SUBSTANTIATING THE OPTIMIZED SHELF LIFE OF PASTEURIZED SAUSAGES WITH THE ELEMENTS OF ACTIVE PACKAGING

Based on the research results, optimization modeling was performed and the shelf life of pasteurized sausage products of the boiled group with the elements of active packaging was substantiated. Re-pasteurization was carried out at the temperature of 85–90 °C for 15–20 minutes in the presence of an oxygen absorber. The dependence regarding the impact of indicators of peroxide and acid numbers on residual content of sodium nitrite accumulation during long-term storage, depending on the formulation composition of sausage products was found.

According to the data of stability of microbiological indicators of pasteurized sausage products and increased values of peroxide and acid numbers, the mathematical dependences to determine the shelf life of sausages were obtained. The dependences substantiate the extended storage for boiled sausage products of the first and top-grade under the condition of using the protective barrier multilayer polymeric materials and the elements of "active packaging".

The conducted optimization modeling in accordance with the obtained experimental data substantiates with high confidence probability the relations between the indicators of quality and safety of sausage products at their shelf life that is longer than normatively recommended. Due to the analysis of response surfaces, an extended shelf life of the high-grade pasteurized sausage products of the boiled group was estimated to be up to 95 days, of the first grade – up to 83 days. The obtained mathematical dependences make it possible to predict the shelf life of pasteurized boiled sausage products, depending on the formulation composition and the use of an oxygen absorber during pasteurization.

The presented prediction and substantiation of the shelf life was performed for sausages, the formulation of which contained the traditional kinds of meat: beef, pork, and poultry. In addition, poultry of mechanical rolling, protein stabilizer and animal proteins based on pig skins, dairy products and spices were included in the composition. In the process of production, sausages were subject to re-pasteurizing at the temperature of 85–90 °C for 15–20 minutes

Keywords: small sausages, pasteurization, storage, residual nitrite, peroxide peroxide value, acid value, microflora

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1. Introduction

Modern trends in ensuring food quality and safety are focused on the development of standardized protocols of production organization. Besides, incoming control of raw materials, delivery, and sale of food products to trading networks, minimizing the risks regarding product safety for consumers remain important [1, 2].

The basic principles of ensuring the safety of food, in particular, based on animal raw materials, rest on the identification of specific contaminant forms of microorganisms and their exposure to bacteriostatic substances [1, 2]. The intensity of their accumulation in the storage process of meat products to a critical level is the main hazard in the consumption of these food products.

The shelf life of foodstuffs under the specified storage conditions [4] is determined by the achievement of the critical values of microbiological contamination, taking into consideration the reserve coefficient [3].

However, besides the maintenance of microbiological safety of products in their long-term storage itself, important quality and safety factors include the minimization of fat spoilage processes [5].

In the fat spoilage process, there is the accumulation of peroxide (PV) and acid value (AV) [6], the critical values of which determine the shelf life and safety of foodstuffs [7, 8].

Thus, the search for effective antioxidants and the use of barrier technologies [8], which slow down the accumulation of PV and AV in the processes of fat spoilage during the storage term, makes it possible to extend the shelf life of food products.

The influence of re-pasteurization on the PV and AV indicators for sausage products of different grades during long-term storage, including using the elements of active packing, was not studied. Research and studying the dynamics of changes in the PV and AV for pasteurized boiled sausages of different grades, with the extended shelf life, will enable prediction of the safety of these products. This research is relevant, as it allows the theoretical and practical prediction of the storage conditions of pasteurized boiled sausage products with the simultaneous use of an oxygen absorber.

2. Literature review and problem statement

The methods for extending the shelf life using pasteurization and sterilization effects have both definite advantages concerning the microflora inactivation, and a series of shortcomings, related to the changes in the quality composition of proteins and fats [3, 6, 7]. In the production of pasteurized boiled sausage products, the normal shelf life is 45 days [3, 4, 8]. To extend the shelf life of meat products, one uses top barrier packaging materials and the elements of active packaging, improving their storage conditions [4, 5]. There is an evidence of a potential possibility of leveling the difference between pasteurization and sterilization effects [8] when it comes to the development of microflora. This creates the prospects of extension of the shelf life of sausage products. However, the systematization of the influence on changes in qualitative chemical composition, primarily lipids, while using re-pasteurization requires further research [3, 6, 7], including the use of antioxidants [2, 8, 9]. The substantiation of the shelf life requires systemic analysis and can be realized based on the analysis of experimental data of safety indicators of sausages, in which reliable factors of influence are raw materials and shelf life [9]. For sausage products of the boiled group, the impact of chemical composition, oleoresins of spices and extracts [10–13], the use of the systems of high-barrier active packaging [14, 15], for a longer period than that recommended by regulations [2, 8, 9], were not studied. In addition, unconventional physical methods

of influencing raw materials [16, 17] are used. Most research into sausage products in terms of their shelf life records the indicators of products without their mathematical analysis and prediction of the food chain safety.

Taking into account the background microbiological contamination in sausage products by the MAFAM level, in the presence of non-meat formulation components or a significant proportion of poultry meat in the composition of products [2, 8, 18] requires further research. In addition, the use of poultry with the specific microflora, plant fillers [18–20], and milk processing products [21, 22] as a part of pasteurized sausages was not studied completely.

Until now, there was no parametric analysis of the further accumulation of MAFAM during storage, changing particles of residual nitrite and kinetics of fat spoilage processes for sausages of boiled group in terms of storage, exceeding the normative.

Conducting such research using mathematical analysis will make it possible to widen the idea of the potential possibilities of their use for sausage products with a significant share of secondary animal raw materials [23, 24]. It is also important to study the effect on the shelf life of non-protein fillers, including hydrocolloids, to prevent the syneresis effect during storage [25].

At high initial values of a_w [26, 27], the problem of influence of variation of pasteurization conditions on a change in acid value (AV) and peroxide value (PV) and the kinetics of MAFAM accumulation during the shelf life of more than 45 days was not studied [2, 28–30].

The study of the influence of "active packaging" on microbiological stability proves the effectiveness of the use of absorbers [31]. However, the available sources do not contain the data on the influence of the elements of "active packaging" on a change in PV and AV when they are used at the pasteurization stage.

Parametrization of dependences and detection of synergy effects using the elements of "active packaging" and re-pasteurization on the stability of physical-chemical and microbiological indicators of sausages with extended shelf life long of sausages require further research.

Statistical validity of these effects will subsequently predict the conditions for pasteurization and substantiate the rational shelf life for boiled sausage products for extended shelf life.

3. The aim and objectives of the study

The aim of this work was to study the influence of pasteurization with the element of "active packaging" – an oxygen absorber on a change in safety indicators of boiled sausage products with a combined composition of raw materials for the prediction of their shelf life.

According to the set aim, the following tasks were set:

– to determine the influence of pasteurization with an oxygen absorber on the residual content of sodium nitrite in the boiled sausage products in the process of storage and to assess the possible relations between the residual nitrate and the value of peroxide number;

– to study and determine the influence of pasteurization with and without the use of an oxygen absorber on a change in peroxide number of sausages of different grades with the shelf life of 45 days, which is longer than the normatively regulated period;

– to determine the dynamics of a change in the acid number of sausages of different grades, pasteurized with and without the use of an oxygen absorber during the storage for 45 days, which is longer than the normatively regulated period;

– to explore and determine the influence of pasteurization with and without the use of an oxygen absorber on microbiological indicators of pasteurized sausages of top and first grades during extended shelf life.

4. Materials and methods for studying sausages pasteurized with oxygen absorber during storage

To optimize the shelf life of sausages, pasteurized with an oxygen absorber, top-grade sausages "Extra" and first-grade sausages "Delicious", which were produced by LTD "Zhytomyr meat processing plant" (Ukraine) by TU U 15.1-32122069-006:2008, were studied [31].

The formulations of the studied products used the traditional types of meat raw materials (pork, poultry, beef, protein stabilizers, animal collagen-containing proteins), and spices [31].

The sausages, cooled to the temperature of 15 °C, were packed on the thermoforming lines "Multivac" (Germany) and "Webomatic" (Germany) by vacuum. They were packed into multi-layer polymer films produced by "Sirius Extrusion" LTD (Ukraine). The samples were packaged with and without sachet-packets of an oxygen absorber according to TU U 20.5-02070938-143:2013 produced by LTD "YUTAK" (Ukraine) and subjected to pasteurization.

Pasteurization was carried out in a thermo-chamber of the "Fessman" brand (Germany) at 85–90 °C for 15–20 minutes. Obtained samples after cooling with water up to the temperature of 15 °C, were additionally cooled to the temperature from 0 to 6 °C.

The samples of pasteurized top and first-grade sausages were stored under standard conditions at LTD "Zhytomyr meat processing factory" (Ukraine) and in parallel at the laboratory of the Problematic scientific research laboratory of the National University of Food Technologies (Ukraine).

The study of microbiologic indicators and residual content of sodium nitrite was carried out in accordance with the requirements of TU U 15.1-32122069-006:2008 by the standard procedures. The number of MAFAM, CFO in 1 g was determined in accordance with DSTU ISO 4833-2:2014 "Microbiology of a food chain. Horizontal method for counting microorganisms" [30, 32, 33].

Preliminary fat extraction was carried out to analyze the sausages and determine their PV and AV. Computation of the PV and AV was performed according to traditional procedures [34].

Modeling and processing of the experimental data were performed using the Mathcad mathematical package and "Data Analysis" (ET) MS Excel.

Existing models of assessment of pasteurization impact on the indicators of sausages of different formulations were reduced to the task of regression analysis of experimental data with the help of package "Data Analysis" (ET) MS Excel and the method of multi-dimensional approximation by means of the Mathcad mathematical package.

To detect the dependences of a change in sodium nitrite on the AV, we used the methodology of response surface with the help of graphic 3D models.

In a general form, the response function is described by the following polynomial:

$$\hat{y}(x,b) = b_0 + \sum_{l=1}^{n} b_1 x_1 + \sum_{k=1}^{n} b_k x_k^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j, \qquad (1)$$

where $x \in R^n$ is the vector of variables, b is the vector of parameters.

To study the values of the AV of the sausages of different grades pasteurized with and without an oxygen absorber in the storage process, the approximation and prediction of the experimental data in the (EM) MS Excel environment using the trendline was performed.

The data of the experimental research are presented in Table 1.

Table 1

Data of experimental research

X_1, shelf life, days	X_2, starch, %	X_3, net weight of an oxygen absorber, g	Residual sodium nitrite, %	AV, mg KOH/g of fat	PV, mMol AK	MA-FAM, CFO in 1 g
1	0	0	0.0029	0	0	50
1	3.12	0	0.0027	0	0	45
1	0	2.5	0.0029	0	0	35
1	3.15	2.5	0.0027	0	0	10
35	0	0	0.0025	3.36	2.8	110
35	3.12	0	0.0025	0.78	0	90
35	0	2.5	0.0025	4.15	6.29	10
35	3.15	2.5	0.0025	2.05	1.94	50
65	0	0	0.0023	3.62	5.11	210
65	3.12	0	0.0022	1.42	2.54	130
65	0	2.5	0.0023	4.41	6.82	15
65	3.15	2.5	0.0022	2.64	4.93	95
94	0	0	0.0021	3.88	9.86	270
94	3.12	0	0.0020	2.11	7.40	210
94	0	2.5	0.0022	6.26	12.30	35
94	3.15	2.5	0.0021	2.40	9.86	12

Table 1 shows the results of the experimental research into the indicators of sausages during the storage process. The results of a change in crucial safety indicators of sausages in time made it possible to perform mathematical analysis of the influence of quantitative input variables to predict the shelf life.

5. Determining the influence of pasteurization with an oxygen absorber on the indicators of sausage products during storage

5. 1. The influence of pasteurization and the PV on residual content of nitrite during storage

According to the experimental data in Table 1 for the control samples of sausages and those that were re-pasteurized with and without the use of an oxygen absorber, the indicators that characterize the safety of products were

determined. Emphasis was placed on a change in the process of storage of residual content of sodium nitrite, the values of acid and peroxide numbers, and the level of microbiological contamination of sausages.

Fig. 1 contains averaged data on the residual content of sodium nitrite in the process of storing the sausages with and without an oxygen absorber.

Fig. 1 shows the absence of a significant difference in the kinetics of a decrease in residual content of sodium nitrite with and without an oxygen absorber up to 65 days of storage.
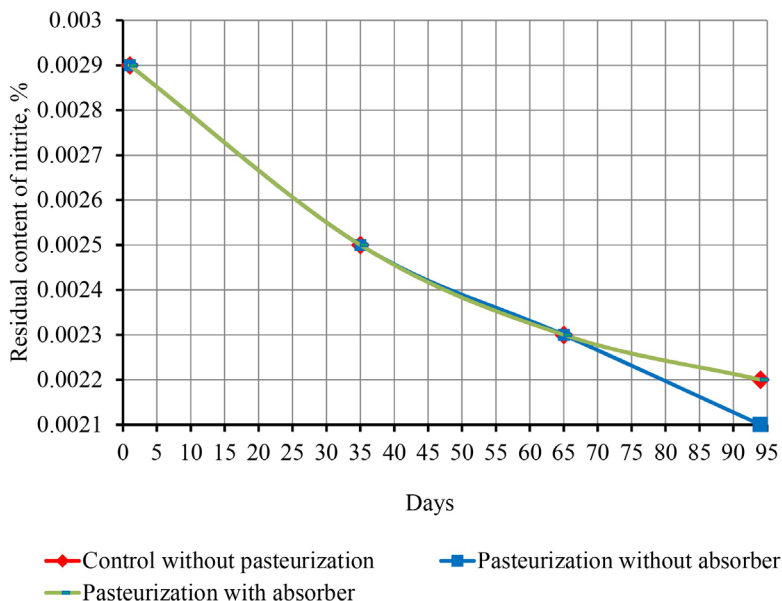
Fig. 1. Change in residual nitrite in the process of storage of pasteurized sausages with and without oxygen absorber

During the storage of pasteurized boiled sausage products, the proportion of sodium nitrite decreases, which may be associated with an increase in the PV values during the storage.

A change in sodium nitrite in the formulations was modeled by the influence of quantitative input variables (peroxide number and the shelf life in given ranges).

The nature of the distribution of the experimental points in factorial space indicates that the dependence may have the form of a polynomial of second degree (Table 1).

$$Z = b_0 + b_1 X + b_{11} X^2 + b_2 Y + b_{22} Y^2 + b_{12} XY, \qquad (2)$$

where b is the constant; X is the peroxide number, mMol AK, %; Y is the shelf life, days.

To assess unknown parameters b_0, b_1, b_2, the least-squares method (LSM) was applied. According to this method, the unknown parameters of the function are chosen so that the sum of squares of deviations of experimental (empiric) values Y_i from their estimated (theoretical) values Y_{ip} should be minimal, that is:

$$S = \sum_{i=1}^{n} \left(Y_p - Y_i \right)^2 = \sum_{i=1}^{n} \left(Y_i - \phi\left(X_i, b_0, b_{1,\dots}, b \right) \right)^2 \to \min. \qquad (3)$$

The resulting equations with calculated coefficients take the form:

– first-grade sausages

$$Z = 0.0029 - 0.00001X - 0.000002X^2 -$$
$$-0.000023Y - 0.000001Y^2 + 0.0000047XY; \qquad (4)$$

– top-grade sausages

$$Z = 0.0027 - 0.000003X - 0.0000014X^2 -$$
$$-0.000082Y - 0.0000047Y^2 + 0.0000021XY. \qquad (5)$$

The resulting graphical 3D models take the form shown in Fig. 2 for equation (5) and in Fig. 3 for equation (4).

The presented 3D models indicate that the values of the PV, increase during the storage at a decrease in the fraction of residual nitrite.

Estimation of the error of approximating polynomials (4) and (5) was carried out from the following formula:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} \left(y_i - \hat{y}_i \right)^2}{n-1}}, \qquad (6)$$

where $\hat{y}_i$ is the values calculated with the help of a regression equation, y_i is the values of the experimental data.

For the indicator of residual content of sodium nitrite of pasteurized top-grade sausages, root mean square deviation is $\sigma = 0.00002$, mMol AK, for the indicator of residual content of sodium nitrite of pasteurized first-grade sausages, it is $\sigma = 0.00001$, mMol AK, which indicates a rather high degree of research results reproducibility with the help of the response area.
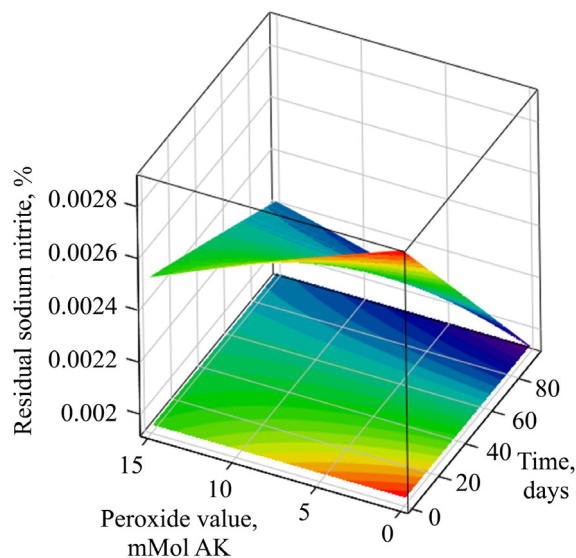

Fig. 2. Dependence between residual content of sodium nitrite and the PV in storage period for pasteurized top-grade sausages
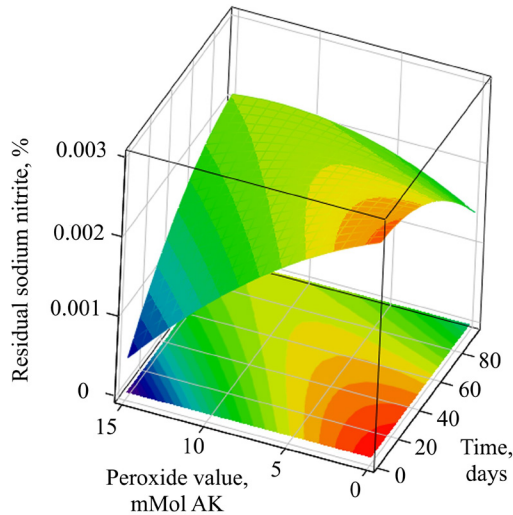
Fig. 3. Dependence between residual content of sodium nitrite and the PV in storage period for pasteurized first-grade sausages

5. 2. Influence of pasteurization on indicators of the PV of sausage products during long-term storage

According to the experimental data, we obtained the dependences of the kinetics of a change in the PV of pasteurized top grade and first grade sausages, which are shown in Fig. 4, 5.

A decrease in the grade of sausages increases the rate of PV accumulation. At the same time, within the samples of equal grades, the highest PV values were observed during the storage of non-pasteurized samples. The use of an oxygen absorber during pasteurization increases the PV more quickly compared to pasteurized sausages without the use of oxygen absorber up to 35 days of storage. However, after that, a change in the PV stabilizes and is better than that of non-pasteurized sausages. In this case, first-grade sausages pasteurized with an oxygen absorber reach the boundary PV values, which corresponds to 10 mMol AK, on day 83 of storage, those pasteurized without an absorber – on day 95. The top-grade sausages pasteurized with or without an oxygen absorber did not achieve the critical PV even on day 95 of storage.
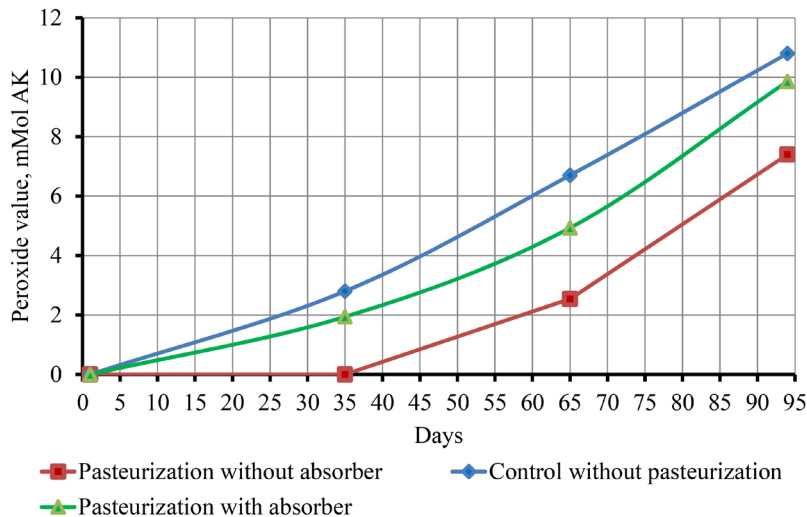

Fig. 4. The kinetics of a change in the PV of pasteurized top-grade sausages in the process of storage
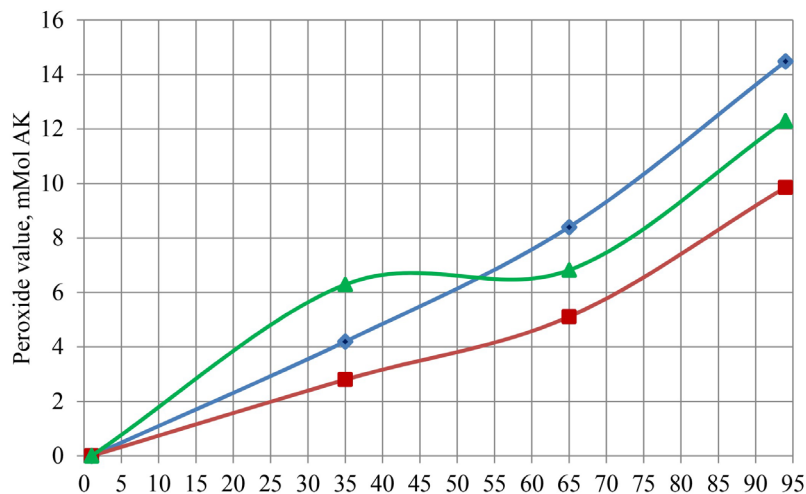

Fig. 5. The kinetics of changes in the PV of pasteurized first-grade sausages during storage

That is why the determining factor of increasing the PV in the storage process is the absence of pasteurization and a decrease in the grade of sausage products.

5. 3. Influence of pasteurization on the AV of sausage products during the long-term storage

The study of the AV of sausages of different grades pasteurized with or without an absorber in the process of storage made it possible to obtain dependences describing the process of its change, depending on a pasteurization method.

The resulting equations with calculated coefficients are as follows:

– AV (Y_1) for first-grade sausages pasteurized without an oxygen absorber is described by equation (7):

$$Y_1=-0.0116+0.0992t, R^2=0.9973; \tag{7}$$

– AV (Y_1) for first-grade sausages pasteurized with an oxygen absorber is described by equation (8):

$$Y_1=0.3656+0.1228t , R^2=0.9899. \tag{8}$$

The kinetics of change in the AV in the process of storage of first grade sausages is shown in Fig. 6.
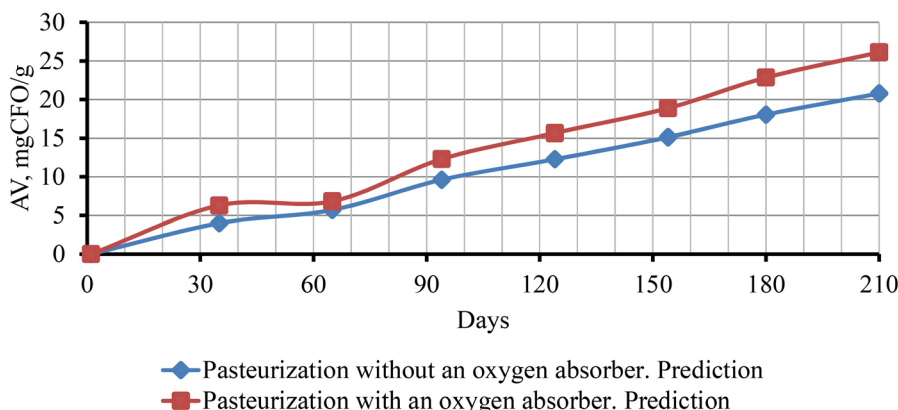

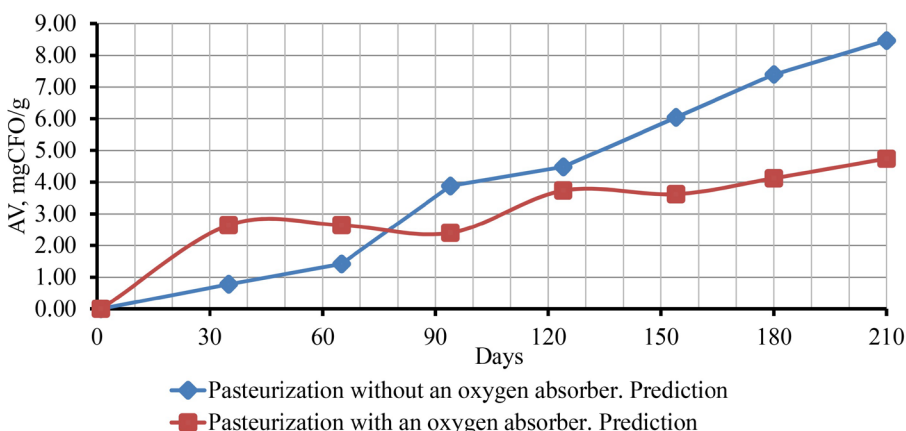Fig. 6. The kinetics of change in AV of pasteurized first-grade sausages in the storage process

Fig. 7. The kinetics of change in the AV of pasteurized top-grade sausages in the process of storage

AV (Y_1) for top-grade sausages pasteurized without an oxygen absorber is described by equation (9).

$$Y_1=-0.5684+0.0429t, R^2=0.9819. \tag{9}$$

AV (Y_1) for top-grade sausages pasteurized with an oxygen absorber is described by equation (10).

$$Y_1=1.0236+0.0182t, R^2=0.9221. \tag{10}$$

The kinetics of change in the AV during the storage of top-grade sausages is shown in Fig. 7.

Changes in the AV of pasteurized sausages more intensively occur for first-grade products and effective use of an oxygen absorber to slow down an increase in the AV is possible when using high quality raw materials in formulation composition. It allows predicting the potential shelf life of up to 120 days for first-grade sausages, taking into consideration the boundary value of the AV of up to 15 mg of KOH/g of product, and for top-grade sausage products for more than 210 days.

5. 4. Influence of pasteurization on the MAFAM values of sausage products during a long-term storage

The dependences of changes in the PV and the AV in the process of storage of pasteurized sausages of different grades are correlated with a change in the values of MAFAM of these products.

Fig. 8, 9 show a change in the MAFAM indicators of pasteurized top grade and first-grade sausages with or without the use of an oxygen absorber during the storage.

The presented dependences of changes in the MAFAM values during storage up to day 95 indicate the compliance with safety requirements of pasteurized sausages with or without using an oxygen absorber. At the same time, in the case of using an oxygen absorber for high grade products, the stabilization of the MAFAM values in dynamics is better than for the first-grade sausages.

For pasteurized first grade sausages, the use of an oxygen absorber makes it possible to prevent more effectively the growth of microflora up to day 65 of storage. At a longer shelf life, the dynamics of microflora growth is more intense, which is consistent with the deterioration of the PV and the AV of first-grade products.
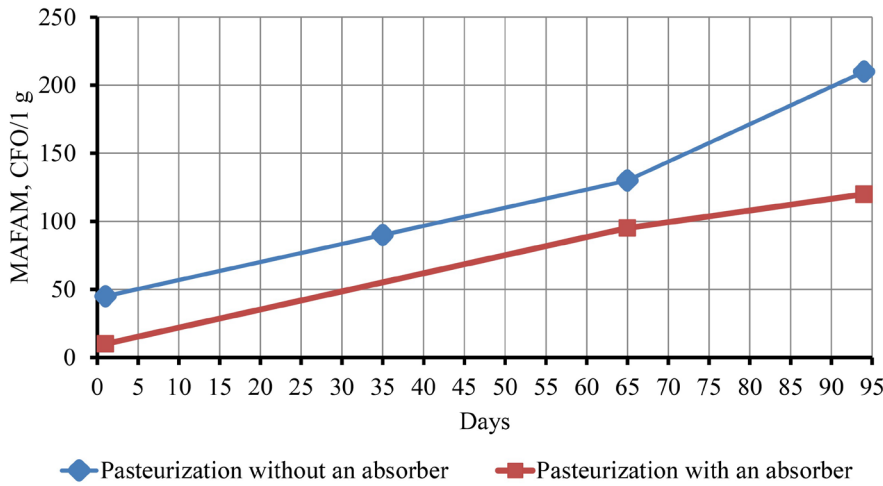
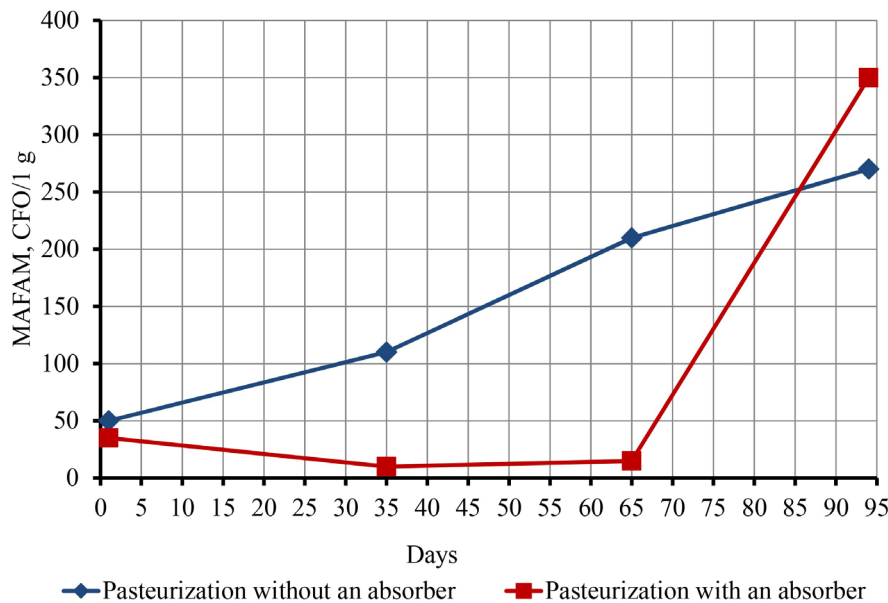Fig. 8. The kinetics of change in the MAFAM of pasteurized top grade sausages

Fig. 9. Kinetics of a change in the MAFAM of first grade pasteurized sausages

6. Discussion of the results of research into the effect of pasteurization on microbiological and oxidative spoilage of pasteurized sausages

Analysis of the presented results of decreasing the residual content of sodium nitrite allowed detection of the relation between an increase in the values of the PV, AV and MAFAM for top-grade and first-grade sausage products during storage.

Thus, on day 65, there was a dynamic increase of the PV, AV and MAFAM indicators for first-grade sausages. This can be explained by partial inclusion of free nitrite to the reaction with active oxygen, which is formed during the process of partial spoilage of fat in sausage products (Fig. 1–3). In addition, nitrogen can be partially used as a nutrient medium for contaminated forms of microorganisms.

Thus, for pasteurized first--grade sausages, the processes causing deterioration in safety indicators do not develop significantly until storage day 65 (Fig. 5, 6, 9). After storage day 65, the intensity of spoilage processes increases. In this case, pasteurized first-grade sausages reach the critical safety values of the PV when using an oxygen absorber on day 83 (Fig. 5). The critical PV value is reached on storage day 95 without the use of an oxygen absorber.

For pasteurized top-grade sausages, both with and without the use of an oxygen absorber, the values of spoilage by the PV and AV indicators were not reached until storage day 95 (Fig. 4, 7).

The boundary values, characterizing product spoilage by the MAFAM value for top-grade sausages also met safety requirements within 95 storage days (Fig. 8). In this case, top-grade sausage products, pasteurized with an oxygen absorber, have more stable values of the MAFAM in the process of long-term storage (Fig. 8) than the first-grade sausages (Fig. 9). This makes it possible to reach potentially much longer shelf life than 95 days during pasteurization with an oxygen absorber.

This proves the effectiveness of re-pasteurization to ensure the level of microbiological stability of boiled sausages on the example of sausages using an oxygen absorber.

The mathematical dependences and parametrization of safety indicators of sausages of different grades pasteurized with the use of an oxygen absorber with the shelf life of more than the normatively regulated period of 45 days were obtained. This makes it possible to predict reliably the shelf life of up to 83 days for pasteurized boiled first-grade sausage products by the value of the PV indicator. For pasteurized boiled top-grade sausage products, it is up to 95 days.

However, to ensure the stability of boiled sausage products using re-pasteurization with an oxygen absorber in a longer range of storage terms, it is necessary to search for the ways to increase the antioxidant potential of products.

In order to counteract the spoilage of fats of boiled sausage products of extended shelf life with the use of oxygen absorbers in the pasteurization process, it is necessary to conduct further search studies regarding effective natural antioxidants. The extracts of rosemary [35, 38], oregano [36, 40], extract of grape pits [39], which are used in the production of boiled sausages, can be used as antioxidants. In addition, to enhance the anti-oxidant potential of meat raw material [37, 41], an effective result may be the search for the ways to enhance the thermal stability of antioxidants and minimize the pasteurization time [42].

Further research will be directed to identification of natural antioxidants– synergists regarding the elements of

active packaging of sausage products and prediction of their influence on quality and safety indicators of pasteurized sausages of the boiled group.

7. Conclusions

1. A decrease in the residual content of sodium nitrite in the process of extended storage of pasteurized boiled sausage products and the relation between a decrease in the content of sodium nitrite in accordance with the values of peroxide number of products were determined. This makes it possible to predict the beginning of spoilage processes in first-grade sausage products at re-pasteurization starting from storage day 65.

2. The use of pasteurization with an oxygen absorber accelerates the PV accumulation compared with pasteurization without an oxygen absorber. For first grade sausages, the PV value limits the shelf life of pasteurized sausages up to 83 days. For top-grade sausages pasteurized with an oxygen absorber, the shelf life is limited to 95 days by the PV indicator.

3. It was found that changes in the AV of pasteurized sausages more intensively occur in first-grade products and it is actually effective to use an oxygen absorber to slow down an increase in the AV, which is possible when using high quality raw materials as a part of formulations. Estimated critical spoilage time according to the AV indicator for first-grade sausages is 120 days, and that for top-grade sausages is 210 days.

4. It was determined that the use of an oxygen absorber during pasteurization for both top grade and first-grade sausages increases the microbiological stability of products. This makes it possible to recommend, taking into account the MAFAM indicator, the shelf life that is longer than 95 days during the storage of boiled sausage products pasteurized with an oxygen absorber.

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