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Functional and technological characteristics of semi-finished products with shell of dough

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Abstract

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Introduction. The aim of the present research was to study the functional and technological properties of semi-finished products with a shell of dough prepared from chicken meat with incorporation of hemp seed flour or hemp protein together with corn starch hydrated by electrochemically activated water.

Materials and methods. White meat of broiler chickens, corn starch, and hemp seed flour and hemp seed protein were used as main raw materials for the production of dumplings. Drinking water, anolyte, or catholyte were used to hydrate the dry ingredients. Moisture content, water activity, pH value, water binding capacity, emulsifying ability of fresh and defrosted dumplings were determined. Thermographic analysis of defrosted dumplings was performed.

Results and discussion. Eight formulations of dumpling fillings based on application of combination of chicken meat with helm processing products and corn starch were studied to find improved composition, which ensured high technological characteristics of the final product. All samples had the moisture content above 60%, which is a sufficient value for this type of product. The samples with corn starch, activated water and hemp seed protein had increased moisture by 3.6–8.0% and with hemp flour by 8.6–18.3 % compared to the corresponding control samples. After defrosting, all samples showed a decrease of moisture content, but this moisture loss was smaller in experimental samples added with corn starch than in control samples without it. Fillings with higher content of corn starch showed lower moisture loss. It was confirmed for dumpling fillings, as well as for dumplings themselves. Water-binding capacity (WBC_w) of the control increased significantly after defrosting compared to the values before freezing. However, the values of the WBC_w for the dumpling fillings with corn starch and activated water remained unchanged after thermal exposure. The dumplings prepared with addition of hemp seed flour or hemp protein had water activity values, a_w , in the range from 0.955 to 0.971. Dumplings containing hemp protein and corn starch had lower a_w values compared to correspondent control. On the contrary, dumplings with hemp flour and corn starch had higher a_w values than correspondent control. Comparison of the samples with electrochemically activated water, showed that lower a_w values were found for the fillings prepared with anolyte. The results of thermographic analysis show that the use of catholyte in the samples makes it possible to obtain thermally stable systems to high temperatures.

Conclusion. Combination of hemp seed and corn starch processing products with different hydration methods allows to obtain semi-finished products with high functional and technological indicators.

Introduction

The use of plant materials in the manufacturing of food products, and in particular meat products, is a new rapidly developing direction in the modern food industry. Plant materials attract the attention of research because they contain proteins, dietary fiber, vitamins, antioxidants, and their addition to traditional foods makes it possible to create functional products that have new qualities and meet the requirements of various groups of the planet's population (Ivanov et al., 2021; Stabnikova et al., 2021). For example, it was proposed to use chia (*Salvia hispanica* L.) flour and chia seeds for partial replacement of fat in burgers, hamburgers, frankfurters, and ham-like products. This replacement allows to decrease the content of fat, increase the content of fiber and omega-3 polyunsaturated fatty acids, improve ratio of omega-6 to omega-3 essential fatty acids, and extend the shelf life of meat products (Stabnikova and Paredes-Lopez, 2024). A number of studies in recent years have been devoted to the use of hemp (*Cannabis sativa* L.) processing products to create a variety of functional foods including gluten-free bakery products (Nissen et al., 2020; Yano and Fu, 2023), hemp seed milk made by homogenizing ground seeds in water (Wang et al., 2018), and meat products (Bozko et al., 2021; Zając et al., 2019).

The nutritional and biological values of hemp seed processing products vary depending on the region and method of hemp cultivation, but in any case remain high (Irakli et al., 2019; Oseyko et al., 2021). Analysis of different literature sources showed that hemp seeds contain, mg/100 g: moisture, 1.1–9.2; protein, 21.3–25.6; fat, 24.5–35.9; carbohydrates, 27.6–38.1; total dietary fiber, 27.6–33.8; insoluble dietary fiber, 22.2–30.9; ash, 3.7–5.9. Hemp seeds are rich in linoleic acid (omega-6) and alpha-linolenic acid (omega-3), having a healthy food preferred ratio 3:1 for ω -6/ ω -3 (Rupasinghe et al., 2020). Besides that, hemp seeds are rich in phenolic compounds, tocopherols, carotenoids and demonstrate antioxidant activity (Farinon et al., 2020). Hemp seed processing products, such as hemp seed flour and hemp protein, produced from defatted hemp cakes, a residue of hemp seed oil extraction, are good ingredients for functional food manufacturing (Mamone et al., 2019).

Flour from hemp seeds has high content of protein, 33% (w/w), low content of fat, 4.5% (w/w), and good profile of fatty acids, where polyunsaturated fatty acids consist 38% (w/w), including α -linolenic acid (omega-3), 8% (w/w) and linoleic acid (omega-6), 27% (w/w). Additionally, hemp seed flour is free of cholesterol, contains dietary fibers, 4% (w/w), polyphenols, flavonoids, tocopherols, terpenes, and possesses antioxidant activity (Nissen et al., 2020). Proteins of hemp seeds contain all essential amino acids and the most abundant amino acids are glutamic acid (3.74–4.58% of whole seed) and arginine (2.28–3.10% of whole seed) (Farinon et al., 2020).

Introduction of plant materials into recipes of meat products is a very popular way to increase their nutritional and biological values (Hinderink et al., 2021; Schreuders et al., 2021; Zhang et al., 2021). However, the application of plant protein as meat analogs could affect the technological and sensory properties of the final product (Boukid, 2021; Cordelle et al., 2022).

It is possible to increase the nutritional value of meat products while maintaining high technological parameters in case when application of hemp seed products is accompanied with addition of corn starch. Corn starch is commonly used as a structuring agent and a substitute for the part of fat in meat products to improve fatty acid profile, decrease lipid oxidation and microbiological count, especially in the case of frozen storage (Eshag Osman et al., 2021, 2022; Romero et al., 2019; Sá Júnior et al., 2021).

The addition of ingredients in powder form, such as corn starch, hemp seed flour and hemp protein, to minced meat is proceeded by the stage of their hydration. During the

hydration, proteins swell to form a viscoplastic mass. The course of this process depends on the properties of the water used for hydration. Electrochemical water treatment could be used to convert water into a metastable excited state. In the process of electrolysis, the catholyte receives a negative potential, the anolyte receives a positive potential because it accumulates near the positive electrode, the anode. According to studies (Marynin et al., 2023), hydration of corn starch with electrochemically activated water allows to produce pates with high rheological properties.

The aim of the present research was study of the functional and technological properties of semi-finished products with a shell of dough prepared from chicken meat with incorporation of hemp seed flour or protein together with corn starch hydrated by electrochemically activated water.

Materials and methods

Materials

White meat of broiler chickens, corn starch, hemp seed flour and hemp seed protein were used as main raw materials for the production of dumplings. Corn starch was produced by AS Group LLC, Kyiv. Flour and seed protein from hemp (*Cannabis Sativa* L.) were manufacturing by Desnaland LLC, Sumy region (Bozko et al., 2021) (Table 1, Figure 1).

Characteristics of helm products

Table 1

Compounds	Hemp seed flour	Hemp protein
Moisture, %	less than 7.0	6.5–7.0
Protein, %	more than 40.0	more than 50.0
Oil, %	less than 16.0	less than 12.0
Ash, %	less than 10.0	less than 10.0
Fiber, %	less than 7.0	less than 15.0

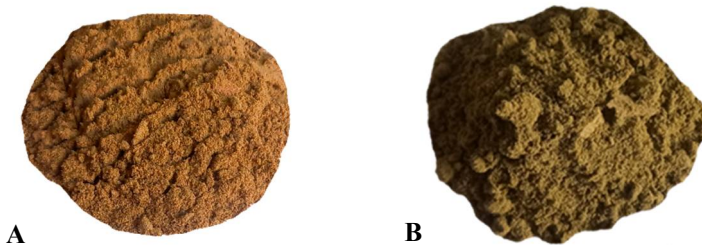


Figure 1. Images of hemp seed flour (A) and hemp protein (B)

Electrochemically activated water: catholyte (obtained by passing a direct electric current through water in the cathode chamber of an electrolyzer) and anolyte (obtained in the process of water oxidation reactions on the anode) (Marynin et al., 2023) was used for hydration (hydromodule 1:2) of hemp products and corn starch instead of drinking water, which was used in control.

Formulations for dumpling fillings are shown in Table 2.

Table 2

Formulations for dumpling fillings

Material	Control		Samples on anolyte				Samples on catholyte			
	1	2	1	2	3	4	5	6	7	8
White meat of broiler chickens,%	74	74	74	74	74	74	74	74	74	74
Hemp protein, hydrated 1:2, %	20	-	14	5	-	-	14	5	-	-
Hemp seed flour, hydrated 1:2, %	-	20	-	-	14	5	-	-	14	5
Corn starch hydrated 1:2, %	-	-	6	15	6	15	6	15	6	15
Onion, %	6	6	6	6	6	6	6	6	6	6

Hydrated helm protein was added in control 1, and meat samples 1, 2, 3, and 4; hydrated helm flour was added in control 2, and meat samples 5, 6, 7, and 8. Onion, 6 %, and spices (salt, 1.7 % and black pepper, 0.6%), were added to each minced meat filling.

Dough composition included, %: wheat flour, 58; chicken eggs, 8; water, 34. Drinking water, catholyte or anolyte were used in dough corresponding to water used for filling preparation.

Dumpling preparation

Broiler chicken meat was ground using a meat grinder (HKN-22SS). Hydration of hemp seed and corn starch was carried out with warm (35–40 °C) drinking water, anolyte pH (5.9) or catholyte (pH 9.7) for 15 minutes, hydro module– 1:2. All ingredients were added to minced meat according to corresponding formulation, and the resulting mixture was kneaded using a mixer (Kenwood KVL8470S). The dough was kneaded using a food processor (Kenwood KVL8470S), and activated water or drinking water was used to prepare the dough. The dumplings were formed using a manual mold. The semi-finished products were frozen using a shock freezer (ASH05K) at a temperature of minus 34-35°C until the dumplings reached a temperature of minus 18°C. Frozen dumplings were stored for 14 days, then they were defrosted and analysed.

Methods

The following parameters were determined in the samples: moisture content, water-binding capacity, water activity, pH, emulsifying ability, and plasticity (Bozko et al., 2021).

Moisture content (W, %) was determined by a thermogravimetric method by drying of the sample to a constant weight at a temperature of 105°C. The moisture content was calculated using the formula:

$$W = (m_1 - m_2) / (m_1 - m), \quad (1)$$

where m is a weight of dry container, g;

m₁ is a weight of container with sample before drying, g;

m₂ is a weight of container and sample after drying, g.

Water activity (a_w) was measured at 25°C using a HygroLab 2 analyzer with an accuracy of $\pm 0.01 a_w$.

pH value was determined using digital pH-meter pH-150MI. To determine pH in minced meat or dough, a sample weighing (5.00 ± 0.02) g was placed into a chemical beaker with a volume of 250 ml. Distilled water, 50 ml, was added and the mixture was stirring for 30 minutes, then it was filtrated through a filter paper, and filtrate was used for pH measurement.

Water-binding capacity (WBC_w , %), the mass fraction of bound moisture in minced meat, was determined by pressing 0.3 g of the sample placed on an ashless filter between glass plates with 1 kg weight for 10 minutes. After this, the contour of the spot is outlined around the compressed sample; the contour of the wet spot appears on its own when the filter paper dries in air. It has been experimentally found that 1 cm² of wet spot area of an ashless filter corresponds to 8.4 mg of absorbed water. The mass fraction of bound moisture is determined by the formula:

$$WBC_w = (M - 8.4S) \times 100/m_0, \quad (2)$$

where M is the weight of moisture in the minced meat by weight, mg;

S is the area of the wet spot, mm;

8.4 is coefficient to transform wet spot area of an ashless filter to mg of absorbed water;

m_0 is weight of minced meat, mg.

Emulsifying ability (EA, %), of the obtained minced meat was determined using centrifugation of a homogenized sample with water and vegetable oil (Bozko et al., 2021). The results were calculated using the following formula:

$$EA = (V_1/V) \times 100, \quad (3)$$

where V_1 is the volume of emulsified oil, ml; V is the total sample volume, ml.

Thermographic analysis was conducted utilizing a Q-1000 derivatograph in an air environment within the temperature range of 15 to 800 °C, with a heating rate of 10 °C/min.

Statistical analysis

Statistical analysis of the experiment results was carried out using Statistica 6.0, Microsoft Office Excel 2007 and Mathcad. Data were expressed as mean \pm standard deviation to define three measurements.

Results and discussion

It is known that the moisture content in meat can reach up to 75%, depending on the type of raw material, and processing can cause its transition from a bound state to a free state, but directly affect the quality of the resulting product (Aboagye et al., 2020). The production of semi-finished products includes the process of freezing, which, if not carried out correctly, destroys the structure of meat tissues (Dang et al., 2021). Such changes cause a deterioration in moisture binding, which in turn worsens functional and technological indicators. Meanwhile, the use of herbal additives in the recipe and the method of their hydration can

significantly affect the functional and technological parameters and reduce the impact of changes caused by technological processing.

The moisture content was determined before freezing and after defrosting, and the study was conducted both for minced fillings and dough separately and for the whole dumpling. The results of the moisture content tests are shown in Table 3, 4 and 5.

Table 3

Moisture content of dumpling fillings

Samples	Moisture content,%		Moisture loss, %
	Before freezing	After defrosting	
Control 1	67.4±2.2	62.5±1.5	4.9
Control 2	65.2±1.4	63.8±2.0	1.4
Anolyte			
Sample 1	75.4±1.6	74.8±1.4	0.6
Sample 2	72.5±2.0	71.6±1.1	0.9
Sample 3	73.4±1.6	72.0±1.8	1.4
Sample 4	74.6±2.6	73.6±1.1	1.0
Catholite			
Sample 5	71.0±1.1	69.5±1.5	1.5
Sample 6	74.9±2.1	74.2±1.6	0.7
Sample 7	74.1±1.2	73.2±1.1	0.9
Sample 8	83.5±2.3	82.4±1.9	1.1

All samples have the moisture content above 60%, which is a sufficient value for this type of product. The samples with corn starch, activated water and hemp protein had increased moisture by 3.6–8.0% and with helm seed flour by 8.6 – 18.3 % compared to the control samples. Among the samples with hemp protein, sample 1 having content of hemp protein 14%, corn starch, 6%, and using anolyte for hydration showed the highest values of moisture content 75.4±1.6%; among the samples with hemp flour, sample 8 with hemp flour, 5%, corn starch, 15% and using catholite for hydration, had the highest moisture content 83.5±2.3%.

After defrosting, all samples showed decrease of moisture content and this moisture loss was smaller in experimental samples added with corn starch than in control samples without it. The meat mixture added with plant material and activated water demonstrated lower moisture loss, and sample 1 with a higher content of protein and anolyte showed a lowest moisture loss, 0.6%, while between the samples added with hemp flour, sample 4 with a higher content of starch had the lowest moisture reduction. The application of catholyte in similar formulations showed the opposite effect: in combination with hemp seed protein, the sample with a higher content of starch demonstrated more significant loss, and in combination with hemp seed flour, the sample with a higher content of flour.

In the production of the dough, drinking water or activated water was used for the corresponded dough formulations. The resulting dough was applied as a shell for the minced meat sample where hydration was carried out with the same type of water. Change in moisture content in dumpling dough shell was also examined, and the results are shown in Table 4.

Table 4

Moisture content of dumpling dough

Samples	Moisture content, %		Increase of moisture, %
	Before freezing	After defrosting	
Dough using drinking water	36.4±1.3	46.5±1.6	10.1
Dough using anolyte	36.6±2.2	42.7±1.3	6.1
Dough using catholyte	35.6±1.2	39.2±1.6	3.6

Initial moisture content of all the dumpling dough was at the same level of 35.6–36.6%. However, after dough defrosting, there was a redistribution of water led an increase in its content in the dough. The largest increase of moisture content by 10.1% was in the control with drinking water. Increase of moisture content after defrosting in dough prepared with catholyte was 3.6 and 6.2% in the dough made with anolyte.

The average meaning of moisture content, namely in minced meat in the dough, allows to assess the changes that occur in the product during the freezing process in general. The results are shown in Table 5.

Table 5

Moisture content of dumplings

Samples	Moisture content, %		Moisture loss, %
	Before freezing	After defrosting	
Control 1	56.0±1.4	53.1±1.6	2.9
Control 2	53.6±1.6	52.5±1.2	1.1
Anolyte			
Sample 1	59.9±1.1	58.0±1.4	1.9
Sample 2	58.1±1.5	57.5±1.8	0.6
Sample 3	58.6±1.4	57.2±1.6	1.4
Sample 4	53.4±1.5	52.6±1.2	0.8
Catholyte			
Sample 5	56.8±1.3	54.4±1.3	2.4
Sample 6	55.2±1.6	53.8±1.5	1.4
Sample 7	54.7±1.6	52.3±1.3	2.4
Sample 8	62.3±1.7	60.9±1.5	1.4

A higher moisture content was observed in experimental samples of dumplings in comparison with control. The highest value of moisture content was found in sample 8 with hemp seed flour and catholyte used for hydration. After defrosting, all samples with a higher content of corn starch (2, 4, 6, 8) showed less moisture loss. It was confirmed for dumpling fillings, as well as for dumplings. These results could be explained by the fact that starch has a gelation capacity of 12%, which allows to form a stable matrix with water (Tafadzwa et al., 2021).

The state of moisture in the experimental samples can be assessed by determining the moisture-binding capacity of dumpling fillings (Figure 2).

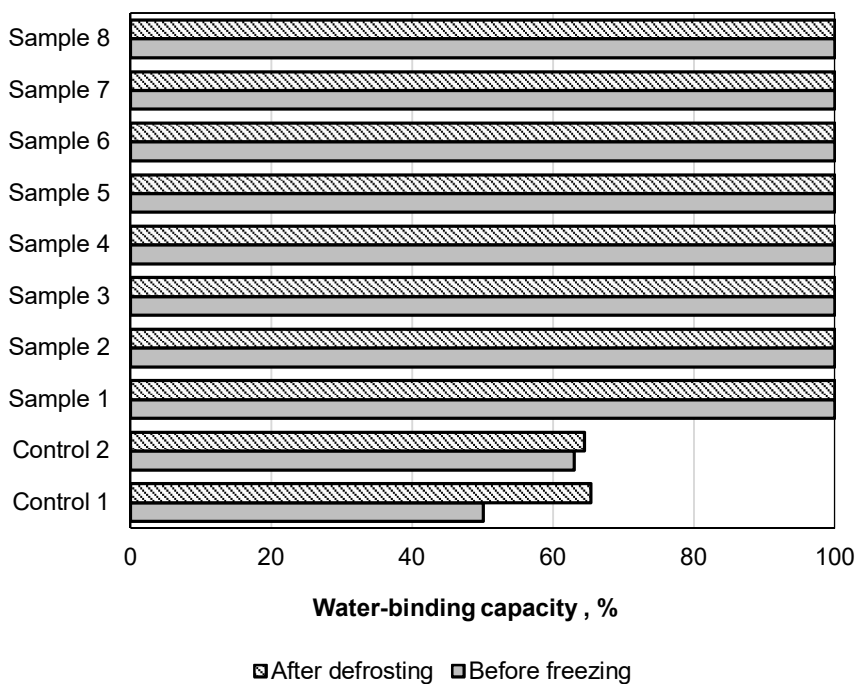


Figure 2. Water-binding capacity of dumpling fillings, %

Water-binding capacity (WBC_w) of the control increased significantly after thawing compared to the values before freezing. However, the values of the WBC_w for the dumpling fillings with corn starch and activated water remained unchanged after thermal exposure. It corresponds to the results of the study (Sá Júnior et al., 2021) which showed that the addition of 2% corn starch can increase the moisture binding in the meat product.

The water activity index (a_w) shows the amount of moisture available for microbial growth and indicates the stability of the sensory properties of meat products. It is known that at a value of water activity below 0.85 the growth of bacteria is impossible. Proliferation of bacteria, yeasts, and mold could be observed at a water activity more than 0.95, meanwhile a_w of fresh meat is found to be around 0.99. The lowering of water activity is preferable for extension of shelf life and prevention of microbial spoilage of the product (Barcenilla et al., 2022). The water activity was measured in the dumpling samples after defrosting (Table 6).

The dumplings prepared with the addition of hemp seed flour or hemp protein had water activity values, a_w , in the range from 0.955 to 0.971. Dumplings containing hemp protein (1, 2, 3, and 4) and corn starch had lower a_w values compared to control 1. On the contrary, dumplings with hemp flour (5, 6, 7, and 8) and corn starch had higher a_w values than control 2. In all samples, regardless of the type of water used to hydrate the components, a decrease in water activity was found with an increase in corn starch content by 0.003–0.009 a_w , which shows the feasibility of introducing starch into the recipe for frozen meat products. Meanwhile, comparison of the samples with activated water showed that lower a_w values were observed in the fillings prepared with anolyte.

Table 6

Water activity values in defrosted dumplings

Samples	Water activity, a_w of defrosted dumplings
Control 1	0.967±0.003
Control 2	0.955±0.002
Anolyte	
Sample 1	0.960±0.003
Sample 2	0.957±0.003
Sample 3	0.965±0.003
Sample 4	0.959±0.002
Catholyte	
Sample 5	0.966±0.001
Sample 6	0.961±0.003
Sample 7	0.971±0.003
Sample 8	0.962±0.001

The development of product formulations with electrochemically activated water with an acidic or alkaline pH inevitably changes this value in the product. Determination of the pH values was carried out in the dumpling filling before freezing and after defrosting (Table 7).

Table 7

pH of the dumpling filling

Samples	pH		Increase of pH
	Before freezing	After defrosting	
Control 1	6.40±0.02	6.40±0.02	0.05
Control 2	5.95±0.05	6.30±0.03	0.05
Anolyte			
Sample 1	5.83±0.03	6.22±0.03	0.39
Sample 2	5.88±0.03	5.98±0.03	0.10
Sample 3	5.86±0.02	5.94±0.03	0.08
Sample 4	5.85±0.04	6.20±0.04	0.35
Catholyte			
Sample 5	5.98±0.01	6.45±0.04	0.47
Sample 6	5.70±0.03	5.85±0.04	0.15
Sample 7	6.00±0.02	6.37±0.02	0.37
Sample 8	6.34±0.04	6.43±0.03	0.10

It was found that all dumpling fillings had initial pH in the range from 5.70 to 6.45. After defrosting, the values in the dumpling fillings did not increase significantly, except for control 1, where the pH did not change. The use of anolyte and catholyte in the formulations did not significantly affect the studied parameters. The difference in the pH values was only 0.15–0.49, and this change was most pronounced for the fillings with hemp seed flour.

The effect of application of activated water on pH of the dumpling dough shell is presented in Table 8.

Table 8

pH of the dumpling dough shell

Samples	pH		Increase of pH
	Before freezing	After defrosting	
Dough using drinking water	6.12±0.03	6.19±0.03	0.07
Dough using anolyte	5.86±0.03	6.51±0.04	0.65
Dough using catholyte	6.26±0.02	6.31±0.04	0.05

The initial pH of the dough did not differ significantly, but slightly decreased after defrosting. In the dough prepared using anolyte, the largest increase in pH value by 0.65 units was observed. The difference in the pH value in minced meat fillings and dough shells is explained by the fact that the pH value of anolyte and catholyte is acidic and alkaline (Liu et al., 2021). Meanwhile, the use of starches in the filling does not have a significant impact on the pH value and its changes during freezing (Coria-Hernández et al., 2022; Eshag Osman et al., 2021).

The ability of minced meat to form emulsions in the protein-water-fat system allows to determine the functional and technological properties of minced meat. The stability and quality of minced meat system can be assessed by determining the emulsifying ability (Table 9).

Table 9

Emulsifying ability of dumpling fillings after defrosting

Samples	Emulsifying ability,%
Control 1	46.8±1.6
Control 2	45.5±1.3
Anolyte	
Sample 1	49.6±1.2
Sample 2	39.2±1.8
Sample 3	51.4±1.6
Sample 4	51.4±1.6
Catholyte	
Sample 5	43.3±1.7
Sample 6	44.5±1.1
Sample 7	45.9±1.9
Sample 8	43.8±1.3

Dumpling fillings had emulsifying capacity values in range from 39.2 to 51.4%. The fillings prepared using anolyte and hemp seed flour (samples 3 and 4) demonstrated the highest emulsifying abilities 51.4%. Filling 3 had the highest amount of hemp seed flour and lowest amount of corn starch, while filling 4 had the lowest amount of hemp seed flour and highest amount of corn starch. This is consistent with the experimental data of other scientists, who showed that vegetable proteins (Zhang et al., 2023) and starch (Genççelep et al., 2017) can be used as stabilizers for meat emulsions.

Thermographic analysis was carried out on dumplings fillings with electrochemically activated water and different contents of hemp products and corn starch. For the study, the formulations 2, 4, 6, 8 were chosen. All these fillings contain 15 % of corn starch and 5% of hemp protein (samples 2 and 6) or hemp seed flour (samples 4 and 8). Anolyte was used for samples 2 and 4, while catholyte was used for samples 6 and 8. The curves obtained for samples 2 and 6, which differed only by activated water taken for hydration are shown in Figure 3.

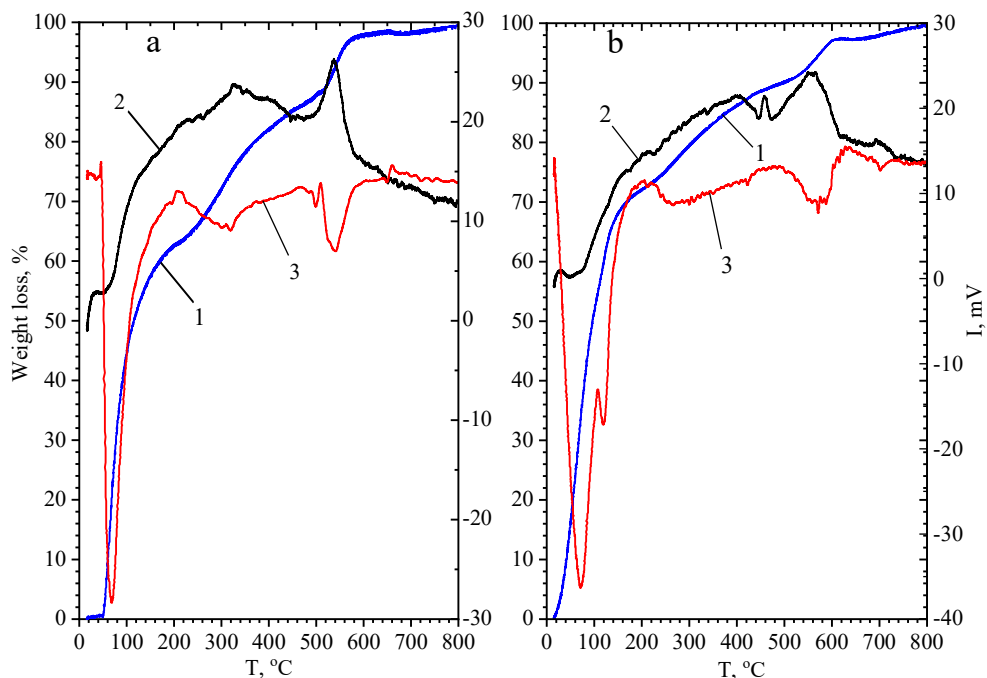


Figure 3 - Derivatization of dumpling filling using hemp protein, 5%, corn starch, 15%, and anolyte (a, sample 2) and catholyte (b, sample 6)
 1, TG, thermogravimetry; 2, DTA, differential thermal analysis; 3, DTG, derivative thermogravimetry

In samples of the same recipe, but differing in water used for hydration of dry components, the maximum rate of mass loss in the samples is within close limits - 73 - 79 °C. At the same time, the change in mass loss (TG curves) shows that for the sample using catholyte (Fig. 2b) the process losses begin at lower temperatures.

Analyzing the DTG curves for two samples 2 and 6, it can be noted that the maximum moisture loss at ~65 °C (accompanied by an endothermic effect on the DTA curve) is present for both samples, however, for sample 6 there is also an additional maximum at ~110 °C, which indicates better retention moisture sample treated with catholyte.

Similarly, the samples show some differences in the DTG curves in the temperature range of 200 – 400 °C, which illustrates the range of complete destruction (partial combustion, since an exothermic effect is observed on the DTA curve) of the protein: for sample 2, maximum weight loss appears at ~320 °C, whereas for sample 6 the maximum weight loss in this temperature range is ~260 °C.

The maxima on the DTG curve in the region of 500–600 °C (accompanied by an intense exothermic peak on the DTA curve) characterize the almost complete combustion of the organic component, and the profile of the corresponding maxima for samples 2 and 6 is slightly different. Finally, the highest temperature low-intensity maximum at ~650°C can be attributed to the complete burnout of residual coke or thermal decomposition of inorganic compounds.

It should also be noted that the TG curves for the studied samples show significant differences. In particular, the share of mass loss due to moisture removal (up to ~180 °C) for sample 2 (with anolyte) is about 60%, while for sample 6 (with catholyte) it is about 72%, which indicates a significantly higher moisture capacity of the latter.

Results of thermographic analysis of dumpling fillings with hemp seed flour are shown in Figure 4.

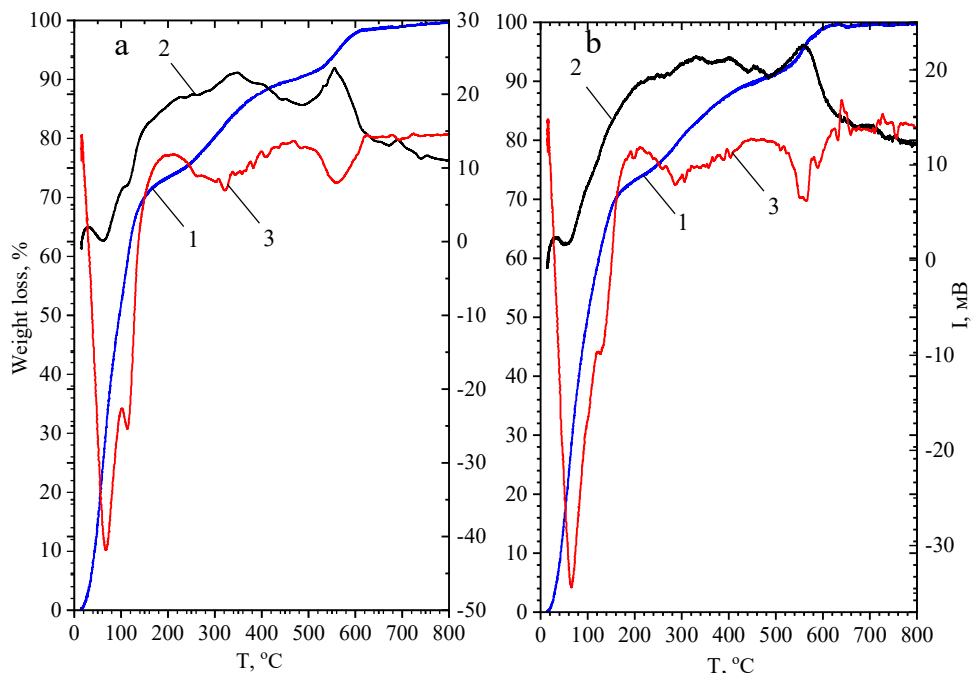


Figure 4 - Derivatization of dumpling filling using hemp seed flour, 5%, corn starch, 15%, and anolyte (a, sample 4) and catholyte (b, sample 8)

1, TG, thermogravimetry; 2, DTA, differential thermal analysis; 3, DTG, derivative thermogravimetry

Dumpling fillings with hemp seed flour show more similar curves of mass change during the heating process, but the process of these changes begins at a lower exposure temperature. The maximum rates of the mass loss in the samples range from 65 to 69°C. The changes in mass loss along the TG curve for both samples are quite similar.

The change in the mass loss rate during temperature exposure in the samples using hemp seed flour and anolyte shows three clear maxima, while the sample using catholyte has three clear maxima and one weakly visible one. For the sample with anolyte, the maxima were at temperatures of: 65°C, 120°C, 320°C, and 560°C, and for the catholyte at temperatures 60°C, 130°C, 280°C, and 560°C. This indicates that despite the fact that the process does not

proceed the same when heating samples with different electrochemically activated water, the temperature of the final decomposition of proteins for the samples is within the same range.

The change in the DTA curve is similar for both samples and has one asymmetric endothermic maximum of water removal at ~ 65 °C and two heating exothermic maxima (decomposition of proteins and their complete combustion) at 340 °C and 560 °C for anolyte and catholyte.

The data obtained prove that the changes under the influence of heat occurring in the structure of minced meat systems depends on the raw material properties as well as on the characteristics of the water used.

Changes in the pH of the medium have a more pronounced effect on the experimental samples using hemp protein, where the sample with catholyte had a higher final conversion temperature. Whereas, when using hemp seed flour, both samples had similar characteristics and temperatures at which the conversion occurred.

Conclusions

1. The addition of corn starch in fillings of frozen semi-finished products helps to increase the moisture content and its binding. However, in case of incorporation of hemp protein, higher moisture binding was found for dumpling fillings with anolyte, but in case of addition of hemp seed flour, catholyte was more effective in increasing the moisture-binding abilities of the fillings. This is maybe due to different content of protein in hemp processing products.
2. Dumpling fillings with higher amounts of help processing products hydrated with anolyte had the highest emulsifying ability.
3. The use of an anolyte or catholyte had no significant effect on the pH of dumplings. However, the lower A_w values were observed in the dumplings prepared with anolyte that ensured their highest microbiological stability.
4. The results of thermographic analysis show that the use of catholyte in the dumpling fillings makes it possible to obtain the higher thermostability of minced meat.
5. Further studies will be aimed at determining the stability of the nutritional and biological value of the developed semi-finished products with a shell of dough during long-term storage.

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Maillard reaction in food technologies

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Abstract

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Introduction. The Maillard reaction is a common reaction that occurs in bakery, confectionary, dairy, meat products, breakfast cereals, and processed fruits as well as in various drinks including wine and beer during cooking, heat treatment, and storage. This reaction determines the sensory properties of food including the taste, colour, and aroma, and consumer preferences largely depend on its intensity.

Materials and methods. The research materials for the present study were scientific publications about the Louis Maillard reaction found in the PubMed, ScienceDirect and Google Scholar databases.

Results and discussion. Information on the chemistry of the Maillard reaction is systematized. The reaction stages leading to the formation of certain compounds, as well as the food products in which these reactions occur, are described. This information will further help to establish in more detail the patterns of the reaction and find out exactly what chemical compounds accumulate in the processed food products.

The Maillard reaction affects the quality of many foods. It has been shown that the Maillard reaction can help create a taste, appearance and aroma that are attractive to consumers, but can, on the contrary, lead to the formation of reaction products with an unpleasant color, taste or even potentially dangerous substances to be consumed.

Meanwhile, for a variety of foods, such as baked bread, grilled meat, or roasted coffee beans, the melanoidin formation is the reaction that will provide the basis for color, taste and odor.

The Maillard reaction is important in the manufacturing of dairy products. It is this reaction that allows the formation of the specific color, smell and taste of baked milk, fermented baked milk or condensed milk, which are valued by consumers.

The Maillard reaction is no less important in food safety. The melanoidin formation can be used to inhibit the growth and development of microorganisms, and has a positive effect on prolonging the shelf life of food products.

Assessing the influence of Maillard reaction products on the formation of the quality and safety of food products involves establishing criteria for its control and management to achieve the specified requirements.

Different Maillard reaction products may have antioxidant, bactericidal, antiallergenic or carcinogenic properties. The formation of certain reaction products depends on the method and duration of food processing. High-temperature processing allows to increase the nutritional value of some food products, while others lose their nutritional value under the same processing conditions.

The Maillard reaction can be used in assessing the quality of food items, namely to identify possible falsification, based on the level of color characteristic of the products formed during this reaction.

Conclusions. The Maillard reaction is of great importance for food production, affecting both the nutritional value and sensory qualities of food. It provides a variety of possibilities for food control, ranging from quality assessment and flavor analysis to nutritional evaluation and adulteration detection.

Introduction

Maillard reaction is one of the most important reactions in the food industry. The first description of the reaction between sugar and an amino acid, which was later called the Maillard reaction, was published more than 100 years ago by Louis Camille Maillard (1912). This reaction is largely responsible for the color, taste, aroma, and texture of the final product in such traditional production processes as baking bread or biscuits, thermal treatment of coffee, cacao beans, meat, and many others. Louis Maillard's discovery became the cornerstone for understanding non-enzymatic reactions that cause the browning of foodstuff during the technological process, mandatory conditions of which are the presence of free amino acids and reducing sugar, as well as high-temperature treatment of the product (Jaeger et al., 2010). Maillard reaction is still under-researched despite the specifics of its course, and usage has been studied for over a hundred years.

Today, the Maillard reaction, its chemistry, impact on the quality and safety of food products and human health are the object of comprehensive studies (Hodge, 1953; Li et al., 2022; Nursten, 2007; Oliver et al., 2006).

The aim of the present study is to determine the prospect of Maillard reaction usage in expertise of foodstuff, namely for identification and detection of falsification of foodstuff.

Materials and methods

The materials for this study were scientific publications about Louis Maillard's reaction. Several questions were examined, specifically: what impact reaction has on the quality and safety of foodstuff and its effect on physiological aspects in the human body.

Separate consideration was given to the questions regarding Maillard reaction usage in the foodstuff falsification identification and detection.

Chemistry of Maillard reaction

Maillard reaction is believed to be hard to control. This is especially noticeable in food technology since the factors tied to the processing methods of raw materials and semi-finished products impact the reaction course. Hodge in 1953 proposed the first constitutive scheme of the Maillard reaction course (Hodge, 1953) (Figure 1).

The reaction course is split into three main stages: early, intermediate, and advanced. At the first stage, a carbonyl group of the reducing sugar (for example, glucose) condenses with the compound with an available amino group (usually with the epsilon-amino group in the lysine residue in the proteins). This glycation reaction leads to aldimine formation – an unstable Schiff base that regroups spontaneously into more stable 1-amino-1-deoxy-2-ketose (ketoamine), also known as the Amadori product.

Acidic hydrolysis of the intermediate product (lactulose-lysine) with HCl leads to the formation of furosine and pyridoxine – compounds that are indicators of the Maillard reaction (Li, 2005; Li et al., 2014; Töpel, 2004).

The subsequent destruction of the Amadori product depends on the activity of hydrogen ions in the solution (pH). Thus, for example, at pH less than 7, the Amadori products primarily undergo 1,2-enolization with the creation of furfural (involving pentoses) or hydroxymethylfurfural – HMF (involving hexoses). At a pH more than 7, Amadori products degrade. This process is argued to include primarily 2,3-enolization that leads to the formation of reductones (such as 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one) and various

products like acetal, pyruvaldehyde, and diacetyl. These compounds have high reactivity essential in later reactions.

Carbonyl groups can condense with free amino groups, resulting in Nitrogen incorporation into the reaction product. Dicarbonyl compounds react with amino acids, forming aldehydes and α -aminoketones. This reaction is known as Strecker degradation. Next, a series of reactions happen in the intermediate stage that includes cyclization, dehydration, retroaldolization, rearrangement, isomerization, and subsequent condensation, which in the advanced stage result in the formation of brown nitrogenous polymers and copolymers more known as melanoidins (Martins et al., 2000).

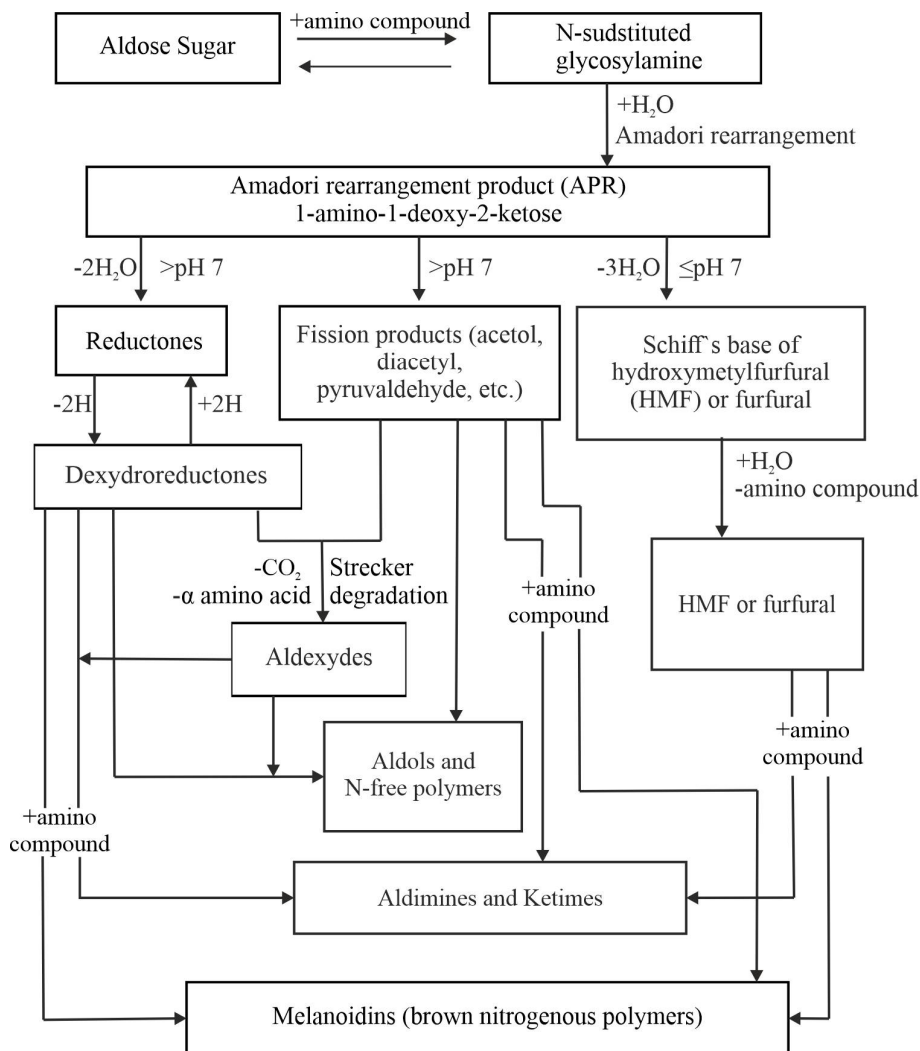


Figure 1. Maillard reaction scheme, adapted from (Hodge, 1953)

Important discoveries took place due to interest in the Maillard reaction. For example, McWeeny and others (McWeeny et al., 1974) discovered that the most important intermediates impacting color are 3-deoxy-2-hexosuloses and 3,4-dideoxyhexosuloses-3-ene. Shortly afterward Ghiron et al. (1988) reported that 3-deoxy-2-hexosuloses, 1-deoxy-2,3-hexodiuloses, and other α -dicarbonyl intermediates can participate in reactions of nucleophilic addition with amino acids in which subsequently decarboxylation takes place resulting in formation Strecker aldehyde.

The Maillard reaction mechanism is described by Hodge and is used to this day, but this hypothesis has some flaws. Firstly, the mechanism describes only the general process of Maillard reaction, while details are not specified. Secondly, some reactions were discovered by other scientists. For example, the work of Japanese scientists Namaki and his colleagues (1975) revealed that carbonyl products of division can also form straight from N-glycosyl amines through an indirect pathway caused by free radicals. This process was named "Namaki Pathway".

1-deoxy- and 3-deoxyglucosones were separated and described from heated Amadori products (Huber et al., 1990). Tressl and others (1995) discovered another perspective on the reaction scheme (Figure 2).

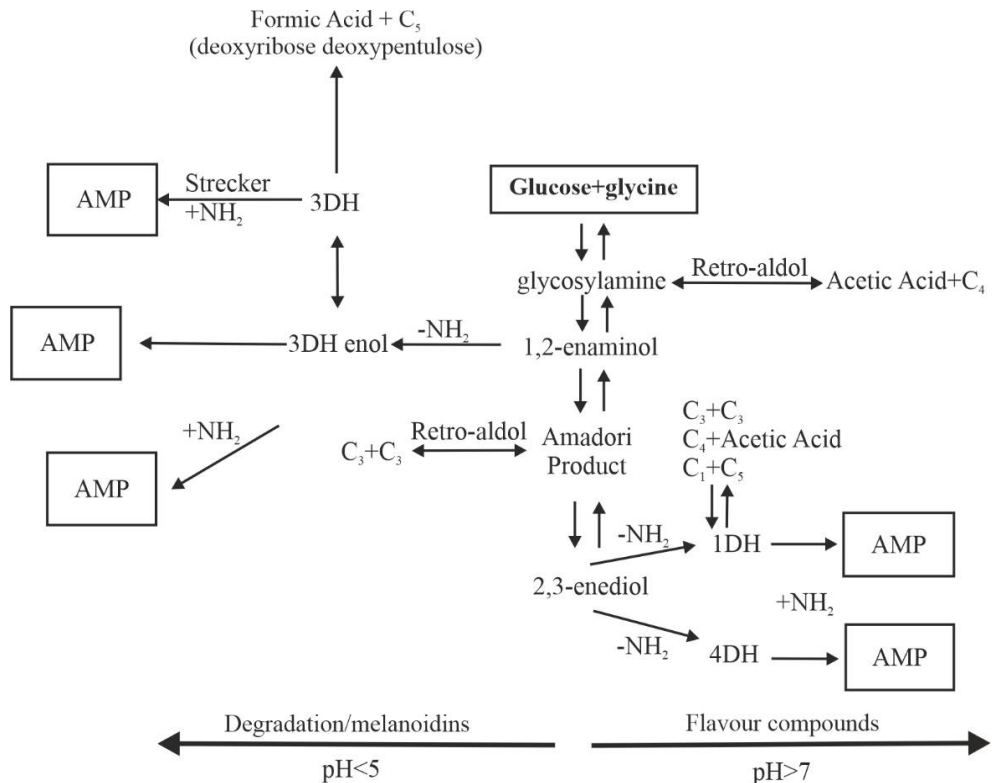


Figure 2. Maillard reaction scheme glucose/glycine

(adapted from Tressl et al., 1995, where AMP (Advanced Maillard Products) are products formed as a result of extended Maillard reaction; 1-DH (1-deoxy-2,3-diketose); 3-DH (3-deoxyaldoketose), 4DH (4-deoxy-2,3-diketose).

At the same time with the enolization reactions, the Amadori product and its dicarbonyl derivatives can be subjected to retro-aldol reactions, resulting in the creation of more reactive sugar fragments C2, C3, C4, and C5, such as derivatives of hydroxyacetone, glyceraldehyde, and diketones. Also, it is worth noting that retro-aldol reactions become more active at higher values of pH.

Huyghues-Despointes and Yaylayan (1996) came to the conclusion that under basic conditions APR (where APR are products of Amadori reaction) can create acetic acid and pyruvaldehyde, as well as lower sugars. The main condition for forming flavor and aroma compounds is the high value of pH in the solution.

Apart from retro-aldol reactions, three redox mechanisms were discovered in which α -hydroxy-carbonyls, α -dicarbonyls, and formic acid are involved. Formic acid as a main product of lactose degradation in the Maillard reaction was reported by Berg and Van Boekel (1994). Van Boekel and Brands (Brands et al., 2000; Van Boekel et al., 2005) indicated that formic and acetic acids are the two main products of glucose and fructose degradation in the Maillard reaction.

Based on Tressl's conclusions, Yaylayan (1997) developed a conceptual view of the processes that occur during the Maillard reaction. According to this view, the Maillard reaction is described as a reaction in which "chemical pools" are being created and interact with each other. The combination of products formed from a clearly defined precursor's decomposition is called the fragmentation pool, and the group of interconnected chemical reactions and their products is called the interaction pool. Fundamental reactions that are the basis of the interaction pool are classified according to the type of chemical transformation that takes place. The importance of this classification is in its ability to predict the formation of Maillard reaction products in the model systems. Also, according to Yaylayan's theory, it has been established that during the Maillard reaction amino acids and sugars also experience independent degradation in addition to ordinary degradation in which the Amadori product is formed.

Sugar isomerization and degradation during the thermal treatment of the milk are more important than the Maillard reaction from a quantitative point of view (Berg, 1993).

Also, the significance of the Amadori product (which has been considered an intermediate product of the reaction) is questioned in the food industry (Molero-Vilchez et al., 1997).

Table 1 shows brief examples of Maillard reaction stages and the results of their study.

Therefore, the chemistry of the Maillard reaction, its course, specifics, and conditions are still disputed among scientists worldwide, and the study of this reaction continues to this day.

In the context of the food industry, the Maillard reaction and its products form characteristics of quality, safety, and physiological consumption aspects.

Table 1

Examples of Maillard reaction stages

Stage of MR	Foodstuff	Reactions/reaction products	References
Early	Beer	Aldehydes	Hellwig et al., 2014
		Carbonyl compounds: glyoxal, methylglyoxal, aldehydes	Maasen et al., 2021
		3-methylbutanal	Cämmerer et al., 2002; Murata, 2021
Early	Malt, children's cookies	Furosine (~N-2-furoylmethylisoinosine) and 2-furoylmethyl derivatives such as GABA (γ -aminobutyric acid)	Erbersdobler et al., 1991; Resmini et al., 1991; García-Banos et al., 2004; Cardenas Ruiz 2004; Del Castillo et al., 2000; Sanz et al., 2000, 2001
Early	Cookies, crackers, breakfast cereals, dry milk	Furocin	Rada-Mendoza et al., 2004
Early	Sterilized milk, curdled milk, condensed milk, liquid infant milk	Hydroxymethylfurfural (HMF) as a marker of the intensity of formation of products of the Maillard reaction	Albalá-Hurtado et al., 1999; Olano et al., 1989; Park et al., 1991; Berg, 1993.
Early	Milk, pasta	5-hydroxymethylfurfural, furosine, maltol and pyridoxine	Christie, 1983; Resmini et al., 1994
Early	Black garlic	2-furomethyl-amino acids (2-FM-AA) as indicators of the Maillard reaction	Ríos-Ríos et al., 2018
Early	Black garlic	2-furoylmethyl- γ -aminobutyric acid and 2-FM-arginine	Ríos-Ríos et al., 2018
Early	Orange juice	2-furoylmethyl derivatives of aminobutyric acid (2-FM-GABA) and arginine (2-FM-Arg) as early indicators of non-enzymatic darkening	Del Castillo et al., 2000
Intermediate	Beer	Carbonyl compounds 1-deoxyglucosone, 3-deoxyglucosone and methylglyoxal	Hodge, 1953
Intermediate	Coffee	Carbohydrates and pyrolysis of organic compounds; melanoidins as a result of polymerization and/or pyrolysis of furans.	Tressl et al., 1998; Belitz et al., 2009
Late	Milk	Condensation, polymerization, degradation, cyclization reactions occur; Fluorescent compounds	Hodge, 1953; Birlouez-Aragon et al., 1998
	Fried fish and grilled meat	Acrylamide and heterocyclic aromatic amines	Friedman, 2003; Carthewa et al., 2010

Table 1 (Continue)

Stage of MR	Foodstuff	Reactions/reaction products	References
Late	Model system of amino acid and sugar	α -hydroxycarbonyls, α -dicarbonyls and formic acid	Van Boekel et al., 2005
Late	Instant coffee, decaffeinated coffee, tea	Dicarbonyl compounds, methylglyoxal, diacetyl and glyoxal	Nagao et al., 1979
Late	Cereal products	2-fluoromethyl-GABA	Marchenko et al., 1973
Late	Roasted coffee, boiled meat	2,3-butanedione, 2,3-pentadione, methylpropanal, 3-methylbutanal, phenylacetaldehyde, 3-hydroxy-4,5-dimethyl-2(3H)furanone (sotolon) and 2,5-dimethyl-4-hydroxy-3 (2H)-furanone; 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine and 2-acetyl-1-pyrroline, 2-furfurylthiol, 20-methyl-3-furanthiol, 3-mercapto-2-pentanone and methional	Lieske et al., 1994

Maillard reaction and its impact on the quality of food products

The positive significance of this reaction was recognized in 1912 when it was discovered that malty aroma during beer brewing forms due to the reaction between the reducing sugars and leucine (Lintner et al., 1912), which later has been confirmed (Helling et al., 2014; Ruckdeschel and Brauw, 1914). But in this regard, Akabori (1927) discovered that aldehydes form with high yield during the decarboxylation of amino acids in the presence of glucose. Other carbonyl compounds, such as glyoxal, methylglyoxal, or diacetyl, also lead to the formation of aldehydes (Neuberg et al., 1927).

Schönberg and Moubacher were the first to demonstrate that vic-dicarbonyl compounds (any diols that have two hydroxyl groups connected to adjacent carbons) are always needed for the “Strecker degradation” (1948). They are formed as intermediate products during the Maillard reaction (Schönberg et al., 1952). This confirms Ruckdeschel’s postulate on the formation of 3-methylbutanal – an important aromatic compound formed in malt from leucine during Strecker degradation (Damn et al., 1964).

The Maillard reaction has 3 stages. In the intermediate stage, different carbonyl compounds are formed from Amadori products, including such dicarbonyl compounds as 1-deoxyglucosone, 3-deoxyglucosone, and methylglyoxal. These dicarbonyl compounds are more reactive than source material or reducing sugar. Reactive dicarbonyls interact with each other and with amino groups in amino acids and proteins, creating aroma and color (Ho, 1996).

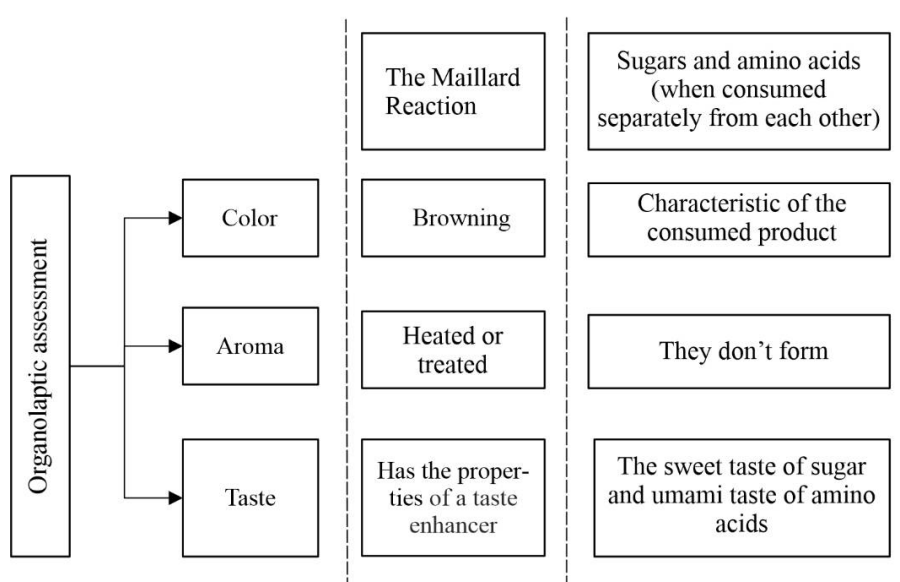


Figure 3. Correlation between Maillard reaction and sensory characteristics of the food product

Figure 3 depicts the correlation between the Maillard reaction and the color, aroma, and taste of food products. It is known that Maillard reaction products are formed due to the heating of sugars, amino acids, or proteins. Thus, it can be said with complete confidence that the brown color and caramelization aroma (typical for this reaction) indicate that the product contains sugar and amino acid or a protein, which is important for consumers, especially for whom sugar is contraindicated. Also, apart from having an impact on browning and aroma, recent studies have shown that different products of the Maillard reaction can act as sweeteners or taste modifiers (Festring et al., 2010; Ho, 1996; Kaneko et al., 2011; Ottinger et al., 2003; Perestrelo et al., 2019; Shima et al., 1998).

A short generalized characteristic of the impact the Maillard reaction has on the quality and safety of food products is shown in Table 2.

Impact of the Maillard reaction on the sensory properties of food products

The origin of the volatile organic compounds responsible for the formation of aroma in food products is hard to identify to this day because of their varied origination and structure. Scientists show great interest in studying this question, especially with the aim of controlling the generation of distinctive aromas and colors of food products.

The development of gas chromatography-mass spectrometry in the last decade significantly intensified the analysis of compounds with a specific odor, including aroma created during the Maillard reaction (Buckholz, 1988; Chuyen, 1998; Ho, 1996; Taylor et al., 1996). Thus, for example, Lane and Nursten (1983) identified 12 amino acids, 5-7 of which, in their opinion, together with glucose participate in the creation of aromas of bread, crunchy cookies, biscuits, and toasts at studied temperatures from 100 to 220°C at selected time intervals up to thirty minutes.

Table 2

Effect of the Maillard reaction on food quality and safety

Quality and safety of food	Food example or explanation	References
Darkening or pigmentation	The color of beer, soy sauce, bread crust and roasted coffee	Murata, 2021; Hayase et al., 2006; Kanzler et.al, 2020
Formation of aroma	Toasted bread, grilled meat and roasted coffee	Lane et al., 1983
Formation of taste enhancer	Boiling beef broth and ripening soy sauce	Shima et al, 1998; Ottinger et al., 2003; Fetting et al., 2010; Kaneko et al., 2011
Antioxidant and antimutagenic activity	Individual structures of enediol and enaminal molecules in melanoidins and various compounds formed by the Maillard reaction; The antimutagenicity of pyrazines contained in Maillard's products correlates with the inhibition of the cytochrome P-450 IA2-linked ethoxycoumarin deethylase mutagen-activating enzyme in microsomes.	Griffith et al., 1957; Chuyen et al., 1998; Eric et al., 2013; Jenq et al., 1994
Loss of lysine	Long-term storage of dry milk	Plakas et al., 1985; Chuyen et al., 1991; Pellegrino et al., 1999
Formation of mutagens	Acrylamide and heterocyclic aromatic amine	Arvidsson, et al., 2005; Nagao et al., 1979; Sugimura et al., 1990; Kovtun et al., 2022

Coffee is one of the most popular drinks among consumers around the world. The desired smell of coffee drinks occurs during the roasting of coffee beans. The typical temperature range for this process is from 180 to 250°C, and the duration of the roasting is from 2 to 25 minutes, depending on the procedure used (Belitz et al., 2009). This results in the Maillard reaction and caramelization, formation of carbohydrates, and pyrolysis of organic compounds. Melanoidins are formed as a result of the Maillard reaction during the roasting as the product of polymerization and/or pyrolysis of furans. They combine among themselves via a poorly understood reaction of condensation polymerization during the intermediate stage of the reaction (Tressl et al., 1998).

In turn, Fors (1983) published a literary review on the sensory properties of the volatile Maillard products and related compounds. This review is centered on the quality of the aroma and description of the taste, color, and sensory threshold values for different compounds classified by their chemical structures.

As for the color, it is known that the brown color typical for the Maillard reaction is caused by the melanoidins. During the last stage of the Maillard reaction, several chemical reactions take place: condensation, polymerization, degradation, cyclization, and so on – which is accompanied by melanoidin formation (which are heterogeneous polymers). The structure of these polymers is not known for certain, and several theories exist on their chemical structure and formation (Wang et al., 2011). Thus, according to one of these theories, the main skeleton of melanoidin contains saturated aliphatic carbon atoms formed from the products of sugar decomposition and branched by amino compounds (Murata, 2021). Hayase and others (1986), with the use of nuclear magnetic resonance spectroscopy, suggested another polymer. It is known that in the Maillard model reaction system with only a monosaccharide and an amino acid the main skeleton of the melanoidin with high molecular mass is considered a polymer product of the sugar decomposition because dicarbonyl compounds such as 1-deoxyglucosone, 3-deoxyglucosone, and methylglyoxal can be condensed with the help of the aldol reaction (Cammer et al., 2002; Maasen et al., 2021; Murata, 2021). But by themselves these basic structures are colorless. Therefore, according to this theory, it can be assumed that melanoidins should have partial structures of different chromophores.

According to the second theory, melanoidins are polymers of low molecular weight pigments formed from sugars and amino acids (Murata, 2021). Hayase and others assumed that melanoidins are formed from heterocyclic intermediate products of the Maillard reaction through the aldol reaction and the Michael 1,4 addition (this is a reaction between Michael donor (an enolate or other nucleophile) and Michael acceptor (usually α,β -unsaturated carbonyl) with the creation of the Michael adduct with the carbon-carbon bond at the acceptor's β -carbon), i.e. they are formed by the aldol condensation and Michael reaction.

Hoffman speculated that melanoidins in food are created by protein crosslinking (Hofmann, 1998, 1999). It was also reported that melanoidins are not characterized by a specific absorption maximum of visible light (380–780 nm), which clearly indicates that melanoidins have mixed chromophores.

Various low molecular weight pigments created as a result of the Maillard reaction were discovered and identified. In some cases, these pigments greatly enhance coloration (Murata, 2021).

On the final stage of the Maillard reaction, colored intermediate products and other reactive precursors (products of enaminal, low molecular weight analogs of sugar, unsaturated carbonyl products) are condensed and polymerized with the amino catalyst creating brown polymers that have furan ring with different functional groups, including carbonyl, carboxyl, amino, amide, ether methyl or/and hydroxyl groups (Ames et al., 1993; Ledl et al., 1990; Tressl et al., 1998).

It should be noted that the discovery and identification of colored Maillard reaction products were being carried out only using model systems, usually for products with low molecular mass (less than 500 Da). Thus, Hashiba (Hashiba, 1982) compared the reactivity of different reducing sugars with a singular amino acid (glycine) and concluded that browning is directly proportional to the reducing ability of sugar and the amount of glycine.

Rizzi (1997) concluded that plenty of colored products are products of (retro) aldolization/dehydration of sugars, which can or can not be connected to the proteins or other sources of amino nitrogen.

Hoffman (1999), using a series of model experiments and chemical, instrumental, and sensory methods, identified some products of carbohydrate decomposition as a precursor of browning (deoxysones, glyoxal, methylglyoxal, hydroxy-2-propanone, 3-hydroxy-2-

butanone, and glycolaldehyde), which fit in with Figure 2, and proved that their reactivity in producing substances that determine color of the product change with thermal treatment.

The degree of browning is often determined similarly to the evaluation of the intensity of the Maillard reaction and generally is measured using absorption at 420 nm (Baisier et al., 1992).

The formation of a golden crunchy crust on the food surface is one of the most obvious signs of fried food. This layer (known as browning) is created as a result of the chemical and structural changes in the product several minutes after the contact with oil. The golden color of the crust is formed due to the Maillard reaction, which causes chemical changes in sugars on the product's surface. In this particular case, the Maillard reaction occurs when high temperatures combine with low moisture content (Skjoeldebrand et al., 1980). In other words, the crust is a dry layer that acts as a barrier between the inner part of the food product and the oil outside. The crust also limits heat transfer.

However, melanoidin creation in food products is not always desirable. For example, during the analysis of various colorants in technological processes of sugar production. Pearson came to the conclusion that melanoidins are the most dangerous colorants from the perspective of final products (Reva et al., 1978).

Utilization of different compounds with amino groups results in the creation of various flavor profiles due to the created compounds. Table 3 shows a possible range of flavors created by heating various amino acids with glucose. Milk proteins usually are rich in amino acids, some of which have residues that can participate in the Maillard reaction without destroying the protein.

Table 3

Creation of possible flavors that occur due to heating of various amino acids with glucose in different conditions (adopted from Van Boekel et al., 2006)

Amino acid	The smell of the product when heated with glucose
Alanine	Fruity, floral, sweet
Arginine	Bitter, sour, fruity
Aspartic acid	Fruity, sweet
Cysteine	Sulphurous, meaty
Glutamic acid	Sour
Glycine	Caramel, sweet, floral
Histidine	Sour
Isoleucine	Burnt, caramel
Leucine	Burnt, caramel
Lysine	Pleasant/sweet, caramel, cardboard, herbal
Methionine	Potato, shrimp
Threonine	Sweet, fruity, tart
Serin	Fruity, sweet
Proline	Fruity, bitter
Phenylalanine	Floral, almond, bitter
Tyrosine	Fruity, floral, tea
Valin	Caramel, biscuit, malt, chocolate, bitter

The hydrolysis process leads to the increase in available amino groups for the Maillard reaction. As can be seen in Table 5, present and available amino acids can cause a number of taste properties (Wong et al., 2008).

Effect of Maillard reaction products on sensory characteristic of milk products

The taste of milk products is one of the most considerable sensory characteristics that consumers take into account. It is well known that fresh and high-quality milk usually has a characteristic mild taste. Therefore, any deviation in taste can be very notable. The main source of the taste components is the milk itself, but lowering the quality of components during processing also has a major impact on the overall taste (Ames, 1998; Nursten et al., 1997).

The Maillard reaction affects the sensory characteristic of numerous food products, especially milk products. Its effect becomes more prominent during heat treatment. This reaction's course can create favorable flavors, appearance, and aromas (Van Boekel et al., 2006). An example of a desirable Maillard reaction in milk can be observed in baked milk (Figure 4) (Mandiuk et al., 2024).

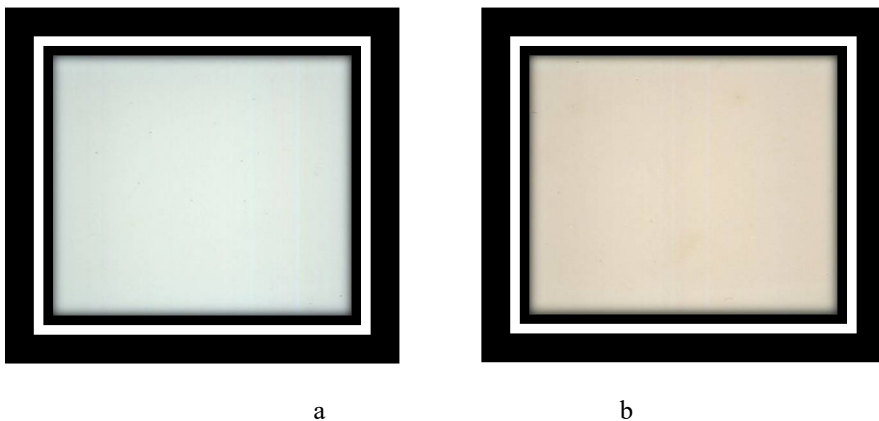


Figure 4. Example of the Maillard reaction in baked milk:
a, pasteurized milk
b, baked milk

This reaction can also cause a reduction in the product quality, undesirable colors, unpleasant tastes and aromas, and potentially create harmful compounds in food products, as well as harmful substances (Keramat et al., 2011; Töpel et al., 2022).

But in the case of milk products, unwanted flavors can be concerning both during the manufacturing and during storage of the milk, especially powdered milk. Thus, reducing the Maillard reaction in dairy products is a priority.

But there are a number of milk products, aromas of baked milk, or pasteurization for which are desirable. Such products are baked milk (Sserunjogi et al., 1998; Yadav et al., 1992), butter, kefir, barbecue cheese, condensed milk, ryazhanka (fermented product typical for Ukraine), taffy, fudge, dulce de leche (Pauletti et al., 1999), and milk chocolate crumb (Muresan et al., 2000).

It is known that the Maillard reaction is a reaction between amino groups and reducing sugars that occurs during the heating process. The main sugar in the milk is lactose, which not only participates in the Maillard reaction but also takes part in the caramelization process.

Maillard reaction and its effect on safety of food products

Mutagenic and carcinogenic products are found in foods that contain significant amounts of proteins. Such mutagenic and carcinogenic products are formed by several mechanisms: caramelisation of sugars, thermal degradation of proteins, amino acid/creatinine reactions and amino carbonyl reactions (Maillard reaction). Available amino groups during the amino acid/creatinine reaction and the aminocarbonyl reaction (Maillard reaction) condense with reducing sugars to form brown melanoid, furanine, carbonylin and other products (Friedman, 1996, 2005).

The Maillard reaction is important for food product safety. Some genotoxic compounds, such as acrylamide and heterocyclic aromatic amines, are produced during this reaction (Friedman, 2003; Carthewa et al., 2010; Bartkiene et al., 2016). Meanwhile, acrylamide is known as a bioavailable neurotoxin (Loso et al., 2016).

In 1994, the International Agency for Research on Cancer classified acrylamide as a probable carcinogenic compound for humans (Huff et al., 2002). Already in 2002, Swedish food researchers at Stockholm University identified significant concentrations of acrylamide in some thermally processed foods, such as bread, coffee and French fries.

The reaction mechanism has a significant impact on the mutagenicity of the reaction products. For example, it was proved that ketose sugars have higher mutagenic reactivity than aldose sugars (Alink et al., 2000). However, because of the complexity of non-fermentative browning reactions and the low stability of the intermediate products, only several well-researched toxic compounds exist, among which the most studied is acrylamide. Acrylamide, also known as prop-2-enamide, is a carcinogen and can cause neurological damage. Acrylamide has been discovered in almost all food products, but fried and baked food treated at high temperatures contain far more acrylamide (Table 4) (Fogliano, 2015).

Table 4

Acrylamide content in some food products

Food product	N*	Acrylamide content ($\mu\text{g}/\text{kg}$)		
		Median	Mean	Maximum
Potato chips	216	490	628	4180
French fries	529	253	350	2668
Cookies	227	169	317	4200
Bread	272	50	136	2430
Breakfast cereal	128	100	156	1600
Coffee	208	188	253	1158
Other products	854	169	313	4700

N* – number of individual data analyzed for each food category.

It has been established that acrylamide is a hazardous chemical compound in foods that are thermally processed at temperatures over 120 °C. A number of studies have been conducted on acrylamide toxicity, mechanism of generation, measurement, reduction and correlation of risk assessment among different foods (Tareke et al., 2002).

The tolerable average dietary intake of acrylamide is 0.3-0.6 $\mu\text{g}/\text{kg}$ daily, but it can lead to its accumulation in the body (Claus et al., 2008). According to modern data on acrylamide, it is possible to argue that:

1. Amino acids split at high temperatures, and products of this split react with reducing sugars and form acrylamide;
2. The first Maillard reaction product – n-glycoside – plays a major role in the creation of acrylamide;
3. α -dicarbonyl compounds react with amino acids and form acrylamide;
4. Strecker degradation contributes to acrylamide generation due to the creation of aldehydes during the degradation;
5. Free radicals also promote acrylamide formation;
6. Acrylamide can be created in several ways. It shouldn't be forgotten that acrylamide is both formed during food processing and can migrate from packaging materials made from polyacrylamide or flocculants (Wang et al., 2012).

In the literature, there isn't much data on the possible role the Maillard reaction can have on the inhibition of microorganisms' growth in food products. Thus, was identified Maillard reaction products through dephlegmation of solutions containing asparagine and xylose and then studied their reactivity on the pathogenic microorganisms and spoilage microorganisms that usually are present in food products. Some inhibition effects on *Staphylococcus aureus* have been noted. But at the same time, an opposite effect could be seen for *Bacillus subtilis* and *Escherichia coli*, and *Candida tropicalis* was found to be practically unresponsive to the Maillard reaction products (Einarsson et al., 1983, 1988; Rufián-Henares et al., 2008).

Table 5 shows data of the impact Maillard reaction products on microorganisms (adopted from ALjahdali et al., 2017).

It is interesting that Maillard reaction products are effective against yeast, which have a positive effect on the safety of food products and their shelf life (Tauer et al., 2004). The negative effect of the Maillard reaction products on the viability of yeasts in alcohol production was first proven by Sattler in 1949 (Sattler et al., 1949; Finot 2005). Ten years later, Krug and others determined LD50 for various products of the reaction between free amino acids and glucose and identified that a mix of lysine and sugar is one of the most toxic ones (Krug et al., 1959).

The most obvious negative effect is the toxic effect of mutagens and carcinogens formed during the thermal treatment of meat and fish (Sugimura et al., 1990). Also, several cyclic amines, obtained as a product of the Maillard reaction in the presence of creatinine, were identified. They belong to the imidazoquinoline and imidazoquinoxaline classes. Others were discovered as a result of heating tryptophan, glutamic acid, or phenylalanine. Thanks to this identification, sensitive detection methods of some heterocyclic amines were created, which made it possible to avoid their creation in the meat industry (Gross et al., 1990).

The loss of the food products' nutritional value is associated with the formation of mutagenic compounds. Nagao and others identified mutagenic substances in instant coffee and decaf coffee (Nagao et al., 1979). They were composed of dicarbonyl compounds, methylglyoxal, diacetyl, and glyoxal, from which methylglyoxal is the most mutagenic. However, there was no quantity correlation with carcinogens.

Mutagenic compounds derived from heterocyclic amines were found in fried meat and fish, especially the grilled ones (Arvidsson et al., 2005). Flavones and flavonoids inhibit the formation of heterocyclic mutagens like amines (Lee et al., 1992). The antimutagenic effect of the Maillard reaction products also has been reported (Lee et al., 1994; Yen et al., 1992).

Table 5

Impact of Maillard reaction products on microorganisms

Product of the Maillard reaction	Microorganisms	Research result	Reference
Acrylamide	<i>Lactobacillus plantarum</i>	Reduction of acrylamide level	Baardseth et al., 2006
	<i>Lactobacillus sakei</i> <i>Pediococcus pentosaceus</i> <i>Pediococcus acidilactici</i>	Reduction of acrylamide level	Chalova et al., 2012
Melanoidins	<i>Salmonella typhimurium</i>	Use of 15% melanoidins as a source of carbon and energy	Chalova et al., 2012
	<i>Escherichia coli</i>	Suppression of growth rates	Rufian-Henares et al., 2008; Yen et al., 1992
	<i>Listeria monocytogenes</i> <i>Salmonella enterica</i> <i>Bacillus cereus</i> <i>Brevibacillus brevis</i>	Inhibition of growth	Kukuminato et al., 2021
Aminoreductone	<i>Pseudomonas aeruginosa</i> <i>Escherichia coli</i> <i>Staphylococcus aureus</i>	Inhibition of growth	Trang et al., 2013
Hydroxymethylfurfural	<i>Salmonella typhimurium</i>	Mutagenicity	Sommer et al., 2003

Regarding the safety of food products, the role of the Maillard reaction in the formation and elimination of mutagens is still a question in need of an answer. There are no data on the correlation of these compounds with cancer.

The Maillard reaction produces antioxidant components as well. Griffith and Johnson were one of the first scientists to report that adding 5% glucose to sugar cookies led to a noticeable browning of the cookies and increased resistance toward oxidative rancidification (Griffith et al., 1957). Since this discovery, Maillard reaction products have been studied in light of their antioxidant properties and ability to protect food from lipid oxidation (Chuyen et al., 1998).

Table 5 shows a short generalized characteristic of the Maillard reaction's impact on the quality and safety of some food products.

Maillard reaction and its impact on physiological aspects

Some studies (Finot et al., 1981, 1990) describe such physiological effects of consuming fried and thermally treated food products or the reaction between sugars and free amino acids or proteins as a decrease in protein-digesting levels and amino acids intake, organ hypertrophy, cellular changes and decrease in activity in intestinal and pancreas enzymes, as well as in liver enzymes responsible for metabolizing medication, serum transaminase and alkaline phosphatase, chelation of metals. All of these effects are connected to premelanoidins (Adrian, 1974).

Also, negative effects of the Maillard reaction in food products can include loss of the nutritional value of proteins that participate in the reaction, which causes a decrease in quality and potentially leads to a decrease in the safety of food products. A number of studies focused on this loss. The loss was explained as a decrease in absorption, destruction, and/or biological inactivation of amino acids including such essential amino acids as lysine and tryptophan, inhibition of proteolytic and glycolytic enzymes, and interaction with metal ions (Ericksson, 1981; Friedman, 1996; Namiki, 1988).

Lysine is the most susceptible to loss during non-enzymatic browning, followed by alkaline amino acids, including L-amino acids like L-arginine and L-histidine. In addition to the reaction between sugars and amino acids, Strecker degradation also results in the loss of amino acids. The formation of complex molecules decreases the solubility of proteins and lowers their nutritional value.

The impact the Maillard reaction has on the availability of amino acids was studied on the rainbow trout (*Salmo gairdneri*). Results showed that in the mix of isolated fish protein and glucose stored at 37 °C for 40 days, arginine and lysine suffered the biggest loss, and notable absorption of particular acids (especially lysine) was lower in trout fed fried protein than trout fed control protein (Plakas et al., 1985).

Additionally, protein molecules can be crosslinked by the Maillard reaction products (Chuyen et al., 1991; Pellegrino et al., 1999).

Also connection was found between the Maillard reaction and lysine loss during the storage of biscuits. Noguchi et al. (1982) discovered that lysine loss increases if biscuit samples are stored at room temperature during long-term storage. Storage effect on the lysine loss in biscuits enriched with protein was studied (Hozova et al., 1997) and assessed by measuring lysine levels and nutritional value of amaranth biscuits and amaranth crackers stored for 4 months in lab conditions (20°C and 62% of relative humidity). Despite the experiment resulting in a slight loss of lysine authors speculated that lysine degradation might continue during prolonged storage and it should be accounted for in relation to the consumers and extension of shelf life.

It is interesting that the physiological effects Maillard reaction products have are not only negative. For example, antimutagenic effects were shown in some Maillard reaction products which somewhat evens out their negative effect.

Therefore, there are a lot of aspects of the quality and safety of food products that are related to the Maillard reaction. The technologist's objective is to balance beneficial and inauspicious effects in the technological process – optimization of nutrition value loss during the heat-moisture treatment, change in taste and color during the milk drying process, maximization of antioxidant generation, etc.

Understanding the Maillard reaction is an additional condition not only for the traditional process of frying, baking, and boiling but also for the development of new technology like microwave ovens and high-pressure processing (Ames, 1998; Shahidi et al., 1998).

Maillard reaction in expertise of foodstuff

Usage of the Maillard reaction in the expertise of foodstuff is prospective.

In the sensory evaluation of the quality of the milk product dulce de leche, popular in the Rio de la Plata region, color is a critical factor that defines a customer's choice. For this, a method of receiving a preliminary structural characteristic of chromophores created by the Maillard reaction was developed (Rodríguez et al., 2019). With its help, it was determined that melanoidins formed during the reaction have molecular mass from 300 to 2000 Da, but the compounds with the bigger molecular mass contribute to the color of the milk product the most.

Identification of furosine – one of the Maillard reaction products and an indirect indicator of the protein-bound lactulose-lysine – is widely used for the evaluation of the quality of pasta (García-Baños et al., 2004) and dry dairy products (Rutherford et al., 2006).

Thus, the identification of furosine (~N-2-furoyl-methyl-lysine) formed as a result of an acidic hydrolysis of the Amadori product created in the early stages of the Maillard reaction (Erbersdobler et al., 1991) is used for malt (Molnar-Perl et al., 1986), pasta (Resmini et al., 1991, Garcia Banos et al, 2001, Cardenas Ruiz 2004), and baby biscuits (Carratu et al., 1993). Other 2-furoyl-methyl derivatives, such as GABA (γ -aminobutyric acid), also were used in the Maillard reaction and suggested as indicators for its early stages (Del Castillo et al., 2000; Sanz et al., 2000, 2001).

The early stage of the Maillard reaction in biscuits, crackers, and breakfast cereals was also evaluated via quantitative analysis of furosine (Rada-Mendoza et al., 2004). Furosine was found in all analyzed samples, but variability was high. Taking into account that a significant amount of furosine was found in powdered milk (Corzo et al., 1994; Guerra-Hernandez et al., 1996, 1999), it is probable that part of the furosine detected in cereal products with powdered milk comes from powdered milk (Rada-Mendoza et al., 2004) that had furosine added. The 2-fluoromethyl derivative – equivalent to GABA – was found in the cracker and breakfast cereal samples but not in most biscuit samples. This compound's presence in breakfast cereals and crackers can be linked to the significant amount of free GABA found in rice and corn used for their production. A considerable amount of free GABA in corn chips has been reported before (Marchenko et al., 1973). Different amounts of powdered milk used in the manufacturing of cereal products, and different levels of free GABA in the untreated grain are the main disadvantages in furosine and 2-fluoromethyl GABA usage as corresponding indicators for differentiation in grain-based commercial products. However, in the grain industry, where the exact composition of raw material is known, measurement of 2-fluoromethyl GABA and formed furosine can be used as an indicator for monitoring processing conditions during the manufacturing of grain products.

Olano and others (Olano et al., 1989) reported differences in the chemical composition of sterilized milk treated at ultra-high temperatures. Levels of HMF created during heat treatment can be used as a marker for the intensity of the Maillard reaction product creation in the manufacturing process of baked or condensed milk. However, the amount of HMF accumulated in milk during ultra-high temperature treatment depends on such factors as the presence of vitamin A, casein, or iron (Albala-Hurtado et al., 1999). The color of the product can be an indicator of Maillard reaction completion (Park et al., 1991)

As noted before, the reaction speed of the Maillard reaction can be controlled using quantitative detection of 5-hydroxymethylfurfural, furosine, maltol, and pyridoxine.

Such Maillard reaction products as 5-hydroxymethylfurfural, furosine, and lactulose are used as “heat load indicators” for the estimation and control of the heat treatment severity. Unlike lactulose, both compounds are already present in raw milk, but the concentration of

5-hydroxymethylfurfural might vary significantly (Table 6). Therefore, for the estimation of heat treatment severity, it is necessary to determine the amount of 5-hydroxymethylfurfural in the raw material.

Table 6
Indicator substances (derivatives of lactose) for the estimation of heat treatment severity of milk
(adopted from Christie, 1983; Resmini et al., 1994; Töpel, 2004)

Product	Lactose, mg/kg	5-hydroxymethidfurfural, $\mu\text{mol/l}$	Furosine, mg/100 g of milk protein
Raw milk	0	2–9	3–5
Pasteurized milk	<50	6–8	–
UHT-milk	100–500	5–20	45–150
Sterilized milk	600–1400	20–100	110–450

UHT milk is milk that has been processed at ultra high temperature (UHT).

Also, created heterocyclic compounds absorb UV light and fluoresce. Fluorescent products are formed through the Maillard reaction when storing food products and biological systems together with brown pigments. These products can be used as early indicators for this reaction. Matiacevich and Buera (2006) demonstrated that under unfavorable conditions (low pH, presence of salts) fluorescent products can be used as adequate markers, including for the early stages of the reaction.

Fluorescent compounds also are formed at the later stages of non-enzymatic browning. Several methods based on measuring fluorescence were used for the estimation of the reaction stage. For example, method FAST (fluorescence of advanced Maillard products and soluble tryptophan) proposed by Birlouez-Aragon with coauthors (1998) corresponds to the molecular structures formed by the reaction between reducing sugars and lysine remnants in proteins. The method is based on the measuring fluoresce emission maximum in an excited state and at the wavelength 330-350 nm. In this case, fluoresce depends on the thermal treatment and is connected to the loss of nutrients in proteins. This method was first validated on milk samples and then was studied on breakfast cereals. Birlouez-Aragon and others (1998) studied the FAST index in manufactured and commercial samples of extruded cereals, as well as the correlation between lysine loss and hydroxymethylfurfural creation. Therefore, the fluorescent method FAST is an interesting alternative for the nutritional value evaluation of grain products subjected to different types of temperature treatment.

The method of molecular fluoresce allows the identification of falsification of milk (Ischenko, 2018) due to changes in absorption specters and fluoresce at 330-420 nm.

In their study, Ríos-Ríos and others (2018) reported the formation of 2-furoymethyl amino acids (2-FM-AA) that indicate the occurrence of the Maillard reaction during the black garlic production. They also determined the content of furosine with the help of ion pair RP-HPLC-UV. Analysis was carried out on samples produced via traditional methods – convective drying (CDP), and ohmic heating (OHP). Besides furosine (2-FM-lysine) 2-furoymethyl- γ -aminobutyric acid and 2-FM-arginine were identified. Furosine levels were higher in the samples created via convective drying (46.6-110.1 mg/100 g of protein) than in ohmic heating samples (13.7-42.0 mg/100 g of protein), probably because of harsher treatment conditions used in the first case. These results highlight the suitability of 2-FM-AA

as chemical indicators in the monitoring of the garlic treatment process for the purpose of obtaining high-quality products.

In the study of different types of orange juice del Castillo and others (2000) showed the formation of 2-furoymethyl derivatives of aminobutyric acid (2-FM-GABA) and arginine (2-FM-Arg) as early indicators of non-enzymatic browning. Thus, in the dehydrated orange juice presence of 2-FM-GABA and 2-FM-Arg was determined after the very first day of storage at 30 °C. In this type of juice, the amount of these two compounds increased with the increase in temperature (30, 50 °C) and storage time (1-7 days). Formation of 2-FM-GABA and 2-FM-Arg in the liquid orange juice heated to manufacturing conditions was not detected. According to the received results, the content of 2-FM-GABA and 2-FM-Arg can be used as an indicator for the evaluation of the main changes caused by the Maillard reaction during the manufacturing process and/or storage of concentrated orange juice.

Aside from the creation of color and taste, Maillard reaction impacts the aroma. However, the key aromatic compounds often are present only in residual concentrations from 1 mcg/kg to 1 mg/kg. Nevertheless, they contribute to the creation of appropriate taste due to the low threshold of smell perception. Even though intermediate Maillard reaction products such as Amadori products and deoxyosones are formed in decent quantities during the model reactions, the yield of the aromatic compounds, especially ones containing nitrogen and sulfur, is often low (0.001-0.01%), which indicates their formation via adverse reactions. Thus, Cerny (2008) claims that volatile Maillard reaction compounds that determine food taste are typically present in small quantities. Oxygen-containing aromatic compounds such as 2,3-butanedione, 2,3-pentanedione, methylpropanal, 3-methylbutanal, phenylacetaldehyde, 3-hydroxy-4,5-dimethyl-2(3H)-furanone (sotolon), and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (furanol; Firmenich, Switzerland) occur in concentrations from 1 mcg/kg for soloton to 100 mg/kg for 3-methylbutanal and furaneol. At the same time, 2-ethyl-3,5-dimethylpyrazine, 2,3-diethyl-5-methylpyrazine, and 2-acetyl-1-pyrroline are examples of nitrogen-containing aromatic compounds. They are present in food in concentrations 0,001-10 mg/kg. Overall, sulfur-containing aromatic compounds of the Maillard reaction are the most powerful aromatic compounds, and despite their small quantities, they often play a dominant role in the taste of boiled meat and roasted coffee. For example, it can be 2-furfurylthiol, 2-methyl-3-furanthiol, 3-mercapto-2-penthanone and methional.

Xu et al. (2019) came to the conclusion that the Maillard reaction in the temperature-influenced water environment combined with vacuum dehydration is a new and perspective way for obtaining intermediate Maillard reaction products (MRIs), such as products of Amadori rearrangement or Heyns rearrangement that are deemed important non-volatile precursors of aroma with stable physicochemical properties compared to the Maillard reaction products (MRP). MRIs obtained from glutamic acid and xylose are a potential replacement for MRP in the manufacturing of artificial flavors.

Fermented hydrolysates are used as reagents for artificial meat flavors (Cheserek et al., 2013; Lieske, 1994; Liu et al., 2012; Song et al., 2008). Lieske and others (1994) reported that peptide fraction 2000-5000 Da in chicken fermented hydrolysate is responsible for the intense aroma of fried chicken. Meanwhile, Liu and others (2015) showed that in the MRP of chicken fermented hydrolysate peptide fraction with less than 500 Da facilitated the fried chicken aroma, peptide fraction with more than 1000 Da, formed by crosslinking peptide fraction with less than 500 Da, added kokumi taste, while peptide fraction with more than 3000 Da contributed to the bitter taste. A study by Kang et al. (2019) demonstrated the possibility of using RP-HPLC (F-3-F-8) fractions as peptide flavor precursors for artificial flavor creation. However, the amount of literary sources regarding structural properties and

action mechanisms of peptides that participate in the meat compound formation via the Maillard reaction is not yet sufficient. Further research in the formation mechanisms of meat aroma and flavor-active compounds from MRP and MRIs is prospective for the identification of flavor compounds.

Paresto's research (2019) refers to the profiling of volatile compounds in Madeira wines and their connection to odor descriptors. A connection between varietal, enzymatic, and aging aromatic compounds and their odor descriptors was established via sensory analysis of Madeira wine. It can be seen that, based on aroma composition, the grape variety is an important parameter that affects the sensory properties of young Madeira wines, while aged wines are greatly impacted by the aging process. The Maillard reaction and oak diffusion were the most influential factors connected to these descriptors. A detailed database of volatile compounds found in Madeira wines and corresponding odor descriptors can be a prospective instrument for winemakers to use for the identification of wine odor, its age, and the grape variety it was made from.

Therefore, Maillard reaction products can be utilized as markers for falsification identification and detection in a wide range of food products. However, the number of developed methods is insufficient, and their use in practical foodstuff expertise remains limited.

It is known that controlling the baking process by color is a key factor for the research of the milk baking process, which is vital for manufacturing such products as baked milk, ryazhanka, and condensed milk.

The Maillard reaction can be used to monitor acrylamide levels in food products (acrylamide content is strictly controlled).

Conclusion

1. The Maillard reaction is important for the food technology reaction based on the interaction between sugars and amino acids. Despite the fact that the Maillard reaction is traditionally associated with cooking and taste development, it has several prospective uses in the study of food products.
2. The Maillard reaction plays an important role in food product quality. For example, this reaction greatly impacts the taste and odor of different food products. Knowing specific compounds that are formed during the browning process via the Maillard reaction, flavor profiles of various products can be better analyzed and evaluated, which is very useful for the development and optimization of recipes for new types of products.
3. The Maillard reaction is responsible for the development of desired color in food products, such as golden-brown crust on bread or saturated brown color of roasted coffee beans. Methods of measuring color can be used for the quantitative identification of browning degree by Maillard, at the same time gaining important information about the quality and texture of the product.
4. The Maillard reaction is widely used in researching safety parameters. It was established that the Maillard reaction products suppresses the growth and development of such microorganisms as *Escherichia coli*, *Listeria innocua*, *Listeria monocytogenes*, *Salmonella enterica*, *Bacillus cereus*, *Brevibacillus brevis*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*.
5. Simultaneously, the Maillard reaction requires control over the heat treatment process at 120 °C since it can lead to the formation of acrylamide, which has mutagenic and carcinogenic properties.

6. Evaluation of nutritional value: the Maillard reaction can impact nutritional composition by changing the availability of specific nutrients and creating new compounds with potential health effects. A more detailed and thorough study of the Maillard reaction in food products can help scientists understand its impact on the bioavailability of certain nutrients, protein absorption, etc.
7. Falsification identification and detection in food products: unique chemical fingerprints created via the Maillard reaction can be used to identify fraud, falsification, and forgery of food products. By analyzing the Maillard reaction products in food samples, researchers can compare them to the established profiles to verify their authenticity and quality.
8. Evaluation of shelf life: monitoring of the Maillard reaction progression during storage can provide an understanding of the shelf life stability of food products. Changes in browning by Maillard with time can indicate the development of off-flavors, texture deterioration, and other quality problems tied to food spoilage.

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Effect of a buckwheat extrudate addition on the quality of multicomponent albumin concentrates

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Abstract

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Introduction. The aim of the research was to determine the influence of the moisture-binding plant ingredient addition on the quality of multicomponent albumin concentrates.

Materials and methods. Albumin mass was obtained from low-fat milk whey with an active acidity of pH 4.4-4.6 by thermoacidic coagulation: time of treatment 90 ± 2 min at a temperature of 95 ± 2 °C. Active acidity was determined potentiometrically; moisture content was measured using a thermogravimetric method; the moisture absorption capacity of milk-plant systems was estimated by the amount of adsorbed water; the effective viscosity of the test samples was determined on a rotary viscometer.

Results and discussion. Multicomponent albumin concentrates with buckwheat extrudate, similar in quality to modern milk protein products with fillers, were used in the present study. An optimal amount of buckwheat extrudate and a method of its preliminary preparation, which involves swelling of the plant ingredient in whey to form a milk-plant system, were proposed. The content of moisture in milk-plant systems with buckwheat extrudate increases from 70.84 to 82.27 % and is linear. Active acidity of a milk-plant system with buckwheat extrudate depends on the pH value of the ingredients. An increase in the heating temperature does not lead to a change in the active acidity of the milk-plant system. The average value of moisture absorption capacity of a milk-plant system is in the range of 58–63% and depends on the quantitative ratio of the components. For buckwheat extrudate, an increase in the water absorption capacity of the milk-plant system is observed with an increase in temperature from 35 to 65 °C, and at a temperature of 95 °C this indicator decreases by an average of 1.25 times. The optimal conditions for the swelling of the milk-plant system with buckwheat extrudate were determined, where the ratio of whey to buckwheat extrudate is 5:1 at a temperature of 63 ± 2 °C and a holding time of 10 ± 1 min. The optimal dose of buckwheat extrudate to albumin mass varies within $4 \pm 1\%$. Thus, the addition of buckwheat extrudate in larger quantities leads to a significant increase in effective viscosity and a decrease in active acidity. It is this amount of buckwheat extrudate, which has technological moisture-binding properties, that increases the moisture retention capacity of the milk-plant system. As a result, a multicomponent albumin concentrate with buckwheat extrudate with a normalized value of the mass fraction of moisture was obtained.

Conclusions. The optimal dose of buckwheat extrudate to the albuminous mass (ratio 1:5) and technological parameters of treatment (temperature 63 ± 2 °C and the exposure time 10 ± 1 min) to preserve the physicochemical and sensory characteristics of multicomponent milk-protein products were determined.

Introduction

The quality of raw materials and technological methods of their processing significantly affect the chemical composition and nutritional value of food products. (Picó et al., 2019). When assessing food diets, it is necessary to take into account their balance in many respects. Thus, the ratio of proteins, fats and carbohydrates in the normal diet of a healthy person should be 1:1.4:4.1 (Kelly et al., 2019).

Whey protein concentrates are biologically valuable food products that are used in the production of bakery and confectionery goods, ice cream and cheeses, cereal and nutrition bars, beverages and fortified functional foods for athletes looking to gain muscle mass (Early, 2012; Ivanov et al., 2021; Kochubei-Lytvynenko et al., 2022; Patel, 2015; Shevchenko et al., 2022).

In everyday life, a person uses a diet, which usually contains both animal and vegetable proteins. A person's daily need for protein depends on its quality: the more inferior the proteins consumed by a person are, the higher the daily rate should be, and vice versa, the closer the proteins are to the ideal in terms of amino acid composition, the lower this rate should be. Although plant proteins are incomplete, they play an important role in human nutrition (Fanzo et al., 2021; Franzoi et al., 2019). The following stages, which are presented in Figure 1.

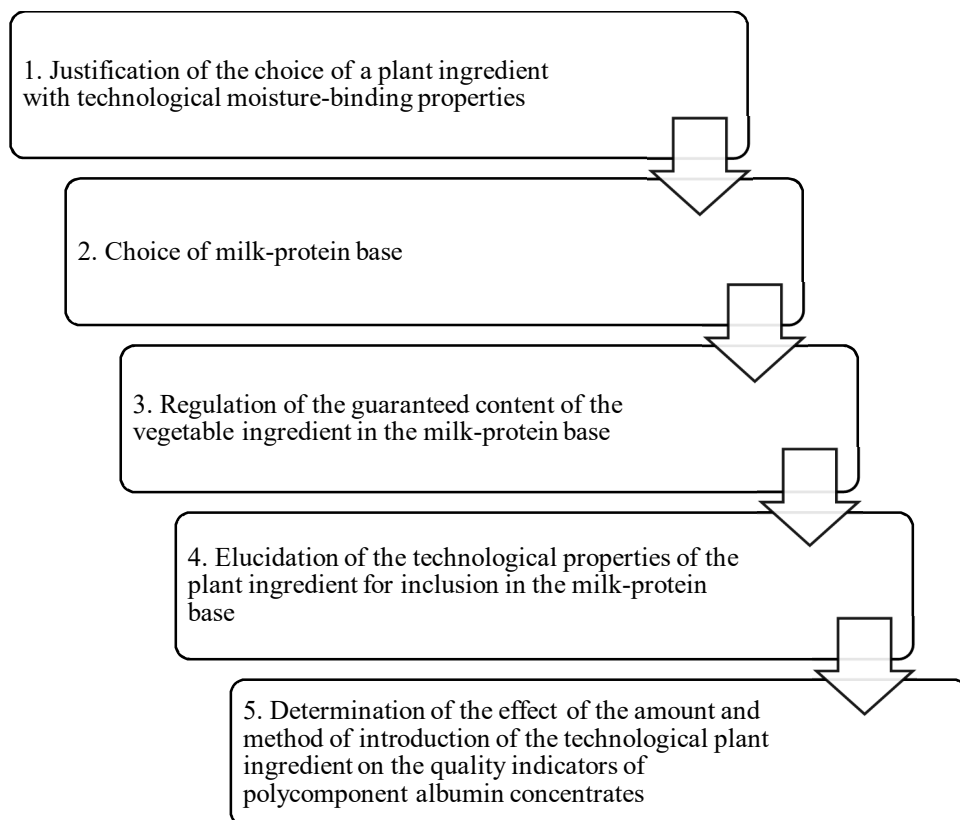


Figure 1. Stages of development of multicomponent albumin concentrates

Taking into account the principles of rational nutrition, for the enrichment of dairy products it is necessary to use ingredients that are in short supply, namely with an increased content of protein, essential amino acids, vitamins, macro- and microelements (Fanzo et al., 2021). The criteria for the selection of plant ingredients are presented in Figure 2.

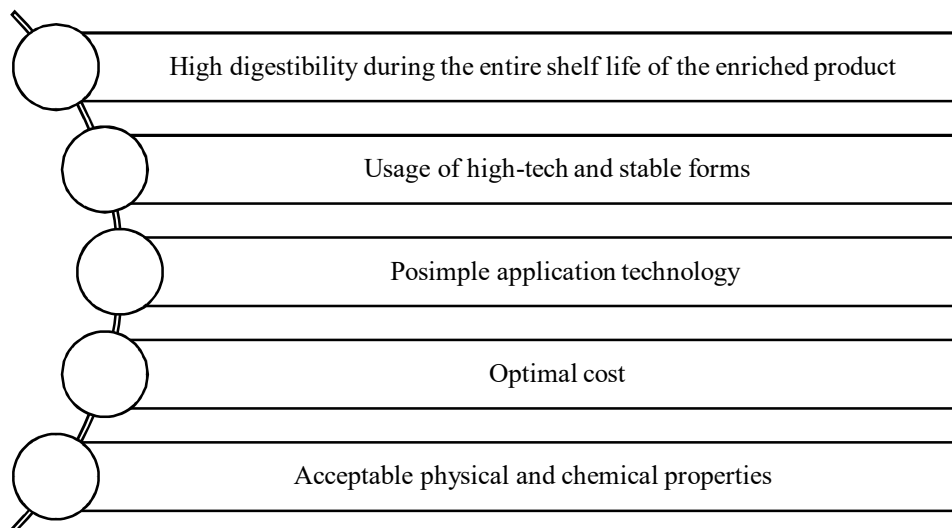


Figure 2. Criteria for selecting a plant ingredient

To expand the range of products and enrich them with nutrients, the dairy industry, along with the main raw materials, uses non-traditional fillers of plant origin, including grain ingredients processed in various ways (extrusion, infrared irradiation, and malting). In addition, they must meet the following requirements: sensory compatibility with the milk base, functional and technological properties, the method of preliminary processing of grain raw materials that increases the digestibility of all grain components, and the presence of dietary fibers.

The most promising are those that have technological moisture-binding properties with high efficiency of action in various food systems - milk and its processing products. From the spectrum of processed grain raw materials, extruded grain products deserve special attention (Grek et al., 2020a, 2020b).

Moist-thermal processing (extrusion) is one of the most common methods of converting native grain raw materials into a more edible form (Brennan et al., 2013). The cooking extrusion process is complex, since the processing of biopolymer compositions, in addition to physical ones, is accompanied by complex chemical transformations. They occur under the influence of various types of mechanical forces under the conditions of the presence of moisture and significant thermal effects in the screw extruder (Sule et al., 2024). Thus, the method of extrusion processing of grain raw materials improves its sensory indicators and increases the bioavailability of all constituent parts of the grain (Singh et al., 2019). In addition, it has a number of advantages: a high sterilization effect (destruction of almost all, even spore-forming, microflora); the possibility of enriching products with various components (protein, fibers, vitamins); low production cost (Ekielski et al., 2007).

As for the selection of products to be fortified, first of all, special attention should be paid to those that are widely consumed, available to all population groups, regularly used in food, which include protein dairy products - multicomponent albumin concentrates.

The aim of the present research was to study the effect of the technological moisture-binding plant ingredient addition on the quality indicators of multicomponent albumin concentrates.

Materials and methods

Materials

Taking into account the selected criteria, buckwheat extrudate (BE) with the composition shown in Table 1 was selected as a multifunctional technological and biologically complete ingredient (Garkina et al., 2021).

Table 1
Characteristics of the native and extruded buckwheat

Characteristics	Buckwheat	
	native	extruded
Chemical composition, % dry weight		
starch	61.50±0.1	52.70±0.1
dextrins	0.17±0.1	2.60±0.1
reducing sugars	0.20±0.1	1.76±0.1
protein	12.60±0.1	11.40±0.1
lipids	3.70±0.1	2.60±0.1
Functional and technological, %:		
moisture binding capacity	180±1	450±1
fat-binding capacity	125±1	230±1

An albuminous mass obtained from low-fat whey with an active acidity of pH 4.4–4.6 by thermoacidic coagulation during (90±2) min at a temperature of (95±2) °C. The protein base had a mass fraction of moisture – 77±2% and titrated acidity - (96±3) °T.

Low-fat milk whey had the following physicochemical parameters: content of fat, 0.2±0.1 %; dry substances, 6.30±0.02 %; titrated acidity, 18.0±0.1 °C, pH, 5.32±0.02.

Methods

Content moisture was determined by the accelerated method on the QUARTZ-21M-33 moisture meter and by the thermogravimetric method on the laboratory electronic scales-moisture meter of the ADS series manufactured by the company «AXIS» (Poland).

Active acidity was measured potentiometrically on a Sartorius PB universal pH-meter.

Moisture absorption capacity (MAC) of milk-plant systems (MPS) was estimated by the amount of adsorbed water, respectively, in the process of infusion and centrifugation of the suspension. The process was carried out at different temperatures in low-fat milk whey.

The moisture absorption capacity was calculated according to the formula, in %:

$$MAC = (c - a) \cdot 100 / m \quad (1)$$

where a is the mass of the supernatant liquid, g; c – mass of added liquid, g; m is the weight of the weight, g.

Effective viscosity of the test samples was determined on a rotary viscometer «Reotest II» (MLW, Germany) with a cylinder-cylinder measurement system by taking the deformation kinetics (flow) curves (Grek et al., 2019a, 2019b). Measurements were carried out in the "a" mode, which was established experimentally taking into account the structural and mechanical properties of the studied samples. Shear stress τ (Pa) was measured at twelve values of the gradient of the shear rate γ in the range from 0.33 to 145.8 s⁻¹ during straight travel, for this, readings of the α value were taken at the maximum angle of deviation of the arrow on the instrument scale. Shear stress (Pa) was calculated using the formula:

$$\tau = Z \cdot \alpha \quad (2)$$

where Z – is the constant of the cylinder, Pa·od. scales; α – readings of the measuring scale of the device.

The effective viscosity (Pa·s) was calculated according to the formula:

$$\eta = \frac{\tau}{\gamma}, \quad (3)$$

where γ – shear rate gradient, s⁻¹.

Moisture-retaining capacity (MRC) of multicomponent albumin concentrates was determined by the Grau-Hamm modified gravimetric method (Grek et al., 2019a). The filter was placed on a glass plate measuring 11×11×0.5. Weighed 0.3 g of the milk protein sample, with an accuracy of 0.5 mg, and transferred it to a polyethylene film with a diameter of 40 mm. From above, the film was covered with a glass plate of the same size, and a load weighing 0.5 kg was placed on it. The contents were pressed for 7 minutes. After that, the filter with the sample was released from the load and the plate. The multicomponent albumin concentrate together with the polyethylene film was removed from the filter paper and weighed. The difference in the mass of the product with the film before and after pressing indicates the mass of the separated serum. The amount of moisture retained by the sample was determined by the formula:

$$MRC = 100 (a - b) / a, \quad (4)$$

where MRC – moisture-retention capacity of multicomponent albumin concentrate, %; a – the amount of moisture in the sample, mg; b - the amount of serum that was released from the test sample, mg.

$$a = 300 W_{tv} / 100, \quad (5)$$

where 300 is the weight of the test sample, mg; W_{tv} is the content of moisture in multicomponent albumin concentrate, %.

Statistical analysis

Mathematical modeling methods (Box-Wilson cube method) were used to optimize the composition parameters of multicomponent albumin concentrates from buckwheat extrudate (BE). The determination of functional dependencies was carried out by the method of least squares.

Data were expressed as means \pm standard deviations for triplicate determination. Statistical analysis was performed using Microsoft Excel 2007.

Results and discussion

Technological characteristics of milk-plant system with buckwheat extrudate

In order to obtain multicomponent albumin concentrates with buckwheat extrudate, approaching in terms of quality indicators to modern milk-protein products with fillers, the task was, first of all, to establish the optimal amount of buckwheat extrudate and the method of preliminary preparation, which involves the swelling of the vegetable ingredient in milk whey lasting 10 ± 1 min with the formation of the milk-plant system. The main technological characteristics of milk-plant system with buckwheat extrudate are given in Table 2.

Table 2
Technological characteristics of milk-plant system with buckwheat extrudate

Ratio of components in milk-plant system (x_1)		Temperature, °C (x_2)	Content of moisture, % (Y_1)	Active acidity, pH (Y_2)	Moisture-retaining capacity, % (Y_3)
Milk whey	Buckwheat extrudate				
3	1	35	70.84 ± 0.10	4.14 ± 0.03	69.47 ± 0.15
3	1	65	70.84 ± 0.11	4.14 ± 0.01	77.28 ± 0.20
3	1	95	70.84 ± 0.05	4.14 ± 0.02	62.24 ± 0.17
5	1	35	78.09 ± 0.12	4.00 ± 0.01	59.68 ± 0.14
5	1	65	78.09 ± 0.11	4.00 ± 0.02	74.89 ± 0.12
5	1	95	78.09 ± 0.05	4.00 ± 0.01	57.43 ± 0.11
7	1	35	82.27 ± 0.20	4.19 ± 0.03	48.91 ± 0.11
7	1	65	82.27 ± 0.15	4.19 ± 0.02	54.59 ± 0.12
7	1	95	82.27 ± 0.17	4.19 ± 0.01	44.02 ± 0.16

The content of moisture in milk-plant systems with buckwheat extrudate increases from 70.84 to 82.27 % and is linear. Active acidity of milk-plant system with buckwheat extrudate depends on the pH value of the ingredients. An increase in the heating temperature does not lead to a change in the active acidity of the milk-plant system. The average value moisture absorption capacity of milk-plant system is in the range of 58–63% and depends on the quantitative ratio of the components. For buckwheat extrudate, an increase in the water absorption capacity of the milk-plant system is observed with an increase in temperature from 35 to 65 °C, and at a temperature of 95 °C this indicator decreases by an average of 1.25 times.

The rheological parameters of milk-plant system with buckwheat extrudate were studied in the temperature range where the moisture-binding properties of the system increase. Changes of effective viscosity at different ratios of ingredients in milk-plant system and temperatures are shown in Figure 3.

The effective viscosity of the milk-plant system with buckwheat extrudate depends more significantly on the ratio of the ingredients. At temperatures of 35 and 65 °C, the viscosity of the milk-plant system does not increase significantly, but when heated to a temperature of 95 °C, this indicator decreases by an average of 1.8 times. This phenomenon can be explained by the fact that during repeated heat treatment, a deeper hydrolytic breakdown of plant proteins and carbohydrates occurs, which affects the reduction of the effective viscosity of the system (Yang et al., 2015).

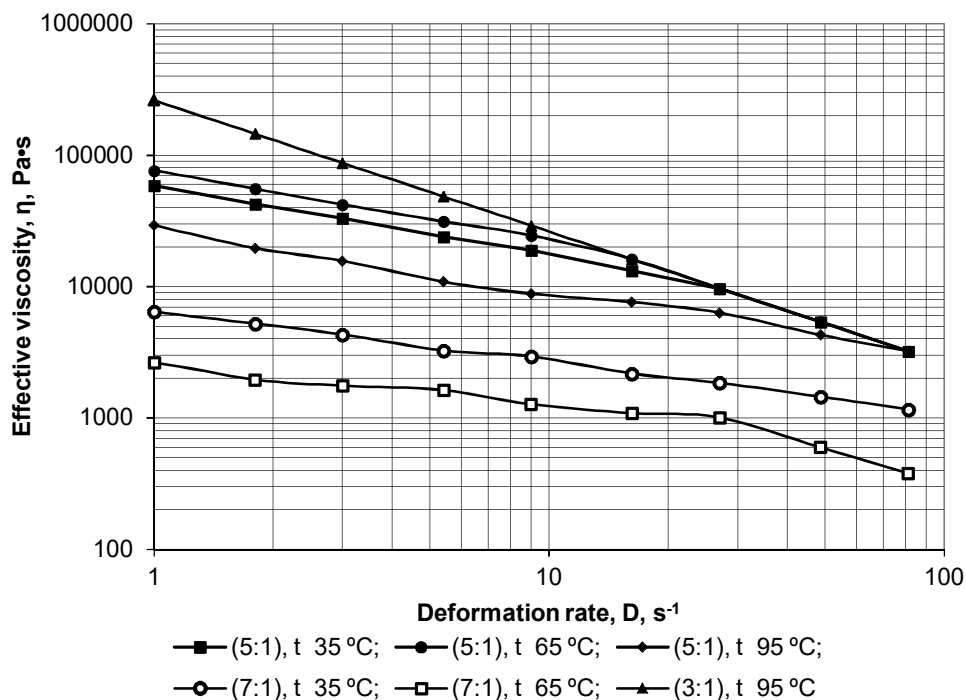


Figure 3. Dependence of effective viscosity of milk-plant system with buckwheat extrudate on the rate of deformation

So, the optimal conditions for the swelling of milk-plant system with buckwheat extrudate were determined, under which the quantitative ratio of milk serum to buckwheat extrudate is 5:1 at a temperature of 63 ± 2 °C with a holding time of 10 ± 1 min.

Optimization of the ratio of components in mixtures of albumin concentrates with buckwheat extrudate

In order to optimize the ratio of components in mixtures of albumin concentrates with buckwheat extrudate, the amount of grain filler was determined to obtain a product with appropriate sensory, physicochemical, and rheological properties. The most objective characteristic of the consistency of multicomponent albumin concentrates is the effective viscosity.

The choice of the optimal dose of buckwheat extrudate was based on the principle of preservation of sensory properties, which are characteristic of modern milk-protein products with fillers and are $4 \pm 1\%$ to the albumin mass. Its smaller amount does not affect the properties of the finished product, while its excess makes the structure inhomogeneous and too dense.

As part of the experiment, a full-factorial experiment was used to determine the optimal amount of milk-plant system with buckwheat extrudate, which must be added to the albumin mass in order to obtain a product with a normalized content of moisture. The physicochemical properties of polycomponent albumin concentrates with buckwheat extrudate were chosen as

optimization parameters. In order to achieve the set goal, complex indicators were chosen that most characterize the effect of pre-prepared buckwheat extrudate on the quality of multicomponent albumin concentrates (Figure 4).

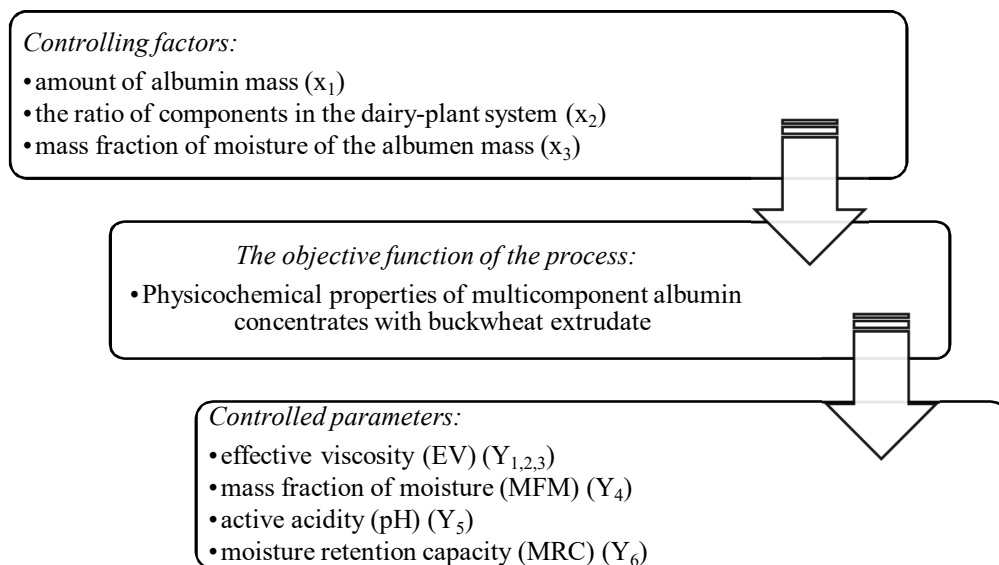


Figure 4. Scheme for optimizing the ratio of components in mixtures of albumin concentrates with buckwheat extrudate

With the help of mathematical and statistical processing of experimental data, regression equations were obtained and their graphical interpretation was given (Figs. 5, 6) for multicomponent albumin concentrates with buckwheat extrudate, which have the following form for:

– the effective viscosity of the test samples, respectively, at the rate of deformation 27, 81 and 243 s^{-1} (η_{ef}), Pa·s:

$$Y_{1(EV)} = 487.06 - 44.15x_1 - 254.14x_2 - 152.68x_3 + 76.33x_1x_2 + 34.13x_1x_3 + 119.12x_2x_3$$

$$Y_{2(EV)} = 291.75 - 31.38x_1 - 142.67x_2 - 87.55x_3 + 44.23x_1x_2 + 31.15x_1x_3 + 72.33x_2x_3$$

$$Y_{3(EV)} = 127.98 - 42.47x_2 - 33.42x_3 + 10.06x_1x_2 + 11.55x_2x_3$$

– mass fraction of moisture (MFM), W, %:

$$Y_{4(MFM)} = 74.01 - 3.10x_1 - 0.45x_2 + 5.19x_3 - 2.65x_1x_2 + 2.09x_1x_3 - 1.50x_2x_3$$

– active acidity (pH):

$$Y_{5(pH)} = 4.03 + 0.04x_1 - 0.07x_2 - 0.20x_3 + 0.04x_1x_3 + 0.02x_2x_3$$

– moisture-retaining capacity (MRC), %:

$$Y_{6(MRC)} = 67.57 + 1.19x_1 - 3.16x_2 - 12.15x_3 - 0.41x_1x_2 - 0.54x_2x_3 - 4.34x_1x_3$$

For the equations given above, the condition $F_p < F_T$ is fulfilled, which makes it possible to draw a conclusion about the adequacy of the obtained equations to the actual state of the process.

According to the specified equations, it is possible to determine with high accuracy the flow of each ingredient in a multicomponent system to optimize the ratio of components in mixtures of albumin concentrates with buckwheat extrudate with normalized physicochemical parameters.

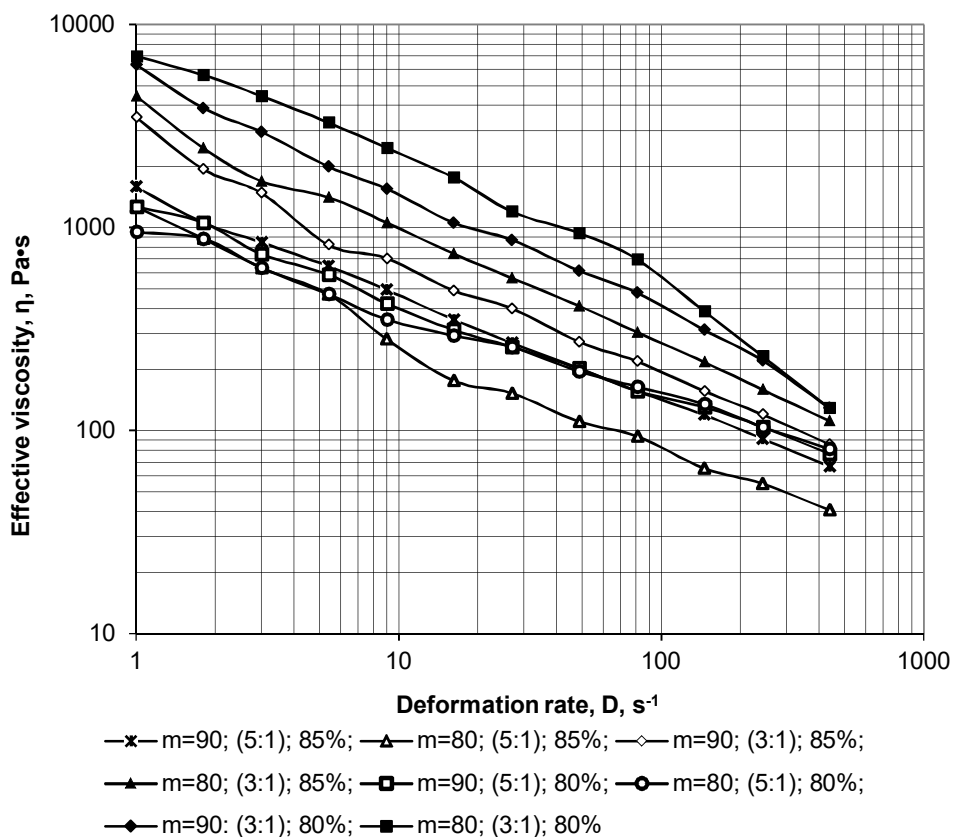


Figure 5. Dependence of the effective viscosity of albumin concentrates with buckwheat extrudate on the rate of deformation

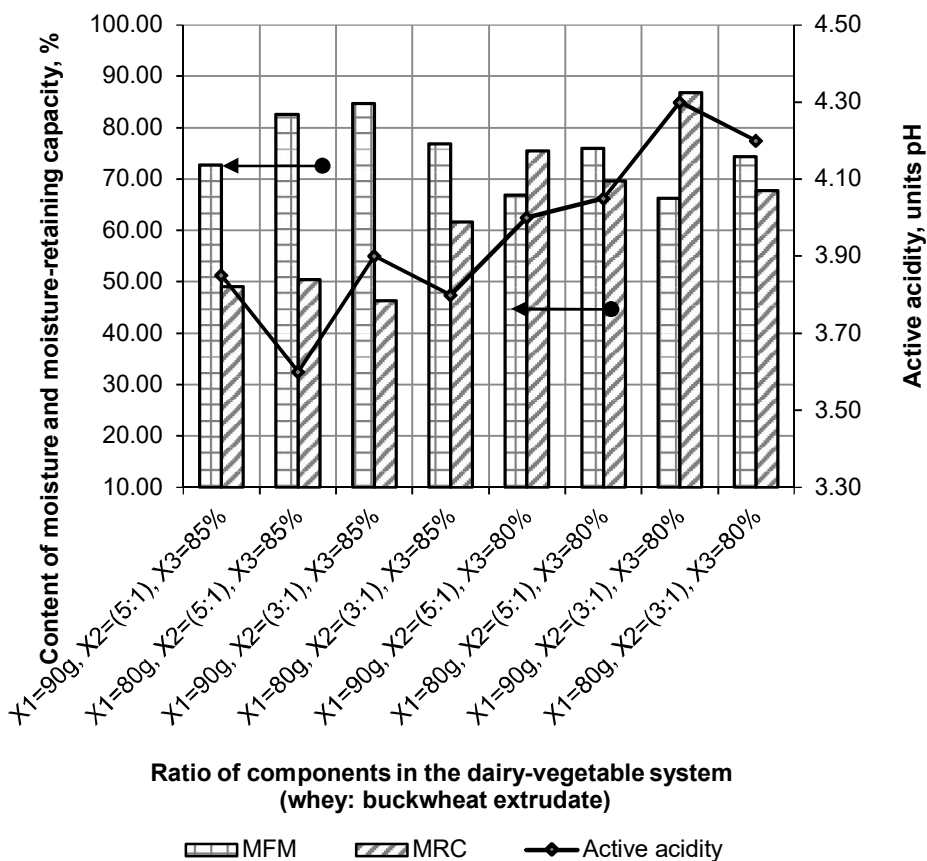


Figure 6. Dependence of quality indicators of multicomponent albumin concentrates with buckwheat extrudate on the ratio of components in milk-plant system

Thus, the optimal dose of buckwheat extrudate to albumin mass varies within $4\pm 1\%$. The addition of buckwheat extrudate in larger quantities leads to a significant increase in effective viscosity and a decrease in active acidity. It is this amount of buckwheat extrudate, which has technological moisture-binding properties, that increases the moisture retention capacity of the milk-plant system. As a result, a multicomponent albumin concentrate with buckwheat extrudate with a normalized value of the mass fraction of moisture was obtained.

Conclusion

1. The possibility of applying a system approach to the development of the technology of polycomponent albumin concentrates with buckwheat extrudate has been confirmed. There is a positive economic effect due to a reduction in the cost of the product; the range of milk-protein products is expanding while maintaining a modern diet.

2. The optimal doses of adding buckwheat extrudate to the albumen mass to preserve the sensory indicators characteristic of modern milk-protein products with fillers have been established - $4\pm 1\%$ to the albumen mass. Their smaller amount does not have a significant effect on the quality indicators of mixtures, while an excess makes their structure heterogeneous and too dense.
3. A feature of the technology of multicomponent albumin concentrates with buckwheat extrudate is the introduction of an additional operation - the preparation of a milk-plant system: the quantitative ratio of whey to buckwheat extrudate is 5:1, the heat treatment temperature is (63 ± 2) °C, the exposure time is 10 ± 1 min. Empirical equations describing the functional-technological properties of milk-plant system depending on the ratio of ingredients and temperature were obtained.

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Improving of thermohydraulic method for calculation of steam contact heat and mass exchange equipment

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Abstract

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Introduction. The complexity of determining the contact surface of phases and the boundaries of the continuous structure of liquid jets complicates the calculation of phase-contact heat and mass exchange mixing apparatuses.

Materials and methods. The condensation process of water steam from a steam-gas mixture on a cylindrical free-falling liquid jet is considered under counter-current movement of the steam phase within a range of flow parameters characteristic of the food industry.

Results and discussion. An empirical dependence for determining the onset of jet structure destruction adequately describes the process of its structural changes and is characterized by the fact that an increase in the Reynolds number leads to an increase in the critical height of jet destruction: the jet becomes more resistant to the action of the steam flow. With an increase in the dynamic pressure of the steam flow, corresponding to an increase in the Weber number, which characterizes a sharp decrease in the dimensionless height of dispersion, the jet intensively disintegrated, was destroyed at the outflow point, and was carried away by the steam flow.

An original system of dimensionless similarity numbers, based on the results of jet hydrodynamics analysis, allows for determining the temperature change along the jet's length, taking into account the geometric characteristics of mixing heat exchanger distribution devices, flow geometric dimensions, steam-liquid flow parameters, and the thermophysical properties of the media.

Empirical dependencies of the heat exchange process, considering the critical height of the existence of the continuous jet structure, are recommended for use in the thermohydraulic calculations of direct phase-contact heat exchange equipment.

Conclusion. The novelty of the results lies in the introduction of empirical dependencies for calculating heat exchange, considering the critical height of the existence of the continuous structure of the liquid jet.

Introduction

Analyzing the most common calculation methods for steam-contact heat and mass transfer mixing equipment in the food industry (Bondar et al., 2015; Forsberg et al., 2020; Lienhard et al., 2024; Sokolenko et al., 2019), where the steam condenses on liquid jets, it was concluded that their use has certain limitations.

This is because any structural calculation of heat exchangers starts with a thermohydraulic calculation. The feature of these calculations is that when determining the heat exchange surface area, the total surface of the continuous jets is considered. It is also assumed that the liquid jet moving in the steam space has a continuous structure (does not break) throughout the heat exchange process and has a cylindrical shape. However, the continuity of the jet structure moving in the steam space depends on the parameters of the liquid and steam flows (Forsberg et al., 2020). Moreover, the liquid jet oscillates, and its outer surface shape differs from the ideal and does not match the shape of the orifice from which the outflow occurs (Bondar V., 2015). Consequently, it is quite difficult, and sometimes impossible, to calculate the cross-sectional area and, accordingly, the contact surface area between the liquid and the steam. Therefore, for these tasks, using classical equations, specifically the Newton-Richman equation (Kim et al, 2021), is not possible. The above implies that it is incorrect to use the traditional concept of the heat transfer coefficient, and thus it is proposed to use a dimensionless complex that describes the degree of temperature change of the liquid along the jet length under certain geometric conditions. Hydrodynamic regimes also determine the conditions for heat and mass energy transfer (Sokolenko et al., 2019).

Thus, using the currently existing classical methods for calculating mixing heat exchangers without considering the above is incorrect.

Research aim – to determine the limits of using the most common thermohydraulic calculation methods for heat and mass transfer equipment with direct phase contact used in the food industry.

Materials and methods

Two-phase steam-liquid flows are studied. The process of water steam condensation from a steam-gas mixture on a cylindrical free-falling liquid jet with countercurrent steam flow.

Theoretical and experimental thermohydraulic study of the process of water steam condensation from a steam-gas mixture on a cylindrical free-falling liquid jet with countercurrent movement of the steam phase within the range of flow parameters typical for the food industry (Bondar et al., 2018).

In the first stage it was analyzed the main methods for calculating heat exchange during steam condensation on the surface of liquid jets. In the second stage it was analyzed the conditions under which the existing methods can be used. The experimental results were processed using statistical methods and mathematical modeling.

Experimental installation

The experimental installation is designed to study the heat exchange process and determine the hydrodynamic characteristics during the condensation of steam on a cylindrical free-falling liquid jet over a wide range of flow rates and operating parameters of two-phase flows (Figure 1).

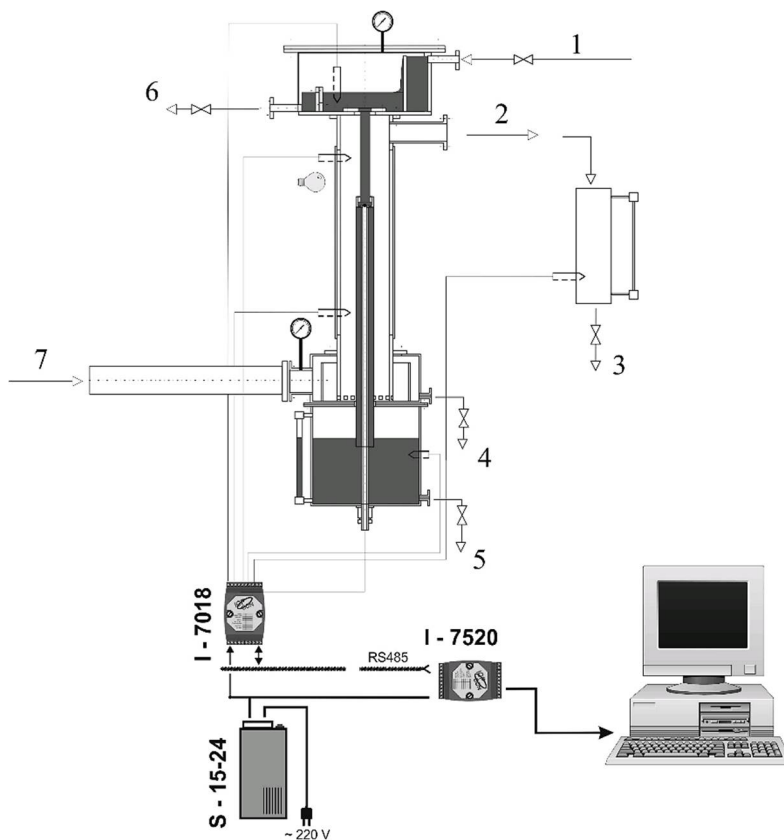


Figure 1. Experimental setup diagram with directions of steam-liquid flows:

- 1 – water supply from the network to the pressure tank;
- 2 – steam movement into the condenser;
- 3 – condensate drainage;
- 4 – drainage of parasitic condensate;
- 5, 6 – liquid drainage;
- 7 – steam supply to the experimental setup.

In the experiments, the initial parameters of the liquid and steam flows varied within the following ranges:

Parameter	Denotation	Units	Limits of change
Heating steam pressure	P_s	kPa	101–114
Steam speed	v_s	m/s	0–1.017
Liquid speed	v_0	m/s	0.29–1.25
Diameter of the orifice	d_0	mm	6, 8, 10
Height of the liquid above the orifice	h_0	mm	60–155
Flow rate of the liquid	G_l	kg/s	0.0015–0.0032
Initial temperature of the liquid	t_0	°C	7–22

The water, on the surface of which the condensation process of water steam took place, enters the pressure tank from the network pipeline 1 through the inlet pipe. Then, the water stream flows out through a calibrated orifice under the action of gravity, enters the steam space filled with dry saturated water steam, and is heated by the heat of phase transition from the condensed water steam on its surface. The water steam enters the steam space above through the steam pipeline 7 from the electric steam boilers installed in a separate room. The heated water stream with condensate enters the liquid collector. The part of the steam that did not condense on the liquid jet enters the condenser through the pipeline 2.

During the hydrodynamic study, measurements of the geometric characteristics of the jets, their trajectories, and the onset of jet dispersion were carried out depending on both the speed of the steam flow and the flow rate of the liquid. Using visual observation and photography, the geometric characteristics of the liquid flow were determined. In the case of counter-current flow around the liquid jet by water steam, the hydrodynamic regimes of the process were determined.

During the heat exchange studies, measurements of the average heat content temperatures along the height of the jet were carried out. For this purpose, at the beginning of the experiment, a washer with a calibrated hole of a certain diameter was installed, the level of liquid above the center of the hole, and the steam pressure were determined. Depending on the diameter of the hole and the level of the liquid above it, the flow rate of the liquid in the setup changed. The level in the pressure vessel was kept constant using an overflow line. The flow rate and, consequently, the steam velocity and its pressure in the apparatus were regulated using regulating valves at the inlet and outlet of the setup. The average steam velocity in the experimental section was taken as the determining velocity of the steam.

When the liquid temperature and steam temperature remained constant, the experiment began. The experiments lasted until the liquid collector was completely filled. Intermediate purging of the experimental setup and draining of the parasitic condensate into the drain were carried out between the experiments.

Results and discussion

In heat and mass transfer equipment used in the food industry, the main hydrodynamic regime for a single liquid jet is its continuous structure along the entire length (Sokolenko et al., 2019). Therefore, when determining empirical dependencies for calculating heat transfer during steam condensation on the surface of a cylindrical liquid jet, heat transfer in jets of this type is present. That is, when calculating heat transfer, only the continuous section of the jet should be considered.

However, a free-falling cylindrical jet has a complex and variable configuration along its height (Bondar et al., 2018). Even if it does not break, it constantly oscillates, and the shape of its cross-section changes, differing from the shape of the distributor orifice from which the outflow occurs.

During heat transfer calculations, which depend on the jet surface area, the energy transfer mechanism within it, and the temperature difference, it is necessary to account for the complex nature of the heat transfer intensity variation along the jet length. This is also evidenced by the experimentally determined temperature changes along the height of the jets, as shown in Figure 1.

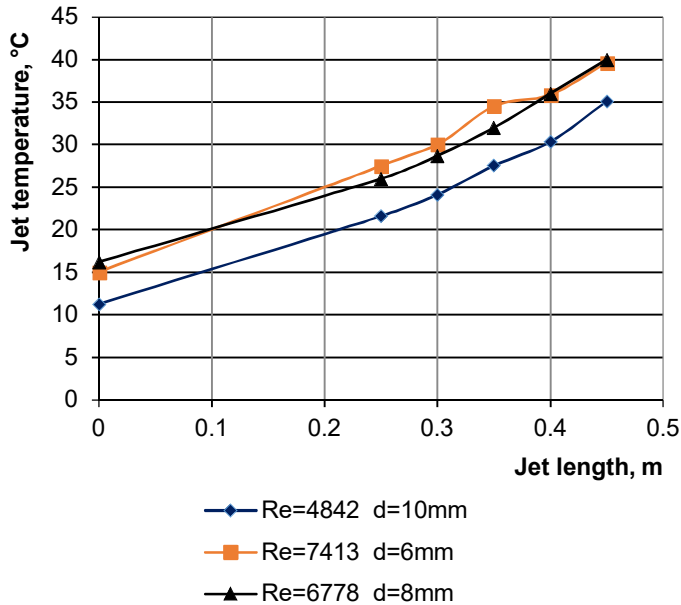


Figure 1. Change in the average water temperature across the height of the jet

According to the above, the use of existing methods for calculating heat transfer in cylindrical single liquid jets to analyze heat exchange in jets of this type is incorrect. This is evidenced by the results of comparing the data from this study with calculations based on existing correlations for both laminar and turbulent flow regimes (Bondar et al., 2018), which show qualitative and quantitative differences.

Under these conditions, it is impossible to construct an adequate mathematical model, and the experimental approach to obtaining an integral calculation method for heat exchange intensity becomes paramount.

When the liquid jet flows out, its shape does not correspond to the shape of the orifice, making it impossible to calculate the cross-sectional area and, consequently, the heat exchange surface area, rendering the use of the Newton-Richman equation is (Kim et al, 2021) impossible. This means that the traditional concept of the heat transfer coefficient cannot be used as a parameter, and instead, a dimensionless complex is proposed to describe the degree of temperature change of the liquid along the length of the jet under the corresponding geometric conditions:

$$4St = \frac{d_0}{y} \ln \frac{T_s - T_0}{T_s - T_p}, \quad (1)$$

where T_s is the saturation temperature of the heating steam, K;

T_p is the current temperature of the liquid, K;

d_0 is the orifice diameter, m.

In addition, considering previous studies on heat transfer during steam condensation on cylindrical jets and using the dimensional analysis method (Kovalenko et al., 2005), the following system of dimensionless parameters can be used in developing empirical correlations:

$$St=f\left(\frac{1}{d_0}; We; Re; K; Pr; \bar{\mu}; \bar{\rho}; \bar{\lambda}; \bar{c}_p\right) \quad (2)$$

where:

- d_0 – jet diameter, m;
- l – jet length, m;
- St – Stanton number of the jet;
- Re – Reynolds number of the jet;
- Pr – Prandtl number of the liquid;
- K – phase transformation criterion;
- λ – thermal conductivity coefficient, W/(m·K);
- μ – dynamic viscosity coefficient, Pa·s;
- ρ – density, kg/m³;
- ν – kinematic viscosity coefficient, m²/s;
- v – jet velocity at the distributor cut, m/s;
- c_p – liquid's heat capacity, J/kg·K.

In processing experimental data, the last four parameters were not considered because the physical properties of the liquid and steam did not change significantly.

The phase transformation criterion (K) accounts for the release of heat from supercooled condensate and the hydrodynamic effects associated with the presence of transverse mass flow on the phase boundary surface.

The selection of determining parameters should consider the influence of characteristics of steam-jet flows, jet length, and the physical properties of the phases.

Analyzing the results of experimental studies within the dimensionless parameter systems (Bondar et al., 2019; Kim et al., 1989), it can be concluded that there is currently no universal system of parameters that can adequately describe the heat transfer process during steam condensation on a cylindrical free-falling liquid jet with sufficient accuracy. Therefore, an original system of dimensionless similarity numbers was developed based on the results of hydrodynamic jet analysis.

According to this system, for one-dimensional modeling, the experimental research results are approximated by the empirical dependency:

$$\frac{d_0}{y} \ln \frac{T_s - T_0}{T_s - T_p} = 0,000897 \cdot \left(\frac{1}{d_0}\right)^{-0,73} \cdot Re_0^{0,99} \cdot We_{\sigma 2}^{-0,53} \cdot K^{-1,66} \cdot Pr^{-2,22} \quad (3)$$

where:

- d_0 – jet diameter, m;
- l – jet length, m;
- T_p – liquid temperature, K;
- T_0 – liquid temperature at the distributor cut, K;
- T_s – steam saturation temperature, K;
- $We_{\sigma 2}$ – modified Weber number,
- Re_0 – Reynolds number of the jet,
- Pr – Prandtl number of the liquid;
- K – phase transformation criterion;
- λ – thermal conductivity coefficient, W/(m·K);
- ν – kinematic viscosity coefficient, m²/s;
- ρ – density, kg/m³;
- σ – surface tension coefficient, N/m.

Furthermore, to describe the onset of dispersion (the transition boundary from wave to dispersed hydrodynamic regime (Bondar et al., 2015)), it is necessary to determine the dimensional quantities that define this transition. A preliminary analysis of the hydrodynamic study of a single jet movement in counter-current flow with water steam concluded that the transition between hydrodynamic regimes depends on the orifice diameter, liquid velocity, dynamic pressure of the steam flow, and the physical properties of the liquid and steam flows. Thus, the height at which jet dispersion begins depends on the following quantities: the liquid jet diameter, the kinetic energy of the steam flow, the liquid exit velocity from the orifice, viscosity, surface tension, and free-fall acceleration.

$$h_{cr} = f((\rho_p v_p^2); v_p; d_o; v_p; \sigma_p; \rho_p; g) \quad (4)$$

The onset of jet structure breakdown is proposed to be described by the following relationship of dimensionless parameters:

$$h_{cr}^* = f[We_{\sigma 1}; Re], \quad (5)$$

where

$$h_{cr}^* = \frac{h_{cr}}{\sqrt{\sigma_p / (\rho_p \cdot g)}}$$

is the dimensionless vertical distance from the orifice center to the plane where jet dispersion begins;

$$We_{\sigma 1} = \frac{\rho_p v_p^2}{\sqrt{\sigma_p \cdot \rho_p \cdot g}} \text{ is the Weber capillary number;}$$

Re is the Reynolds number of the jet;

$$Re_0 = \frac{v_o \cdot d_o}{v_p}$$

where v_o is the liquid velocity at the orifice exit, m/s;

v_p is the steam velocity in the steam space, m/s;

h_{cr} is the height at which dispersion begins, measured from the point of outflow, m;

d_o is the orifice diameter, m.

It is also necessary to consider the change in the ical parameters of the liquid and steam flows by introducing a dimensionless complex, such as the Prandtl number (Pr). Flow parameters for constructing dimensionless complexes were selected based on practical considerations. In heat exchange equipment, it is possible to measure the orifice diameter rather than the jet diameter and calculate the liquid and steam flow velocities at the orifice exit.

The experimental data are satisfactorily approximated by the dependence (Bondar, 2015):

$$h_{cr}^* = 14,10840 \cdot Re_0^{0,180938} \cdot \exp(-55,54866 \cdot We_{\sigma 1}). \quad (6)$$

A comparison of experimental and calculated values using the empirical dependence (6) is shown in Figure 2.

The proposed dependence accurately adjusts the experimental data within a 10% error margin, with a determination coefficient of 98.11%.

To further verify the proposed empirical dependence, we will examine how the dimensionless height of jet dispersion onset changes with flow parameters. As previously discussed, flow parameters are accounted for by the dimensionless complexes Re_0 and $We_{\sigma 1}$. The comparison results are shown in Figure 3.

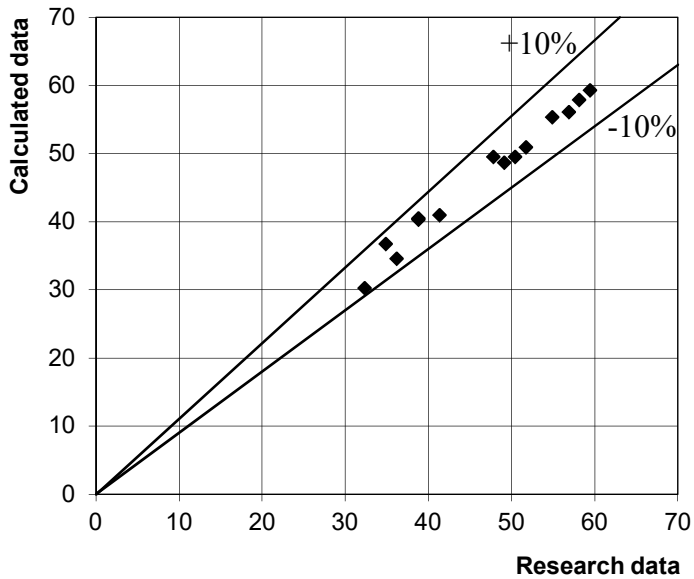


Figure 2. Comparison of calculated and experimental values of h_{cr}^*

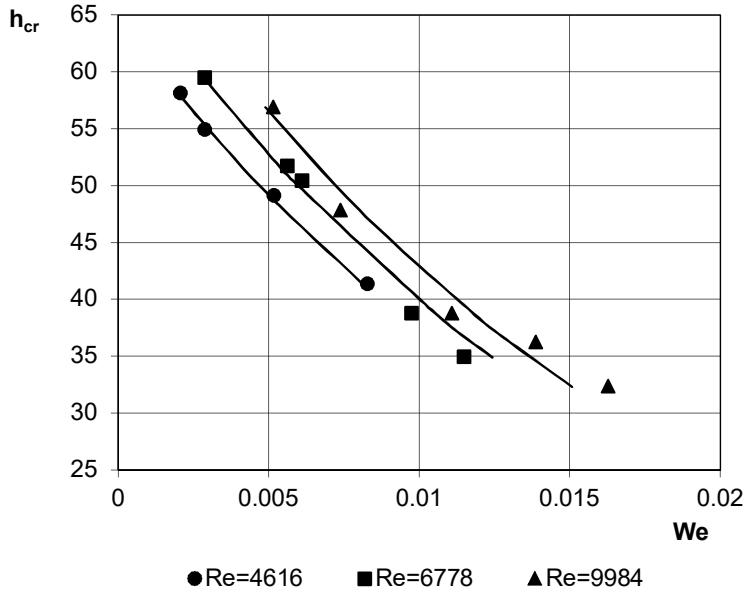


Figure 3. Effect of the We_{eo1} criterion on the dimensionless height of dispersion onset. Calculated data by formula (6) are shown as lines, and experimental data are shown as points for corresponding Re values.

Analyzing the graphical dependence, we conclude that the experimental values systematically vary by Reynolds number. An increase in Re causes an increase in h^*_{cr} , meaning the jet becomes more stable against the action of the steam flow.

As the dynamic pressure of the steam flow increases and thus $We_{\sigma 1}$ rises, there is an initial sharp decrease in the dimensionless height of dispersion, followed by intensive jet fragmentation and destruction at the outflow point, leading to it being carried away by the passing steam.

We can conclude that the empirical dependence for determining the onset of jet structure breakdown adequately describes the process of its structural change.

Summarizing the above, we propose using the research results when designing new heat exchange equipment with direct phase contact.

Currently, there are many methods for calculating mixing heat exchangers. For example, the method of calculating a barometric mixing condenser is proposed to be improved, which consists of the following steps:

1. Determining the cooling water flow rate from the heat balance equation:

$$G_w = W \frac{(h_s - c_w \cdot t_{cond})}{c_w \cdot (t_2 - t_1)}, \quad (7)$$

where W is the steam flow rate entering the condenser, kg/s;

h_s – the specific enthalpy of the steam, kJ/kg;

c_w – the specific heat capacity of water, kJ/kg·K;

$t_{cond} = t_2$ is the temperature of the condensate, °C;

t_1 and t_2 are the initial and final temperatures of the cooling water, °C.

2. Determining the diameter and height of the barometric condenser. The condenser diameter is determined from the flow rate equation:

$$D_{b.c.} = \sqrt{4Wv / (\pi\omega_s)}, \quad (8)$$

where v – the specific volume of the steam, m³/kg;

ω_s – the steam velocity in the condenser, m/s.

The obtained value $D_{b.c.}$ is rounded to the standard, based on which all dimensions of the condenser are selected.

A simplified calculation of the number of trays and the height of the condenser was conducted by assuming that the distance between trays is the same for all trays, and the amount of liquid dripping from each tray is equal $G_w + W$

The height of the condenser is determined by the formula:

$$H = (n + 1)h, \quad (9)$$

where n is the number of trays,

h is the distance between trays, which is chosen within the range of 350–550 mm.

The number of trays is determined by the formula:

$$n = \ln \frac{T_s - T_1}{T_s - T_2} / \frac{T_s - T_0}{T_s - T_p}, \quad (10)$$

where T_s – the saturation temperature of the steam, °C,

T_1, T_2 – the initial and final temperatures of the cooling liquid, °C.

Knowing the flow rate of the liquid, we assume that the fraction of liquid dripping through the cylindrical openings is equal to $0,3(G_w + W)$.

3. It is checked the condition of the jet continuity:

$$h_{cr}^* = 14,108 \cdot Re_0^{0,181} \cdot \exp(-55,55 \cdot We_{\sigma_1}) \quad (11)$$

where $h_{cr}^* = \frac{h_{cr}}{\sqrt{\sigma_p / (\rho_p \cdot g)}}$,

h_{cr} – the height at the start of dispersion;

$h_{cr} = h, m$;

If this condition is not met, the jet breaks down, and a new distance between trays is set.

4. The heat transfer on cylindrical liquid jets was calculated using the empirical dependence:

$$\frac{d_0}{y} \ln \frac{T_s - T_0}{T_s - T_p} = 0,000897 \cdot \left(\frac{1}{d_0}\right)^{-0,73} \cdot Re_0^{0,99} \cdot We_{\sigma_2}^{-0,53} \cdot K^{-1,66} \cdot Pr^{-2,22} \quad (12)$$

5. The heat transfer for the liquid flowing out through a slit distributor is calculated using the dependence (Vasylenko, 2003):

$$\frac{d_e}{y} \ln \frac{T_s - T_0}{T_s - T_p} = 8,59 \cdot 10^{-17} \cdot (y^*)^{-0,849} \cdot We^{-0,023} \cdot Pr_p^{-3,661} \cdot Re_{de}^{4,108} \quad (13)$$

where y^* – is the dimensionless distance from the water overflow edge,

$$y^* = y / \left[\sigma_p / (\rho_p g) \right]^{0,5}$$

d_e is the equivalent diameter of a single jet, m;

$$d_e = 4 \cdot b \cdot h / (2h + b);$$

b is the width of the slit distribution device, m;

Re_{de} is the Reynolds number of the jet flowing from the slit,

$$Re_{de} = v_{0j} \cdot d_e / \nu_p$$

We is the Weber number,

$$We = \rho_p \cdot v_p^2 \cdot d_e / \sigma;$$

b – width of the distribution device, m.

6. At the end of the calculation, a check is made to ensure that the liquid jet heats up to the set temperature, which flows through the slit and cylindrical distribution devices to the same temperature. If not, a new distance between trays is set.

Further calculations of the dimensions of the barometric pipe and the calculation of the vacuum pump are carried out using classical methods.

Conclusions

1. When it is calculating the heat transfer in free cylindrical liquid jets during the condensation on their surface of stationary steam and steam from the countercurrent

flow, it is recommended to take into account the limits of the existence of a continuous structure of the jet.

2. It is recommended to calculate the heat exchange according to the dependencies given in the article, the adequacy of which is confirmed by comparative analysis.
3. A scientifically substantiated methodology for the thermohydrodynamic calculation of steam-contact heat and mass transfer devices has been developed. The feature of methodology the feature of methodology is that before calculating the heat transfer, the condition of the existence of a solid jet structure is checked, and the heat transfer is calculated according to the obtained empirical formula.

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Automation of a sugar plant diffusion station with a subsystem for resolving conflict modes

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Abstract

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Introduction. The aim of the present study was to improve of the automated control system of the sugar plant diffusion station, which does not respond adequately to violations of the technological regime when changing the quality indicators of raw beet materials and the rhythm of work.

Materials and methods. The paper considers the data of the diffusion station and the lab for testing of raw materials of the Zhdanivkyi Sugar Plan, Vinnytsia region, Ukraine. To improve the automation system, it is proposed to include a subsystem for resolving conflict modes, and the method of bimatrix non-antagonistic game is used.

Results and discussion. Uncontrolled parameters worsen the quality of raw beet materials and chips, disrupt the movement of chips in the scalding unit and column, and affect machine loading. Contradictions arise: an increase in productivity reduces storage losses, but leads to an increase in sugar losses with the cake because higher throughput reduces the time for optimal extraction. Changes in the condition of the raw beet materials decreases the processing quality and plant productivity.

For the studied sugar plant, changing chip thickness from 6 to 9.5 m/100 grams of beet caused the voltage on the column motors to vary from 135 to 375 V, leading to changes in plant productivity from 2033 to 2358 t/day and sugar losses from 0.39 to 0.65% by weight of processed beets.

An approach to the automation of a diffusion station was proposed. This approach involves supplementing existing systems with a subsystem for resolving conflict modes of operation. The subsystem uses information from the automatic control system, operator inspections, and laboratory data. By applying game theory, it controls the performance of the diffusion station. This algorithm minimizes the total loss of sugar during the storage and processing of beet. It also forms control actions to adjust technological parameters. The methodology involves presenting the problem as a non-antagonistic bimatrix game. In this game, one party aims to increase plant productivity during processing. The other party focuses on reducing losses during processing. The set of strategies involves changing the thickness of the chips. The payoff functions for the parties are productivity and sugar losses during processing.

Conclusion. The use of game theory to optimize the productivity of a sugar plant takes into account sugar losses during beet storage, processing sequence, temperature, beet quality, and changes in sugar losses at different plant productivity.

Introduction

The process of sugar extraction from beet chips is a key part of sugar production. This process significantly impacts the cost of sugar production, energy consumption, and sugar losses (Mabeta et al., 2023; Zayets, 2003). Despite the simplicity of the technological scheme, the dehydration process is complex. It involves different operations including mass transfer, heat transfer, and physicochemical processes.

At most sugar plants, the diffusion station is controlled by an automation system based on modern microprocessor technology (Sidletskyi et al., 2020). These systems reliably maintain the regulated values of the main process parameters (temperature, material balance, level, pressure, and pH). However, existing automation systems cannot always respond adequately to process disruptions (Sadílek et al., 2016; Sidletskyi et al., 2020). This can be explained by the fact that the automation system does not take into account a number of uncontrolled parameters that significantly change the technological regime of the plant and reduces the efficiency of its operation. The quality of beets and chips, the movement of chips in the scalding unit and column, and the loading of the devices are all crucial factors. If there are changes in the technological regime, it is necessary to adjust the technological parameters. Without automatic correction algorithms, the operator must make the decision to change these parameters (Geng et al., 2015; Korobiichuk et al., 2017; Machková et al., 2017; Sidletskyi et al., 2020; Srivastava et al., 2013).

The following issues require additional research:

1. To develop methods for selecting the capacity of the diffusion station and forming a plan for sugar beet processing to minimize total sugar losses during storage and processing.
2. Develop the structure, algorithmic, and software of the subsystem for resolving conflict modes when adjusting the operation of a diffusion station
3. To develop ways to integrate the subsystem for resolving conflict modes into existing automated control systems of the diffusion station.

The aim of the research was to improve the efficiency of the diffusion station for the sugar extraction from beet chips. This was achieved by enhancing the automated control system of the diffusion process through the development and inclusion of a subsystem for resolving conflict modes.

Materials and methods

Object of research

The diffusion station of the Zhdanivkyi Sugar Plan (Vinnytsia region, Ukraine) was used in the study (Fig. 1).

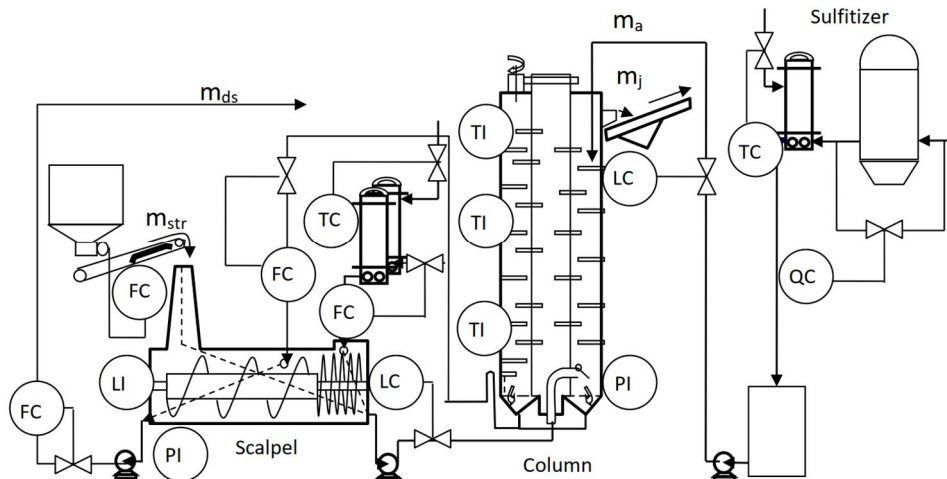


Figure 1. Simplified automation scheme of a diffusion station:

Positions FC - flow control loop, TC - temperature control loop, LC - level control loop, QC - control loop, TI - control loop, RI - control loop, LI - control loop, m_a - feed water material flow, m_j - material flow of cake, m_{ds} - material flow of diffusion juice, m_{mstr} - material flow of chips

The automation scheme of the column diffusion unit provides for the implementation of the following control loops (Fig. 1):

- maintaining the ratio of diffusion juice extraction from the mass of processed beets;
- maintaining the ratio of consumption of diffusion and circulation juice;
- maintaining the temperature regime in the scalding unit and the column by stabilizing the temperature of the feed water and circulating juice;
- maintaining the level of juice in the agitator and scalding column.
- To provide the operator with additional information about the state of the technological process, the parameters are monitored:
 - juice pH in the column and water treatment station;
 - pressure drop on the sieves in the column and scaler;
 - specific load on the electric motors of the scalding unit and column drives;
 - sugar losses in the pulp;
 - quality of the diffusion juice;
 - matter content of the diffusion juice at the scalding unit outlet.

Data sources

Sensors and actuators are placed directly on the processing equipment. The quantity and types of these devices are chosen based on the monitoring and control algorithms used at the specific technological site. The automation system in the diffusion department is structured as a hierarchical three-level automated control system. At the first level, there are sensors and actuators; at the second level, there is an industrial controller, and at the third level, there is an automated workstation for the process operator (operator workstation) (Fig. 2).

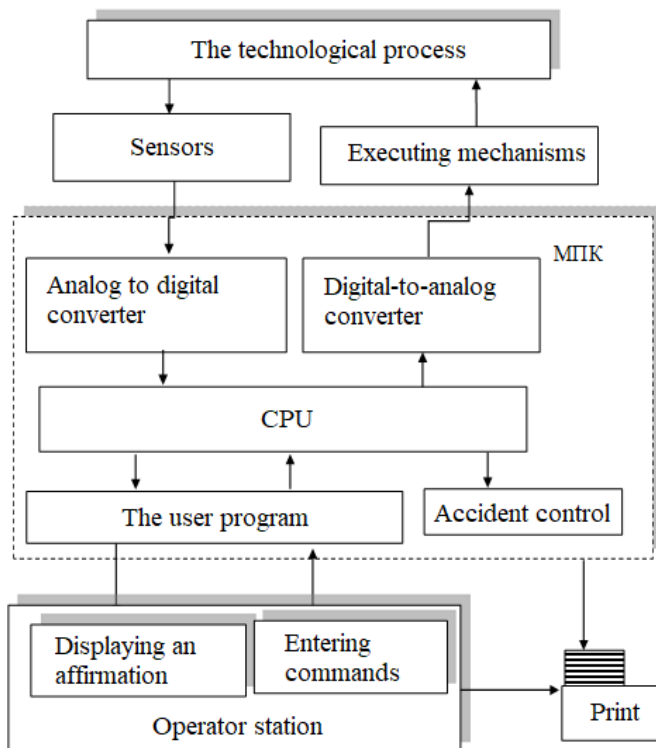


Fig. 2. Functional structure of the automated control system of the diffusion station

Such a system provides the following functions: polling and subsequent processing of signals from sensors, execution of operating control algorithms, production and emergency alarms, development of control actions on actuators, transmission of signals from sensors, positions of actuators, diagnostic signals to the operator station, providing the operator with the ability to change the set values for regulators and manual control of actuators, archiving of values of technological parameters and parameters of equipment operation, and maintaining.

Research methods

The study is a bimatrix non-antagonistic repeated game for two players with a Nash equilibrium search (Cruz et al., 2005; Du, 2008; Kontogiannis et al., 2009).

Results and discussion

Conflicting regimes of operation of the diffusion station.

A complex indicator of disturbances in the operation of a diffusion plant is the decrease of its quality indicators, which are determined in the process of laboratory analysis of

diffusion juice, pulp or determination of total sugar losses (Zayets, 2003). The complexity of the operator's work lies in the fact that deviations in the technological regime and deterioration of the process quality indicators can be caused by various reasons (Korobiichuk et al., 2018; Srivastava et al., 2013). At the same time, decision-making to eliminate them is also ambiguous.

For example, as noted above, the quality of diffusion juice can be changed by the pumping coefficient α , which in turn can be changed either by the amount of diffusion juice m_{dc} that is pumped out or the amount of beet chips m_c that is fed for processing, i.e. by changing the productivity of the apparatus (Sidletskyi et al., 2020).

At first glance, changing the productivity can be done very simply by changing the speed of the column's conveying body. But the column's performance also depends on the specific load of the column and the conditions of chip movement in it:

$$Y = f_y(R, V, Z), \quad (2)$$

where Y is the productivity of the diffusion apparatus, R is the specific load, V is the shaft speed, and Z is the chip movement in the apparatus.

In turn, the specific load R depends on: shaft speed V , chip flow F , level in the machine L , chip quality W , and is characterized by the load of the electric motor I) (Sidletskyi et al., 2020):

$$R = f_r(V, F, L, W, I) \quad (3)$$

In this case, the movement of chips in the apparatus Z depends on: the specific load in the apparatus R , the pH of the water P , the quality of the chips W , and the temperature T (Sidletskyi et al., 2020):

$$Z = f_z(R, P, W, T) \quad (4)$$

To maximize the column's performance, it is necessary to operate at the maximum turbine speed, maintain the maximum specific load and chip movement in the apparatus. Considering 2, 3 and 4:

$$\begin{cases} R = f_r(V, F, L, W, I, O_1) \\ Z = f_z(R, P, W, T, O_2) \\ Y = f_y(R, V, Z) \end{cases} \quad (5)$$

A graph was developed (Fig. 3) showing the effect of specific load and chip movement on the productivity of the diffusion station.

The graph shows that it is impossible to change the productivity by the speed of the tube without taking into account the state of the chips, which affects the load and movement of the chips in the apparatus.

Therefore, the role of the operator-technologist in the diffusion station control system is very important. The quality of management depends on his/her professional qualities and the time allotted for decision-making. An untimely or erroneous decision can lead to damage to process equipment, an increase in the cost of production, and a deterioration in its quality. This is especially true for sugar production, which is seasonal in nature, in which the operator's experience either does not have time to accumulate or during the period when the sugar plant is not working, his professional skills are lost.

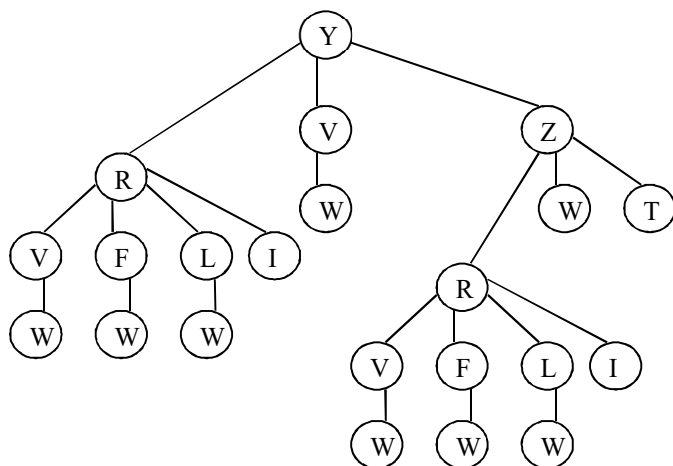


Fig. 3. Influence of factors on the performance of the diffusion apparatus

The analysis shows that the performance of the diffusion station significantly affects both the quality of the diffusion process during sugar beet processing and sugar losses during the storage of raw materials. At the same time, there are some contradictions in decision-making. If there is a need to reduce sugar losses during storage, it is necessary to increase the rate of processing of raw materials, i.e. to increase the productivity of the diffusion department. But this can lead to an increase in sugar losses in the pulp and a deterioration in the quality of the diffusion process. On the other hand, changes in raw material condition indicators lead to changes in the technological conditions of the extraction process and significantly affect the quality indicators of the diffusion process. This may require a change in the residence time of the chips in the column, which will change the productivity of the plant and disrupt its rhythmicity (Geng et al., 2015; Sadilek et al., 2016; Sidletskyi et al., 2020). And this, in turn, will affect the shelf life of raw materials and, accordingly, sugar losses during storage. Therefore, the choice of performance control algorithms is an important task.

It's important to note that simply reducing individual sugar losses during storage and processing may not always achieve the desired outcome. For example, if bad weather causes higher sugar losses in stored beets, increasing the processing rate may seem like a solution, but it can actually lead to higher sugar losses during processing. In some cases, it might be better to adjust the processing methods to minimize overall sugar losses, even if it means accepting higher losses in certain areas, like the pulp (Sidletskyi et al., 2020).

There are two ways to change the performance of a diffusion station (Sidletskyi et al., 2020):

- increasing the voltage on the motors of the tube column, which leads to an increase in the speed of chips passing through the machine and reduces the time spent in the machine;
- reduction of chip length (increase in geometric dimensions), which leads to the need to increase the time spent in the machine. This is because coarser chips move better in the machine, and therefore the machine can be filled with more chips. However, this increases the thickness of the diffusion layer, which requires an increase in the diffusion time, i.e. a decrease in the voltage on the column motors.

- Therefore in the process of finding management decisions to change the productivity of raw material processing while maintaining sugar losses within specified limits, a non-antagonistic conflict situation arises, in which two parties can be distinguished (Abalo et al., 2004; Enkhbat et al., 2021; Fletcher et al., 2007; Kontogiannis et al., 2009):
- The first is interested in increasing productivity by increasing the voltage on the column motors;
- The second is interested in reducing losses during sugar beet processing by increasing the length of the chips.

The length of the chips depends on the quality of the raw material and the setting of the beet cutters (Sidletskyi et al., 2020; Zayets, 2003), i.e. it is a parameter that cannot be controlled in an operational manner. Therefore, the task of the system will be to find such values of motor voltage at which the maximum productivity of the station will be achieved for the available chip length, provided that sugar losses during storage are not affected.

Presentation of station operation modes in the form of a non-antagonistic game

Assuming that each value of voltage on the column motors v and chip length d will correspond to both productivity A and sugar losses B , it is necessary to find a situation in which productivity is maximized and losses are minimized:

$$\begin{cases} A = f_1(v, d) \\ B = f_2(v, d) \end{cases} \quad A \rightarrow \max, B \rightarrow \min \quad (6)$$

No mathematical expression was found that could be used to obtain the dependence of productivity on the voltage on the column motors and chip length, since a change in the voltage on the column motors does not lead to a proportional change in productivity (Geng et al., 2015; Sadílek et al., 2016; Sidletskyi et al., 2020; Zayets, 2003). This can be explained by the fact that productivity primarily depends on the processes that affect the movement of chips, which, as shown in the previous sections, depend on a significant number of factors. It should be noted that in the process of operation, the operator always finds a mode that can be called steady-state, in which the specified performance indicators of the diffusion station were achieved at different voltage on the shaft of the column motors, different chip length and at different productivity (Sidletskyi et al., 2020). Based on this, using the experimental data of the diffusion station operation, a matrix was formed (Table 1), which could be used to determine what productivity was characteristic of the voltage of the column motors v and the chip length l (Sidletskyi et al., 2020).

Table 1
Productivity values (a) depending on column motor voltage and chip length

Voltage of column motors	Chip length l				
	l_1	...	l_i	...	l_n
Diffusion station capacity, tons					
v_1	a_{11}	...	a_{1j}	...	a_{1n}
...
v_j	a_{1j}	...	a_{ij}	...	a_{in}
...
v_m	a_{1m}	...	a_{mi}	...	a_{mn}

The symbols (...) are used to indicate that a certain part of the table has been omitted, but similar information follows.

Similarly, for sugar losses during processing, a matrix was formed (Table 2) that characterized sugar losses β depending on the voltage of the column motors v and chip length l .

Table 2

Sugar loss values (β) depending on column motor voltage and chip length

Voltage of column motors	Chip length l				
	l_1	...	l_i	...	l_n
	Sugar loss				
v_1	β_{11}	...	β_{1j}	...	β_{1n}
...
v_j	β_{1j}	...	β_{ij}	...	β_{in}
...
v_m	β_{1m}	...	β_{mi}	...	β_{mn}

To solve this problem, we can consider condition (6) as a non-antagonistic bimatrix game:

$$G = (N, \{X_i\}_{i \in N}, \{H_i\}_{i \in N}) \quad (7)$$

in which $N = \{1, 2, \dots, n\}$ is the set of players, X_i is the set of strategies of player i , H_i is the payoff function of player i .

We view the recycling process as a game of G , in which there are two sides.

$$G = (X_{11}, X_{12}, H_{11}, H_{12}) \quad (8)$$

One party is interested in increasing the productivity of processing and for which the set of strategies is to change the voltage on the column motors $X_1 = \{v_1, v_2, \dots, v_m\}$, the other party is interested in reducing the losses during processing and for which the set of strategies is to change the length of the chips $X_2 = \{d_1, d_2, \dots, d_n\}$. The gain functions for the parties will be $H_1 = P(v, d)$ and $H_2 = C_2(v, d)$ for productivity and sugar losses during processing, respectively. Then the tables of sugar losses during processing and processing productivity, depending on the voltage and chip length, will take the form of game matrices G :

$$H_1 = \begin{matrix} & \begin{matrix} |l_1 & \dots & l_i & \dots & l_n \end{matrix} \\ \begin{matrix} v_1 \\ \dots \\ v_j \\ \dots \\ v_m \end{matrix} & \begin{vmatrix} a_{11} & \dots & a_{i1} & \dots & a_{n1} \\ \dots & \dots & \dots & \dots & \dots \\ a_{1j} & \dots & a_{ij} & \dots & a_{nj} \\ \dots & \dots & \dots & \dots & \dots \\ a_{1m} & \dots & a_{im} & \dots & a_{nm} \end{vmatrix} \end{matrix} \quad (9)$$

$$H_2 = \begin{matrix} & \begin{matrix} |l_1 & \dots & l_i & \dots & l_n \end{matrix} \\ \begin{matrix} v_1 \\ \dots \\ v_j \\ \dots \\ v_m \end{matrix} & \begin{vmatrix} \beta_{11} & \dots & \beta_{i1} & \dots & \beta_{n1} \\ \dots & \dots & \dots & \dots & \dots \\ \beta_{1j} & \dots & \beta_{ij} & \dots & \beta_{nj} \\ \dots & \dots & \dots & \dots & \dots \\ \beta_{1m} & \dots & \beta_{im} & \dots & \beta_{nm} \end{vmatrix} \end{matrix}$$

For a game G , the equilibrium situation is the value of v and d for which the condition is satisfied:

$$G = (v, d) \rightarrow \left\{ (v^*, d^*) \left| \begin{array}{l} H_1(v, d^*) = \max_{X_{11}} H_1(v, d) \\ H_2(v^*, d) = \min_{X_{12}} H_2(v^*, d) \end{array} \right. \right\}, \quad (10)$$

Assuming that for a game G the full set of probabilities of the first party using its pure strategies is mixed strategy $X_{11} = \{v_1, v_2, \dots, v_m\}$ and $X_{12} = \{d_1, d_2, \dots, d_n\}$ - the mixed strategies of the second party. Then the average payoffs of the first and second parties will be equal:

$$\begin{aligned} G(H_1, v, d) &= \sum_{i=1}^m \sum_{j=1}^n a_{ij} v_i d_j \\ G(H_2, v, d) &= \sum_{i=1}^m \sum_{j=1}^n \beta_{ij} v_i d_j \end{aligned} \quad (11)$$

The equilibrium situation for a given bimatrix game will be a pair (v, d) of mixed strategies of the first and second party that satisfy the inequalities:

$$\begin{aligned} \sum_{j=1}^n a_{ij} d_j &\leq \sum_{i=1}^m \sum_{j=1}^n a_{ij} v_i d_j \quad (i = 1, \dots, m) \\ \sum_{i=1}^m \beta_{ij} v_i &\leq \sum_{i=1}^m \sum_{j=1}^n \beta_{ij} v_i d_j \quad (j = 1, \dots, n) \end{aligned} \quad (12)$$

According to [114], for a situation (v^0, d^0) to be an equilibrium situation in the mixed strategies of a bimatrix game G , it is necessary and sufficient that there exist sets $H_1^0 \subseteq H_1$, $H_2^0 \subseteq H_2$ and the numbers u_1, u_2 , for which the conditions are met:

$$\left\{ \begin{array}{l} \sum_{j \in H_{22}^0} a_{ij} v_j^0 = u_1 \quad \forall i \in H_1^0, \\ \sum_{j \in H_{22}^0} a_{ij} v_j^0 \leq u_1 \quad \forall i \notin H_1^0, \\ \sum_{j \in H_{22}^0} v_j^0 = 1, v_j^0 \geq 0 \quad \forall j \in H_2^0, \end{array} \right. \quad (13)$$

$$\left\{ \begin{array}{l} \sum_{j \in H_{22}^0} d_j^0 \beta_{ij} = u_2 \quad \forall j \in H_2^0, \\ \sum_{j \in H_{22}^0} d_j^0 \beta_{ij} \leq u_2 \quad \forall j \notin H_2^0, \\ \sum_{j \in H_{22}^0} d_j^0 = 1, d_j^0 \geq 0 \quad \forall i \in H_1^0, \end{array} \right. \quad (14)$$

Resolving conflicting modes of operation on the example of Zhdanivkyi Sugar Plant

To verify the approach, we took archival data from the Zhdanivkyi Sugar Plant's control system and information from the lab for testing of raw materials. Based on these data, matrices of the dependence of productivity and sugar losses during beet processing on the voltage of the column motors (the time the chips stay in the apparatus) and the length of the chips were constructed.

The payoff matrices for each side are given in the form of tables; for the first side, the net strategies are $X_1=\{135, 145, 155, 165, 175, 185, 195, 205, 215, 225, 235, 245, 255, 265, 275, 285, 295, 305, 315, 325, 335, 345, 355, 365, 375\}$, and for the other side, pure strategies will be $X_2=\{6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5\}$.

Table 3

Productivity depending on column motor voltage and chip length

		Chip length, m/100 g							
		6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
		Diffusion station capacity, tons/day							
Voltage of column diffusion apparatus motors, V	135	2033	2109	2150	2008	2075	2096	2082	2023
	145	2020	2021	2152	2176.98	2027	2113	2055	2088
	155	2213	2089	2143	2020	2049	2063	2091	2091
	165	2142	2201	2168	2093	2025	2025	2085	2139
	175	2058	2233	2137	2046	2157	2019	2030	2021
	185	2198	2011	2171	2022	2010	2063	2164	2117
	195	2103	2059	2050	2185	2186	2078	2201	2111
	205	2005	2165	2146	2236	2141	2109	2184	2121
	215	2226	2269	2120	2103	2072	2003	2082	2146
	225	2169	2048	2274	2278	2216	2118	2104	2127
	235	2303	2322	2149	2171	2206	2224	2032	2019
	245	2282	2205	2074	2029	2089	2041	2232	2103
	255	2267	2316	2235	2082	2218	2162	2196	2103
	265	2122	2003	2256	2075	2158	2184	2156	2176
	275	2287	2032	2007	2065	2115	2169	2197	2045
	285	2036	2214	2325	2261	2008	2133	2284	2102
	295	2038	2413	2327	2160	2294	2207	2160	2066
	305	2471	2261	2212	2116	2170	2331	2164	2151
	315	2153	2047	2058	2343	2313	2283	2229	2214
	325	2256	2038	2002	2326	2142	2020	2321	2070
335	2330	2451	2046	2332	2341	2030	2164	2049	
345	2448	2305	2429	2064	2144	2081	2185	2260	
355	2444	2080	2294	2039	2304	2112	2103	2341	
365	2479	2408	2348	2321	2181	2061	2049	2231	
375	2278	2519	2158	2333	2138	2055	2027	2358	

Table 4

Sugar loss depending on column motor voltage and chip length

		Chip length, m/100 g							
		6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5
		Sugar losses during beet processing, % by weight of beet							
The voltage of column diffusion apparatus motors, V	135	0.39	0.35	0.28	0.26	0.21	0.27	0.23	0.21
	145	0.47	0.34	0.35	0.25	0.23	0.24	0.23	0.23
	155	0.43	0.42	0.30	0.29	0.28	0.28	0.24	0.23
	165	0.42	0.34	0.40	0.28	0.32	0.26	0.30	0.22
	175	0.56	0.45	0.36	0.38	0.33	0.26	0.29	0.26
	185	0.60	0.36	0.34	0.33	0.31	0.37	0.29	0.30
	195	0.53	0.51	0.38	0.32	0.35	0.31	0.30	0.36
	205	0.50	0.51	0.47	0.37	0.33	0.31	0.36	0.33
	215	0.61	0.52	0.51	0.45	0.39	0.43	0.33	0.37
	225	0.74	0.57	0.45	0.38	0.36	0.33	0.34	0.36
	235	0.55	0.52	0.43	0.40	0.36	0.43	0.43	0.32
	245	0.73	0.69	0.53	0.56	0.37	0.43	0.46	0.39
	255	0.59	0.55	0.58	0.43	0.52	0.45	0.36	0.48
	265	0.60	0.72	0.62	0.53	0.42	0.42	0.38	0.47
	275	0.91	0.56	0.64	0.47	0.53	0.48	0.48	0.36
	285	0.83	0.68	0.60	0.62	0.53	0.54	0.52	0.38
	295	0.69	0.71	0.62	0.55	0.48	0.44	0.46	0.49
	305	0.81	0.85	0.58	0.53	0.46	0.48	0.45	0.42
	315	0.96	0.81	0.72	0.52	0.60	0.51	0.49	0.49
	325	0.84	0.84	0.73	0.58	0.50	0.67	0.52	0.59
335	1.00	0.81	0.64	0.67	0.65	0.56	0.56	0.57	
345	1.08	0.89	0.68	0.78	0.70	0.52	0.56	0.63	
355	1.03	0.86	0.85	0.71	0.68	0.57	0.66	0.55	
365	1.19	1.02	0.64	0.69	0.57	0.57	0.50	0.60	
375	0.88	1.04	0.75	0.81	0.68	0.59	0.68	0.65	

To find an equilibrium situation in biquadratic games, algorithms for rejecting strictly dominant strategies are used (Abalo et al., 2004; Enkhbat et al., 2021; Fletcher et al., 2007; Kontogiannis et al., 2009). To do this, it is necessary to find the dominant rows of the H_1 matrix and columns in the H_2 matrix, while distinguishing between strict and weak dominance.

In a bimatrix game, the strategy of the first side i_1 is strictly dominant over strategy i_2 ($i_1 > i_2$) on the set $\overline{H_2} \subseteq H_2$, if $a_{i_1 j} > a_{i_2 j} \forall j \in \overline{H_2}$. Weak dominance ($i_1 \geq i_2$), if $a_{i_1 j} \geq a_{i_2 j} \forall j \in \overline{H_2}$. Similarly, for the second party, strategy j_1 strictly dominates strategy j_2 ($j_1 > j_2$) on the set $\overline{H_1} \subseteq H_1$, if $d_{ij_1} > d_{ij_2} \forall i \in \overline{H_1}$ and weak dominance ($j_1 \geq j_2$) if $d_{ij_1} \geq d_{ij_2} \forall i \in \overline{H_1}$ $d_{ij_1} \geq d_{ij_2} \forall i \in \overline{H_1}$ (Abalo et al., 2004; Enkhbat et al., 2021).

Using the definition of dominant strategies, the procedure of sequential exclusion of strictly dominant strategies was carried out. In the process of excluding dominant strategies,

two sequentially nested sets were constructed $H_1 = H_1^1 \supseteq H_1^2 \supseteq \dots \supseteq H_1^\kappa$ and $H_2 = H_2^1 \supseteq H_2^2 \supseteq \dots \supseteq H_2^\kappa$.

If the following conditions are met for $l=1, \dots, \kappa-1$:

$$\forall i_2 \in H_1^l \setminus H_1^{l+1} \exists i_1 \in H_1^{l+1} : i_1 > i_2 \text{ на } H_2^l; \quad (15)$$

$$\forall j_2 \in H_2^l \setminus H_2^{l+1} \exists j_1 \in H_2^{l+1} : j_1 > j_2 \text{ на } H_1^l. \quad (16)$$

After the procedure of eliminating all dominant strategies, mixed Nash equilibria remain (Du, 2008; Cruz et al., 2005):

1. If the set $\bar{Z} = \bar{H}_1 \times \bar{H}_2$ strictly dominates the set $Z = H_1 \times H_2$ in mixed strategies, then for any equilibrium situation (v^0, d^0) conditions (Abalo et al., 2004; Cruz et al., 2005; Du, 2008; Enkhbat et al., 2021; Kontogiannis et al., 2009) are met:

$$i \notin \bar{H}_1 \Rightarrow v_i^0 = 0 \quad (17)$$

$$j \notin \bar{H}_2 \Rightarrow d_j^0 = 0 \quad (18)$$

2. If the set $\bar{Z} = \bar{H}_1 \times \bar{H}_2$ weakly dominates the set $Z = H_1 \times H_2$ in mixed strategies and (\bar{v}, \bar{d}) is an equilibrium situation for a game with matrices (Du, 2008; Cruz et al., 2005; Enkhbat et al., 2021; Kontogiannis et al., 2009):

$$\bar{A} = (a_{ij})_{i \in \bar{H}_1, j \in \bar{H}_2}, \bar{B} = (\beta_{ij})_{i \in \bar{H}_1, j \in \bar{H}_2} \quad (19)$$

Then there will be mixed strategies:

$$v^0 : v_i^0 = \begin{cases} \bar{v}_i, & i \in \bar{H}_1, \\ 0, & i \in H_1 \setminus \bar{H}_1; \end{cases} \quad d^0 : d_j^0 = \begin{cases} \bar{d}_j, & j \in \bar{H}_2, \\ 0, & j \in H_2 \setminus \bar{H}_2, \end{cases} \quad (20)$$

where v^0, d^0 are equilibrium situation for the game G_I .

For the technological process, it is best to have the longest residence time and the longest chip length. However, the increase in chip length increases the load on the machine (Cruz et al., 2005; Du, 2008; Enkhbat et al., 2021; Kontogiannis et al., 2009), and therefore it is necessary to reduce the amount of chips in the machine, i.e. either to reduce the residence time or to feed coarser chips. In turn, the supply of coarser chips (reduction in length) or reduction of the chip residence time in the apparatus leads to an increase in sugar consumption with pulp (Sidletsyky et al., 2020).

Block diagram of the diffusion station control with the module for controlling the performance of the diffusion station

The analysis of the functions that should be performed by the module for generating recommendations for managing processing productivity made it possible to identify the following elements that should comprise its structure:

- a block for assessing the condition of raw materials, which calculates possible sugar losses during storage of raw materials;
- a block for calculating the plan for supplying raw materials for processing, taking into account the quality indicators of raw materials and sugar losses during storage;

- a block for calculating processing capacity, taking into account raw material losses during storage.

The solution to this problem can be achieved by including an additional module for controlling the performance of the diffusion station in the automation system of Fig. 1 (Sidletsnyi et al., 2020).

Data from the diffusion station is used to analyze productivity and sugar losses during processing, considering column motor voltage and chip length. This analysis aims to find optimal motor voltage values for maximizing productivity and minimizing sugar losses.

Meanwhile, the raw material lab provides information on raw material quantity and condition for storage. This data is input into units calculating sugar losses during storage and planning raw material supply.

For each level of productivity, we calculate storage and processing losses to find the productivity level with the lowest total losses. Then, based on the productivity and processing losses, we determine the voltage needed for the column motors. The analysis of the diffusion station's efficiency highlights productivity as the main factor influencing total sugar losses. Using formulas for average daily weight and sugar losses of sugar beets, along with stock management methodology, we derived a formula to predict sugar beet state changes based on daily temperature. The analysis also shows that productivity can be adjusted by changing column motor voltage or chip length. The productivity control system aims to find optimal motor voltage values for maximum plant productivity, considering chip length and minimizing sugar losses during storage, using game theory. It's worth noting that other researchers have tackled similar problems using game theory (Abalo et al., 2004; Enkhbat et al., 2021; Fletcher et al., 2007; Kontogiannis et al., 2009).

Conclusions

The use of game theory in calculating the optimal productivity of a sugar factory allows for accounting for sugar losses during storage and their dependency on: the sequence of processing each batch, ambient temperature, raw material quality indicators. It also enables considering changes in sugar losses ranging from 0.39% to 0.65% of the processed beet mass during processing when productivity varies between 2033 and 2358 tons per day, by adjusting the geometric parameters of the chips within the range of 6 to 9.5 meters per 100 grams of chips and the residence time of the chips in the apparatus, which depends on the voltage on the motors of the column diffusion apparatus ranging from 135 to 375 V.

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Problem of survivability of energy associations as specific property of complex systems

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Abstract

Keywords:

Electric
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Introduction. This study examines the factors contributing to the survivability of energy associations, particularly their ability to withstand emergency disturbances and prevent widespread consumer supply disruptions.

Materials and methods. The study employs a systematic approach using quantitative indicators to measure survivability levels. The methodology involves analyzing transient modes of the Unified Power System (UPS) through simulation modeling. This model calculates long transient processes and post-emergency modes, accurately representing system dynamics and considering failures in relay protection, anti-emergency automation, and switching devices.

Results and discussion. The developed simulation model provides an in-depth analysis of the transient behaviors and stabilization processes of the UPS under various emergency conditions. By accurately simulating these dynamics, the model demonstrates the ability to represent the energy systems' performance with satisfactory accuracy. Key findings indicate that the approach effectively identifies potential failures and their impacts, supporting the development of strategies to enhance system resilience. The model's comprehensive accounting for failures in critical components like relay protection and anti-emergency automation highlights the importance of detailed scenario-probabilistic analysis. This method enables a thorough understanding of system vulnerabilities and the effectiveness of preventive measures. The results show that incorporating these detailed analyses into survivability assessments can significantly improve the reliability and robustness of energy associations. The research underscores the necessity of continuous monitoring and updating of simulation models to adapt to evolving system dynamics and emerging threats. By focusing on ergodic scenario-probabilistic approaches, the study provides a robust framework for future research and practical applications in enhancing the resilience of electric power systems.

Conclusions. This methodology offers valuable insights into energy system dynamics, helping identify vulnerabilities and implement effective measures to ensure stable energy supply and resilience.

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Introduction

The urgency of addressing the survivability of energy associations is driven by several factors: the existing centralization of electricity production and distribution, the growing influence of renewable energy sources, and the operational challenges of energy systems and associations under wartime conditions (Li S. et al., 2022; Liu J. et al., 2021). These issues are under continuous investigation by scientists and experts in the energy sector (Abedi et al., 2022; Li L. et al., 2022; Yao et al., 2022).

A significant outcome of this ongoing research is the quantitative and qualitative enhancement of the Electric Power Systems (EPS) emergency management system, a critical and integral component of energy associations that ensures their normal functioning (Liu D. et al., 2022). However, these challenges increase the stress on the Unified Power System's (UPS) electrical modes and the operating conditions of all major electrical systems' equipment, which function with minimal permissible stability reserves and limited operational power reserves (Khan et al., 2022; Soni et al., 2022).

These trends elevate the likelihood of significant disturbances occurring and propagating within the EPS as initial emergency situations develop and escalate. Experience with modern power units demonstrates that abrupt, significant disturbances originating in one part of the unit can spread over large areas (due to the increasing "connectivity" of EPS elements and their operating modes). The nature and duration of the resultant transient processes become more complex, leading to cascading (chain) accidents that can disrupt the electricity supply to large populations (Alam et al., 2022).

The reliability of the energy system is a multifaceted property defined by its ability to perform the functions of production, transmission, distribution, and supply of electrical energy to consumers in the required quantity and standardized quality. This is achieved through the interaction of generating units, electrical networks, and consumer electrical installations. The energy system must:

- Satisfy the total electricity demand at any time (both current and prospective).
- Resist disturbances caused by failures of power system elements, including the cascading development of accidents and force majeure conditions.
- Restore its functions after disruptions.

The last function, the ability to return to operational mode after various disturbances, characterizes the system's stability (Zhong et al., 2023). The survivability of the energy system can thus be defined as its ability to withstand emergency disturbances and prevent the cascading development of accidents that cause widespread consumer supply disruptions.

Cascading accidents are characterized by the successive disconnection of a power grid or station equipment due to the activation of relay protection or emergency automation triggered by unacceptable operational conditions. While such serious system accidents are relatively rare (occurring once every few years), they can have the scale of national disasters. In such events, power supply disruptions can affect large areas with several million populations, resulting in tens of millions of kilowatts of power and hours-long outages, leading to significant material losses. An example is the February 2021 Texas, USA, energy crisis, where extreme cold led to failures in the electric power, gas supply, and water supply systems, with the interconnected nature of these systems exacerbating the impacts (Niet et al., 2022; Parrado-Hernando et al., 2022).

Literature review

In the energy system survivability analysis task, it is advisable to highlight two issues: methodical approaches and indicators for quantitative measurement of the level of the Unified Power System survivability (Zhong et al., 2023). The idea of approaches that consider the survivability of a system as a property that manifests itself exclusively under external influences of an undefined nature (intentional or extreme natural influencing factors) was most clearly expressed by I. Ushakov (Agajic et al., 2021; Avramenko et al., 2011), who, in this way, formulates the concept of the survivability indicator, which does not use probabilistic characteristics. Let $\Phi_j(l_i)$ be an indicator of the quality (efficiency) of the functioning of the j th variant of the system under the influence of l_i . The survivability index $L_j(E)$ of the system for a set of possible external influences L is written in the form:

$$L_j(E) = \Phi_j(l_i) \quad (1)$$
$$l_i \in E$$

Thus, in conditions of uncertainty in quality fuse survivability, worst-case functioning is accepted. Optimization systems (according to the indicator survivability) are found during design by finding such an option system from the number of possibilities that L_j have the maximum value.

Concerning electric power systems, the reduction of equal functioning is to be measured by the amount of load paid off during the course accident (Liu J. et al., 2021); maybe her clarification at the expense of accounting for depth outages load. Based on analysis more than 100 types electricity consumers received averaged dependencies specific damage consumers of large power stations from depth emergency shortage capacity. Note that at a depth (Abedi et al., 2022) deficit equal to 60%, the steepness of these characteristics is sharp and growing. It needs to be addressed, and attention to what full indicator survivability (Khan et al., 2022) takes into account duration violation electricity supply, there is a shortage electricity consumers taking into account different importance different components short leave There is a comparison technique options development of the EPS according to the criterion survivability (Soni et al., 2022) This approach allows consider development accident at the expense of violation dynamic stability. Results testify that (Liu D. et al., 2022) this moment, considered a measure of increased adequacy used in the EPS model, significantly impacts the assessment of survivability energy association, separate in parts of which there are large losses capacity. Do not use probabilistic characteristics and indicators, which are determined by the number of large disturbing influences during which the unacceptable development of emergencies occurs (Li S. et al., 2022; Yao et al., 2022). Such an indicator accurately reflects the essence of the concept of survivability, which characterizes achieving the maximum permissible state of the system. However, the practical determination of such indicators based on the analysis of the performance function as the solution of a system of logical equations expressing the dependence of the achievement of the goal (providing power to consumers) on the performance of elements and external disturbances, can be effective only for relatively compact systems limited in number of elements: autonomous systems (ships, airplanes, etc.), switching schemes of generators and power plants of own needs, etc (Khan et al., 2022; Niet et al., 2022). Thus, there is a certain limitation of the scope of application of logical-probabilistic methods modified for the analysis of the survivability of the Electric Power System, which is reflected in taking into account the imposition of external disturbances and calculating the conditional probability of

the degree of damage to the system or accounting for the probability of the development of an accident following the failure tree due to possible failures of relay protection and emergency control automatics (Alam et al., 2022).

A regressive factorial model is an extremely generalized form of description of survivability energy systems. Its essence is that it is based on retrospective data to determine shared different factors and their connections to the cause of the beginning and development chain accidents at different depths, shared accidents with an excessively high number of degrees of development, and shared accidents with unsuccessful action anti-emergency automatics. Implementing such an approach may do more justified expert evaluations of settlement influences and rejections concerning those necessary to determine the survivability of the EPS (Yao et al., 2022).

The complex, dynamic nature of the reaction of modern energy unions to resentment and rejection prompts search decision tasks. Analysis of their survivability means imitative modeling, based on which calculations are laid out lasting transitional processes in energy systems. The method also deserves attention when calculating sustainability submission based on annual or seasonal schedule load in the form of equivalent per diem and coverage of these graphics stations. As a result, a seasonal or yearly graph load will be released that (Soni et al., 2022) characterizes the entire spectrum of normal stationary modes. Probability violation emergency stability disconnection line is defined as relationship duration excess admissible under stability overcurrents (Zhong et al., 2023). This approach considers static stability and provides previous definition regimes that are marginal in terms of stability in all respects and intersects, and therefore, is oriented mainly on long ones' energy association.

A method designed for analysis of process development emergencies in concentrated energy systems is as follows. In such systems, the maximum bandwidth ability lines power transmission because of their relatively small length is not determined by a static stability system and is beyond the limits of the transferred one thermal capacity stability elements (Abedi et al., 2022). When this occurs overload, they have turned off protection and the duration of action, which may be calculated as minutes or dozens of minutes. Because load in the system causes overload lines, there are random processes and sequence disconnection lines, which significantly affect development (Parrado-Hernando et al., 2022) accidents, and the consequences are also random. Therefore, instead of a probabilistically deterministic model proposed for research (Agajie et al., 2021) cascading accidents in the power association, which have comparatively weak intersystem connections, developed and used a probable non-stationary mathematical model of electrical long-term load time intervals (up to an hour), using determined probabilities of system transition from one state to another due to emissions overcurrent above a certain level. Note that appropriate imitative modeling is carried out separately from each of the chosen ones' most difficult initiating disturbances, i.e., it is considered a single-rooted tree. Process modeling lasts until it remains in the system branches with overload more than permissible, i.e., before reaching "absorbing" states. As a result of calculation, you can determine that probably not until the holiday electricity as a result of development cascading accidents in the system, and based on analysis of "narrow seats" (min intersections) in graphs of transition states outline measures, thanks to which system with the largest the probability will be to switch to those states which lead to termination further development accident (Avramenko et al., 2011).

The aim of this study is to delve into the issue of energy associations' survivability as a distinctive attribute of complex systems, delineating their capacity to maintain and reinstate fundamental functions even amidst extreme conditions. Additionally, the objective is to establish a comprehensive methodology for scrutinizing the survivability of energy associations through the utilization of simulation modeling techniques.

Materials and methods

The research focuses on power associations, electric power systems, emergency modes, and transitional modes. Simulation modeling serves as the primary research method, understood here as computational experiments conducted on a computer using a digital mathematical model. This model is designed to reflect the properties and features of complex associations in terms of their survivability with necessary completeness and sufficient accuracy for practical purposes. It accounts for all physical processes and emergency control mechanisms essential for accident development, representing major elements of the power association, such as large power plants, load nodes, main power transmission lines, and converting elements (e.g., direct current inserts). The model incorporates a variety of disturbing influences and failures.

The solution involves adequate physical processes, mathematical descriptions, and effective software and computational implementation (Avramenko et al., 2011). Simulation modeling allows for the examination of disturbances and failures in multiple ways: statistically, via pre-defined scripts, or dynamically, with active human participation in the computational experiment. The study focuses on a scenario-based approach to analyze the reliability and survivability of energy associations.

The simplest model of a synchronous machine, which considers its dynamics when calculating electromotive force (EMF) in the EPS but does not explicitly consider electromagnetic processes and automatic excitation regulation, is the representation of a constant EMF machine with some reactivity. In this case, the transient process of the machine is described only by the equation of the mechanical motion of the rotor, which can be written down as

$$\frac{ds}{dt} = \frac{P_t - (P_{el} + I^2 R_g) - K_d S \cdot P_n}{T_j P_n (1+s)} \quad (2)$$

$$\frac{d\delta_E}{dt} = s \quad (3)$$

$$P_{el} = \frac{E_{sm} U \sin(\delta_E - \theta)}{x_{sm}} \quad (4)$$

where s – rotor slip; T_j - inertia constant; P_{el} - electric power (active); P_t - mechanical power (active); P_n - rated power (active); I – electric current of the generator, R_g – resistance of the generator; U, θ - are module and angle with respect to the reference axis (for example, the voltage vector of the balancing node in the calculation of the pre-emergency mode) of the voltage vector at the machine terminals; δ_E is an angle of electromotive force relative to the same axis; E_{sm} is electromotive force; k_{ds} is damping coefficient, intended for simplified consideration of electromagnetic and other damping moments proportional to the deviation of the absolute speed of rotation of the machine rotor; x_{sm} - synchronous machine reaction resistance.

The calculation of the transition process involves taking into account the electrical mode of the power system and its effect on the load in the Unified Power System nodes. The

dynamics equations of individual machines in the electrical network nodes of the power system are numerically integrated separately, one by one, based on the model of individual movement. The use of implicit methods of numerical integration (methods of forecasting and correction) allows you to combine the differential equations of the dynamics of synchronous machines and their excitation and speed control systems with a system of algebraic equations in a complex form that describes the quasi-steady state of the Electric Power System. The apparatus of such unification is the iterative process of calculation of integrated variables at the stage of corrections, which is combined with the iterative process of calculation of the system of nonlinear algebraic equations of the steady-state Electric Power System.

Traditionally, in the calculations of the dynamic stability of the Unified Power System, fast-moving electromagnetic processes in the electrical network and stator windings of synchronous machines are neglected. This leads to the fact that the Electric Power System dynamics model turns into a degenerate system

$$\frac{dX_1}{dt} = F_1(X_1, X_2, t) \quad (5)$$

$$F_2(X_1, X_2) = 0 \quad (6)$$

where X_1 is a vector of variables to be integrated; X_2 is a vector of variables that are not integrated; F_1 is a vector function that characterizes a subsystem of variables determined by numerical integration of differential equations; F_2 is a function that determines the quasi-stationary electrical mode of the Electric Power System at any instant of time t .

Fixing at time t the conductivity of nodal loads according to the static characteristics or slip of an equivalent induction motor, which is an integrated change in the case of using dynamic load characteristics, and using the EMF of synchronous machines, which reflect the electromagnetic state of the machine at time t , leads to the linearization of the system of quasi-steady-state equations:

$$YU = GE \quad (7)$$

where Y is a square symmetric matrix of electrical network conductances; G is the diagonal matrix of the conductances of the generators; U is a column vector of stresses at the nodes; E is the electromotive force column vector of generators.

The solution of the linear system is performed by the method of ordered Gaussian elimination, using an efficient algorithm that takes into account the high sparsity of the conductivity matrix of the electrical network.

As the basic method of numerical integration, the implicit Adams method of the second order is chosen, in which the forecast is made by the Euler method, and the corrections are made by the trapezoidal method.

The method is modified by increasing the order of the prediction and correction formulas for the rotor motion equation (i.e., with respect to the slip s) and implementing the numerical analytical solution for the equations of the machine's electromagnetic state and automatic regulators of excitation and frequency of rotation of generators.

Implementing this approach involves significant challenges, particularly in forming a set of initial modes that accurately reflect the loading of intersystem connections within the Unified Power System (Avramenko et al., 2016; Kuznetsov et al., 2018). This implementation is based

on developed methods and programs for calculating the reliability of parallel power system operations, especially with weak intersystem connections during emergency power imbalances caused by mutual shutdowns of power plants and loaded transmission lines (Baliuta S., Zinkevych P., 2022).

Results and discussion

The operational experience of power systems underscores that within a well-designed and properly operated power system, even the failure of the most critical element (such as the disconnection of a major power unit, busbars, or an overloaded line) constitutes a controlled disturbance and should not precipitate unplanned consequences. Only an accident's cascading, chain-like progression can result in such outcomes, highlighting the system's inadequate survivability.

To elucidate the concept of cascading accident progression, it's essential to consider three distinct types of emergency processes:

1. **Deterministic Cascading Shutdowns** entail successive shutdowns of Unified Power System elements (e.g., lines, transformers) triggered by sequential overloads or the surpassing of protection or automatic settings. The deterministic nature of these shutdowns relies on the physical properties of the system and the characteristics of relay protection and emergency automatic devices. A set of Unified Power System elements that disconnect deterministically form a calculation group of dependent failures.
2. **Probabilistic Cascading Failures:** This involves failures of relay protection, emergency automatics, and switching devices intended to localize the consequences of primary and previous failures. Given the probabilistic nature of these devices' reliability, the corresponding failure chains have a probabilistic characteristic, making this type of accident development probabilistic.
3. **Multiple Failures due to External Influences:** This type is typical for extreme natural events (e.g., hurricanes, thunderstorms, earthquakes) or deliberate actions, where subsequent impacts occur before the consequences of previous ones are resolved. The nature of these influences is highly uncertain.

The behavior of power plants significantly influences the development and exacerbation of accidents, particularly concerning parts that are inadequately controlled by anti-emergency control devices or operate inefficiently in complex emergency modes (e.g., during asynchronous operation). With their increasing share in generating capacity, nuclear power plants impose stringent requirements on electricity quality. Consequently, accidents characterized by increased frequency, especially in cases of UPS separation from the rest of the power association, have become common in power systems with nuclear power plants.

For instance, in one power system containing a nuclear power plant, the disconnection of a power transmission line led to synchronous oscillations lasting 25 seconds and an asynchronous mode concerning the UPS. This event resulted in the system's isolation for isolated operation, causing the system frequency to increase to 52 Hz, leading to the shutdown of nuclear power plant units and sharp frequency decreases, necessitating emergency system operation modes (Baliuta S., Zinkevych P., 2022).

It should be noted that a similar incident also occurred in a highly redundant system powered by a large hydroelectric power plant, albeit due to the failure of emergency automatics. Significant system accidents demonstrate that the emergency shutdown of power units with severe technological process violations at thermal power plants and nuclear power plants complicates their restart and restoration to normal mode, thereby magnifying the

consequences of such incidents. The ability to swiftly restore the scheme and regime of energy systems and power supply to consumers following emergency violations is a key aspect of survivability, and the duration of system restoration indicates UPS survivability. Another factor affecting the survivability of energy associations is the effectiveness of operational dispatch personnel (Kulkarni and Shingare, 2016; Machowski et al., 2008). Correct or incorrect actions, as well as personnel inactivity, can significantly impact accident development and its subsequent consequences. It is worth noting that the growth of energy associations objectively exacerbates the survivability challenge, particularly evident in cascade accidents where the properties of a complex closed system can undergo significant changes, potentially rendering dispatcher actions ineffective based on their experiences under normal conditions.

The methodology for analyzing the survivability of energy associations is based on calculations of transient modes of the Electric Power System. The dynamic nature of the EPS response to disturbances and failures, along with the complexity of transient processes, warrants the use of simulation modeling. At the core of this approach lie calculations of the EPS's transient modes, including long transient processes and self-setting post-emergency modes. Experience from EPS operations and calculations confirms the significant increase in transient process duration in large power plants and the notable spread of emergency disturbances. This necessitates the development of a simulation model based on calculations of long transient processes, not solely focused on dynamic stability.

Another aspect of the simulation modeling challenge lies in the effectiveness of mathematical modeling of the EPS as a complex dynamic object. Certain essential features of the EPS make it practical to utilize the adaptive dynamics model (ADM) of the EPS, which automatically forms EPS models at various transition stages, considering the fundamental nature of movement at each stage. The use of ADM allows for a significant reduction in computational costs without sacrificing decision accuracy, which is crucial for analyzing EPS survivability, which demands numerous transient mode calculations during varying disturbances and failures (Okakwu and Ogujor, 2017; Petinrin and Shaaban, 2016). Furthermore, simulation modeling involves automating computational experiments and processing their results, tasks largely addressed by specialized programs developed at the Institute of Electrodynamics of the Academy of Sciences of Ukraine for analyzing disturbed modes of complex power systems.

The first principle of the methodology for analyzing the survivability of energy associations underscores the necessity of employing simulation modeling, ensuring satisfactory accuracy in representing the dynamics of energy systems and enabling comprehensive accounting of relay protection, emergency control automatics (EA), and switching devices failures through EPS transient mode calculations. The second principle of the methodology involves focusing on an ergastic scenario-probabilistic approach to survivability analysis. This approach entails partially predefining and partially determining during calculation the type, location, magnitude, and sequence of external disturbances and system element failures based on intermediate result analysis by the technologist. The resulting emergency frequency is determined by the frequency of primary disturbances and the probabilities of secondary failures (disturbances), thus concentrating on disturbances and failures of an uncertain nature. Essentially, this approach represents a refinement of UPS reliability analysis methods, considering secondary failures comprehensively and the dynamics of UPS element interaction.

In contrast to existing approaches, our proposed egoistic scenario approach centers on the consideration of system emergency automatics. It anticipates scenarios where, following emergency control automatic (EA) failure, the emergency process evolves in a challenging-

to-predict, formalized manner, initiating EA action in remote areas of the power association, requiring technologist analysis to assign a new failure, determining the energetic and human-technical nature of the situation (Liang, 2017; Dhamanda and Rawat, 2019). EPS survivability is assessed based on a predefined set of disruptive influences, including sudden disconnection of the most powerful generating unit (power unit), group of units, or entire power plant in the receiving system of the power association; disconnection of the most heavily loaded line or the line with the greatest bandwidth in the congested intersection of intersystem connections; occurrence of excess power in the transmission surplus energy system due to disconnection of powerful consumer connections; and disconnection of bus differential protection of all system connections (sections) of buses of a potent nodal substation. The assignment of these disturbances considers the specific scheme-regime situation in the association. As a sequence of disturbances and failures for assessing EPS survivability, scenario formation relies on a retrospective analysis of cascading system accidents and the generalization of their development mechanism. This analysis illustrates a generalized diagram of accident development and localization in energy associations, as shown in Figure 1.

The diagram depicts the failure of switching devices in only one instance, yet switching device failures may accompany any Electric Power System element disconnection. Similarly, repeated short circuits, false activations, and redundant disconnections can occur in any intermediate post-emergency mode. The final post-emergency mode on the diagram represents the established mode meeting technical operation requirements for voltage, frequency, and equipment overloads, serving as the starting point for restoring the power system's normal circuit and mode of operation (reintegration). Modern power units feature a sophisticated emergency management system, with another group of emergency automations serving as backups for individual device failures. For instance, in cases where stability is compromised due to primary fast-acting protection failure or automatic protective device system failures of IPA type (instability prevention automations), the resulting asynchronous mode is addressed by asynchronous mode elimination automations. Automatics intervene to halt accident progression in specific areas, restoring active (or reactive) power balance (automatic unloading by frequency, frequency start of hydro generators, automatics limiting frequency increase, automatics limiting frequency increase or decrease), and supplying power to critical consumers with acceptable parameters. However, there are instances (posing a challenge to Unified Power System survivability) where successive failures of Relay Protection, emergency automation, and circuit breakers form a chain of accidents resulting in significant emergency consumer disconnections. From the perspective of forming scenarios for survivability analysis, both the quantity and severity of failures are crucial. Analysis indicates that in large-scale system accidents, the presence and combination of 3-4 severe failures (considering factors such as the initial mode's reduced stability margin due to dispatcher instructions to increase flows or unscheduled equipment repairs) significantly impact the scenario's severity.

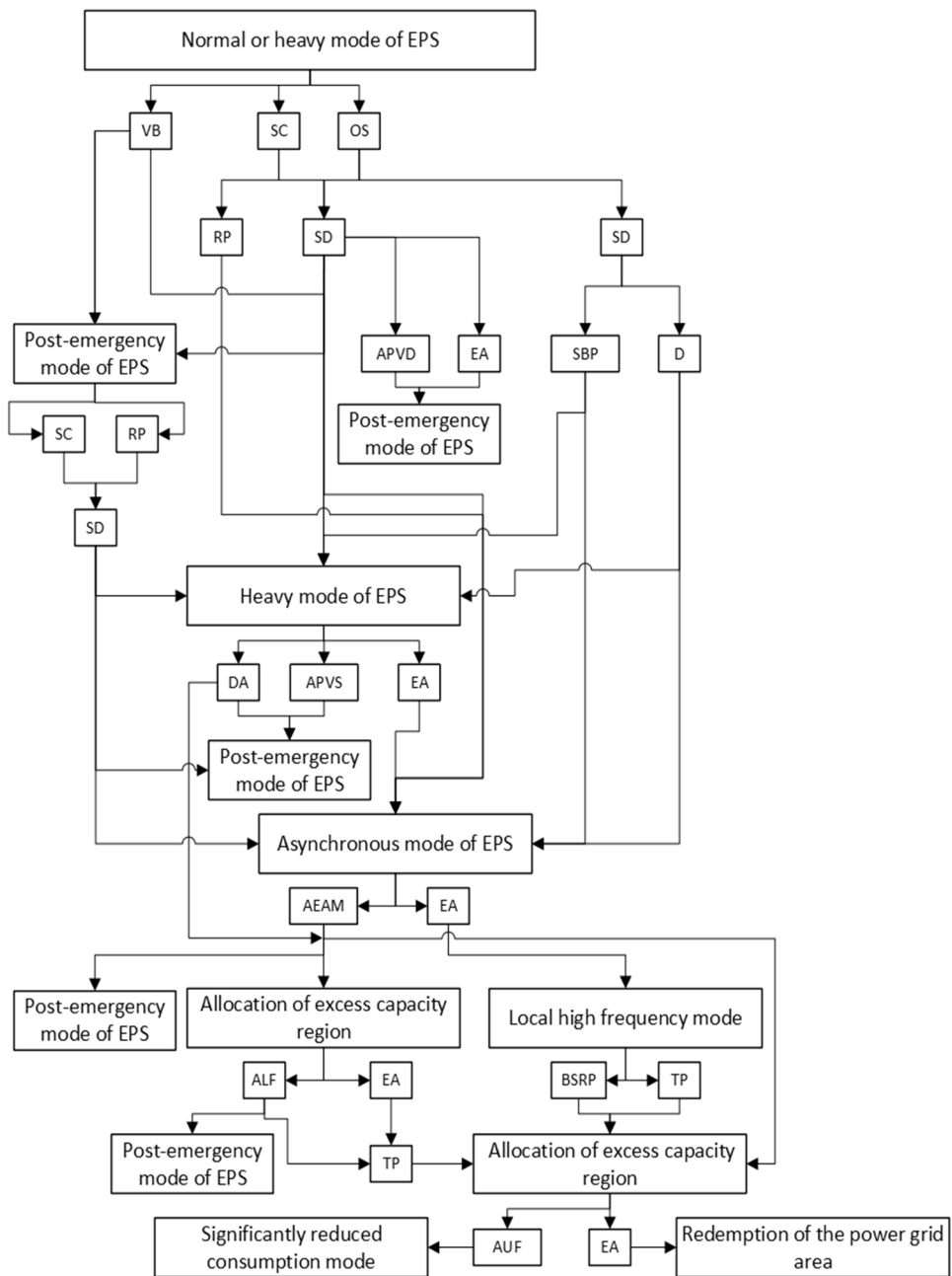


Figure 1. Scheme of accident development and localization in energy associations.

Marking in the Figure 1:

- VB, violation of the balance of active power in the system due to loss of generating power, disconnection of the external intersystem line, or heavy load;
- SC, short circuit, on EPS elements;
- OS, operation system (RP, relay protection, EA, emergency control automatic, operational personnel), failures of which lead to the disconnection of lines;
- RP, relay protection, failure of RP and EA type of erroneous or unnecessary disconnection of EPS elements;
- SD, switching devices;
- D, failure of the circuit breaker failure backup device;
- APVD, automatic for preventing violation of the dynamic stability of the UPS, which affects the disconnection of part of the generators, electrical braking of the generators, as well as the emergency power management of steam turbines;
- APVS, automatic for preventing violation of the static stability of the EPS, which includes automatic unloading and loading of power plants and special automatic load disconnection and provides unloading of intersystem connections;
- DA, dividing automatic, divides the power pool into electrically unconnected non-synchronous parts in the event of exceeding the overcurrent at the intersection of the specified value;
- AEAM, automatic elimination of asynchronous mode, which prevents or terminates such mode by dividing the scheme into non-synchronously working parts;
- ALF, automatics of limiting the increase of frequency, which affects the disconnection of part of the generators;
- AUF, automatic unloading by frequency;
- BSRP, backup sets of relay protection or automatics;
- TP, technological protections, of power plants, leading to disconnection of generating equipment.

The proposed scenario for analyzing the survivability of energy associations focuses on severe failures, including:

- A primary disturbance of significant magnitude leading to stability violation or a decrease in cleanliness in the segregated area, possibly combined with a large output load mode or other failures.
- Failure of one of the main protections.
- Failure of one of the main switches.
- Rejection or absence of instability prevention automatics.
- Rejection of the asynchronous mode elimination automatic.
- Failure or insufficiency of automatic unloading by frequency.
- Serious errors by operational dispatch personnel, equivalent in consequences to the failures mentioned above.

To form this scenario, it is suggested to rely on the most reliable statistical information about cascading accidents, considering three consecutive failures in the chain, including a generalized failure (such as deterioration of the initial mode leading to decreased stability reserves or significant weakening of the scheme) as a standard. The application location and type of primary disturbances, as well as the second rejection, are determined by the

technologist for implementing calculations of electromechanical transitional processes. The task involving the third rejection typically requires calculating transitional processes under the given conditions of two rejections and identifying specific emergency control automatic devices (most often asynchronous mode elimination automatics) expected to function simultaneously. The technologist selects the refusals likely to result in the most serious consequences and repeats the calculation with three refusals. This approach results in a multi-rooted rejection tree, with different roots corresponding to various primary disturbances and branches reflecting potential paths of accident development based on the identified refusals.

Conclusions

The methodology for analyzing the survivability of power associations has been presented, with its primary principle being the use of simulation modeling based on calculations of transient states of the Unified Power System. This ensures satisfactory accuracy in representing the dynamics of electrical power systems and allows for the consideration of relay protection failures, emergency automation, and switching devices. This methodology is oriented towards an ergodic scenario-probabilistic approach to survivability analysis and, unlike those discussed in the literature, has the advantage of adapting to the changing structure and operational conditions of the Unified Power System of Ukraine during wartime. This is achieved by utilizing the most adequate mathematical models of elements, which are implemented in software packages for analyzing Unified Power System operating modes.

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Materials and methods briefly describe the materials and methods used in the study (3-5 lines).

Results and discussion describe the main findings (23-26 lines).

Conclusion provides the main conclusions (2-3 lines).

The abstract should not contain any undefined abbreviations or references to the article.

Keywords. Immediately after the abstract provide 4 to 6 keywords.

Text of manuscript

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Introduction. Provide a background avoiding a detailed review of literature and declare the aim of the present research. Identify unexplored questions, prove the relevance of the topic. This should be not more than 1.5 pages.

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Ivanov V., Shevchenko O., Marynin A., Stabnikov V., Gubenia O., Stabnikova O., Shevchenko A., Gavva O., Saliuk A. (2021), Trends and expected benefits of the breaking edge food technologies in 2021–2030, *Ukrainian Food Journal*, 10(1), pp. 7-36, <https://doi.org/10.24263/2304-974X-2021-10-1-3>

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Mendeley, J.A., Thomson, M., & Coyne, R.P. (2017), *How and when to reference*, Available at: <https://www.howandwhentoreference.com>

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Arych M. (2018), Insurance's impact on food safety and food security, *Resource and Energy Saving Technologies of Production and Packing of Food Products as the Main Fundamentals of Their Competitiveness: Proceedings of the 7th International Specialized Scientific and Practical Conference, September 13, 2018*, NUFT, Kyiv, pp. 52–57.

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Мінімальний обсяг статті – **10 сторінок** формату А4 (без врахування анотацій і списку літератури).

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