	65
plastic	32		33		41		33	
elastic	14		15		20		16	
48 hours,								
general	30	53.6	29	38.2	31	38.3	33	37.1
plastic	20		22		23		23	
elastic	10		7		8		10	
72 hours,								
general	21	37.5	24	31.2	29	35.8	30	33.7
plastic	16		19		20		23	
elastic	5		5		9		7	

Table 2

Changes in the hydrophilic properties of bread crumb during storage n=3, p≤0,95

Time after baking, hours	Bread samples			
	Control 1 (dense ferment)	Control 2 (addition of the acidulant «Ibis»)	Addition of «Optimum 1»	Addition of «Optimum 2»
Crustiness, %				
4	1.35	1.9	0.84	1.1
24	1.5	2.1	1.2	1.4
48	1.8	2.6	1.98	2.9
72	2.5	6.4	2.8	3.7
Hydration properties of crumb (swelling), %				
4	388	410	341	323
24	371	390	275	315
48	354	370	240	259
72	336	360	215	231

Hydrophilic properties of bread are characterized by a wetting coefficient of bread crumb.

According to the results obtained, it is evident that the "Ibis" additive has a higher wetting capacity compared to MCA 1 and 2, which exceed control indicators for the traditional technology. This is explained by the introduction of additional formulation components and by the formation in the process of preparation of compounds that have vividly or moderately expressed hydrophilic properties.

The data obtained during analysis of crustiness and hydrophilic properties of the crumb fully agree with the results of a deformation change. That is, bread with the addition of the developed MCA demonstrated better properties to maintain freshness compared with the control prepared by the accelerated technology, but somewhat inferior to the control made by the traditional technology.

Changes in the forms of moisture binding and their redistribution in the process of storage were studied in the analysis of staling intensity of rye-wheat bread products.

The main forms of moisture binding in bakery products are the adsorption (bound moisture) and the osmotically-bound (swelling moisture), which is considered to be free. Additionally, adsorption moisture has a greater binding energy, as opposed to that osmotically-bound [20, 21].

Flour biopolymers bind moisture in a different way. Starch binds it absorbingly, proteins bind it mostly osmotically, and only a small amount - absorbingly. Retrogradation of starch and denaturation of proteins occur during storage of products. This results in the release of part of the bound water and affects the condition of the crumb and the preservation of freshness. Redistribution of bound and free moisture is carried out in the process of storage of bread – free water evaporates; thus, the system acquires a new equilibrium state. One can determine the degree of staleness by a change in the ratio of free and bound water while storing bread products [22].

The research was carried out by a thermogravimetric method using the derivatograph Q-1500. Heating of the samples of bread crumb was conducted at a rate of 2.5 °C/min in the temperature range 20…250 °C. It is believed that when the sample is heated from 15 to 115…118 °C, the free water is released, while at a higher temperature the bound water evaporates [18]. As the heating temperature increases, the bound water is removed. A change in the ratio of free and bound moisture was determined after 4 and 48 hours after baking (Table 3).

Table 3

Content of the free and bound water in bread crumb, % (n=3, p≤0.95)

Samples	Storage duration, hours	Mass fraction of moisture, % to total amount		Loss of bound moisture, % to total amount
		Free	Bound	
Control 1 (dense ferment)	4 48	76.6 79.0	23.4 21.0	2.4
Control 2 (addition of the acidulant «Ibis»)	4 48	71.5 74.6	28.5 25.3	3.2
Addition of «Optimum 1»	4 48	73.2 76.0	26.8 24.0	2.8
Addition of «Optimum 2»	4 48	70.7 73.4	29.3 26.6	2.7

Bread made by the accelerated technology contains more absorbingly-bound moisture and better keeps it during storage due to the MCA components. Probably, due to the addition of guar gum to the composition of MCA mixes, the loss of moisture in samples with the developed additives is smaller compared to the control that contains "Ibis". The sample with "Ibis" lost 11.2 % of bound water after 48 hours of storage; the sample with "Optimum 1" – 10.5 %, and the sample with "Optimum 2" – 9.2 %. The total amount of free moisture in the samples made by accelerated technology is greater. In rye-wheat bread, which contains "Optimum 2", an increase in the amount of adsorption bound moisture is provided. Glucose oxidase provides destruction of sulfhydryl groups of proteins, which leads to a decrease in the binding properties of dough [9, 15] in composition with "Optimum 1" MCA. Results of the research given in Table 3 show that the bound moisture losses in bread samples with the developed MCA are lower than those in samples prepared by the existing accelerated technology with the acidulant "Ibis".

The flavor of rye-wheat bread is one of the main organoleptic indicators of product quality. It motivates the choice of this type of products by consumers, which is why its quality and stability during storage is an essential feature. Pleasant taste and flavor of bread contribute to increased secretion of enzymes in the gastrointestinal tract, and this provides faster and better assimilation of nutrients.

The formation of taste and flavor of products depends on ingredients of the formulation and substances created during maturation of dough and baking dough semi-finished products (products of the interaction between sugars and other carbonyl compounds and amino acids and proteins) [23].

Reducing the length of production process leads to a decrease in the content of bisulfite binding agents. Therefore, their content in the crust and the crumb of rye-wheat bread made by the accelerated technology with the use of MCA was determined. It is known that the total content of carbonyl compounds in the crust and the under-crust layer of bakery products is 4…6 times higher than that in the crumb. Determination of the content of bisulfite binding agents was carried out in line with the Tokarev and Kretovich method, which is based on binding the carbonyl compounds by sodium bisulfite

[24]. A change in the content of bisulfite-binding compounds was investigated after 4 and 48 hours after baking. The short storage duration of the products is explained by the fact that the developed MCA are recommended for restaurant facilities, which a short storage of bread products is implied.

It was established (Table 4) that there were more aromatic substances in the bread crumb baked according to the traditional technology, but 47 % of their amount is lost during storage period.

Table 4

Effect of acidulants on the formation of bisulfite binding agents $n=4$, $p\leq 0.05$

Storage duration, hours	Control 1 (dense ferment)	Control 2 (addition of the acidulant «Ibis»)	Addition of «Optimum 1»	Addition of «Optimum 2»
	Content of bisulfite binding substances in bread, mg-equiv./100 g			
Crumb				
4	5.64	2.73	3.98	3.89
48	3.00	2.64	3.09	3.05
Crust				
4	11.1	10.27	10.03	11.47
48	7.27	7.27	8.73	10.00

Aromatic substances are lost less intensely in the products with MCA, despite their lower initial content (the sample with "Ibis" contains 51.6 % less than the control prepared by traditional technology, with the MCA "Optimum 1" – 29.4 % less, with the MCA "Optimum 2" – 31 % less). The sample with "Ibis" is inferior by 12 %, while samples with the developed additives exceed the content of aromatic substances by 3...4 %, respectively, after 48 hours. The amount of bisulfite binding agents in the sample crust with the MCA "Optimum 2" is greater than that in the control by 3.3 %.

This is explained by the higher content of reducing substances in bread with acidulants due to the deeper hydrolysis of starch under the action of enzymes in the MCA composition and the presence of dry whey as a source of amino acids. These components are the main components of the melanoid formation reaction, which ensures the formation of a significant amount of aromatic and taste substances. Products made by the accelerated technology preserve the flavor better compared to the products prepared by the traditional way of cooking.

Addition of the MCA "Optimum 1" and "Optimum 2" helps to preserve better the flavor, both in crumb and crust of the tested samples, compared to the control. The higher content of carbonyl compounds in rye-wheat bread with MCA during storage correlates with the more intense taste and flavor of products and the color of crust.

This is explained by an increase in the amount of substances that form the aroma during maturation of dough and baking of dough semi-finished products.

6. Discussion of results of applying the developed multicomponent acidulants to preserve freshness of products

It was established that the use of MCA "Optimal 1" and "Optimal 2" in the amount of 2 % by weight of flour contributes to preservation of freshness and flavor of rye-wheat bread prepared by the accelerated technology.

Achievement of the desired effect of longer-term preservation of freshness of products, compared with existing accelerated technologies, occurs due to the content of organic acids (citric acid and dry whey as the source of lactic acid) in the developed acidulants, enzyme preparations that promote deeper hydrolysis of starch and non-microcrystalline polysaccharides (pentosane).

Prolonged preservation of freshness of products is also predetermined by the content of guar gum in the MCA composition. It helps to keep moisture during storage of bread due to the high water absorption capacity of the additive.

In the production of rye-wheat bread, the best preservation of freshness is noted in products prepared according to the traditional technology on liquid or dense rye ferments. If one considers the accelerated technology to bake bread with the use of acidulants, it can be stated that the developed MCA "Optimum 1" and "Optimum 2" contribute to the preservation of freshness of bread better than the existing accelerated technologies.

A more detailed analysis of influence of the developed MCA and their components on the structural and mechanical properties of rye-wheat dough might be possible in further studies.

During storage, both in the control and experimental samples of the products, the carbonyl compounds content is reduced, especially in the crust, due to the weathering of the bisulfite binding compounds in the environment, as well as partial diffusion into crumb. In the case of introduction of MCA, the loss of bisulfite-binding compounds during storage is smaller, compared with the traditional technology, due to the components of the developed MCA. The use of enzyme preparations of amylolytic action accelerates the process of fermentation, which results in the release of a greater number of carbonyl compounds.

Production of rye-wheat bread with MCA "Optimum 1" and "Optimum 2" will expand the range of rye-wheat bread products in restaurants and mini-enterprises.

The presented study results make it possible to expand the methods of production of rye-wheat bread with the preservation of freshness and flavor of bakery products in the process of storage.

7. Conclusions

1. It was established that the samples of bread prepared by the accelerated technology, in the case of using MCA "Optimum 1" and "Optimum 2", have high values of elastic and plastic deformation parameters of bread crumb throughout the whole storage period.

2. It was proved that the bound moisture losses make up 9.2–10.5 % in bread samples with the developed MCA, which is lower than those in the samples prepared by the existing accelerated technology.

3. It was established that the content of aromatic substances in bread with the addition of MCA "Optimum 1" and "Optimum 2" after 48 hours of storage is greater, compared to the control, by 3–38 %.

Thus, the obtained results show the expediency of using MCA "Optimum 1" and "Optimum 2" in the technology of rye-wheat bread varieties in order to accelerate the technological process and to extend their shelf life.

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