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Original scientific paper

DEVELOPMENT AND USE OF COMPOSITIONS FROM PRODUCTS OF DEEP PROCESSING OF SECONDARY MEAT RAW MATERIALS

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Abstract
The development of protein ingredients based on the composites from secondary collagen-containing meat raw materials and obtained by the methods of deep processing attracts increasing attention of specialists.
In the presented work, the composite and mass composition of the protein ingredient from hydrolysates of beef hide split, pork skin and blood plasma in a ratio of 45:45:10 was established. The improved amino acid composition of the protein ingredient due to addition of dry blood plasma suggests an increased biological and nutritional value of the developed product. Addition of up to 15 % of the protein ingredient instead of beef in the technology of minced semi-prepared products improves the rheological and organoleptic characteristics of the finished product.

Introduction

The main direction in processing of agricultural raw materials is an increase in efficiency of present-day production, the development of non-waste technologies of animal raw material processing and involvement of the secondary raw material resources into the commercial-economic turnover.

At present, specialists and technologists of the meat industry pay close attention to a search for new methods for processing of secondary raw materials that remain in the meat processing industry for their more effective use in production of high quality meat products.

The rational use of proteins of collagen-containing raw materials makes it possible to solve many questions of meat production, namely: to compensate a deficiency of soluble proteins, to reduce prime cost of the finished products without a decrease in the nutritional and energy value, to increase the yield of the finished product and to stabilize quality with simultaneous reduction of meat raw material expenditure [1].

The main direction in the rational use of collagen-containing raw materials from the slaughter products of the meat industry is their transformation in order to obtain protein ingredients of different fractional compositions for further use in meat product manufacture.

Nowadays, collagen proteins entering meat processing enterprises are presented by an insignificant number of domestic manufacturers. At the territory of the Russian Federation, the protein containing components of foreign manufacturers or their mixtures are mainly sold by the representatives of different manufacturing organizations and, often, the prices on these protein ingredients are much higher than the prices on the domestic products; however, it is necessary to note that functionality of the preparations from the Russian manufacturers in not inferior to the foreign samples. The proportion of import of collagen proteins both as «pure» mono-ingredients and in the composition of complex food additives or the constituents of the brine preparations exceeds 56 % in volume terms [2].

Taking into consideration an increasing demand of the meat industry for the collagen proteins, the negative attitude of consumers towards plant ingredients in meat products and evolving instability of import supply of food ingredients as a result of the economic sanctions, organization of the system approach in the domestic competitive sector of protein production from secondary products seems to be vitally important.

The fundamental trend in the modern consumer market of food development specified by PNST 329–2018 «green standards» is creation of new food ingredients, which demand is oriented towards the ultimate customer. To this end, the ready complex decisions are necessary including problems regarding the rational use of raw material (meat) components and creation of protein ingredients and their mixtures obtained upon secondary raw material processing [3].

Of particular importance in the use of complex food additives under the conditions of present-day production of meat products is the wide application of protein preparations that significantly affect organoleptic indicators (color, taste, aroma of products) and functional-technological, rheological indicators (brine viscosity, finished product yield, consistency, elasticity, bite properties, strength and so on). For example, the systems based on the connective tissue proteins increase hydration of meat proteins, their

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emulsifying capacity or capacity to bind and hold water and fatty raw materials.

Today, the agro-industrial sector of the Russian economy faces a systemic challenge that predetermines the necessity to update and improve scientific-informational, technical and technological base of the agro-industrial complex on the qualitatively new basis, and the necessity to transfer to an innovative type of the development.

The state program of the development of the agro-industrial complex for the period up to 2024, envisages the most rational use of all types of resources of the food industry; a special attention should be paid to processing of secondary raw materials in the sphere of the agricultural complexes. It is also important to note that the specific weight of raw materials of animal origin in prime cost of the finished products achieves about 60 %, which suggests an importance of its commercial use. The expedient use of secondary raw materials of the meat industry is important as it allows solving problems of the development of non-waste ecologically pure and safe technologies in the continuous commercial conditions [1].

Collagen fibers, which form all types of the connective tissue, support general physical and structural integrity of the body and take part in protective, metabolic and receptor functions.

Collagen prevails in derma, cartilages, bones and vessel walls. Collagen constitutes about 30 % of total protein mass in mammals, and cutaneous covering accounts for about 40 % of it [4,5]. Collagens of cutaneous covering contain large concentrations of proline and oxyproline (about 20 % of the sum of all amino acid residues), glycine and alanine (more than 50 % of the sum of all amino acids) [4].

Healthy people, as a rule, do not show a deficiency of nonessential amino acids (proline and oxyproline). For gerontological patients and people with disorders of collagen metabolism of different types, regular intake of amino acids that are contained in collagen at the maximum level is vitally important.

Therefore, investigations aimed at the development of protein ingredients with multicomponent composition and increased amino acid content seems to be topical.

The aim of this work was the development of a protein ingredient obtained from a mixture of collagen containing secondary products of the meat industry and its use in the technology of minced semi-prepared products.

The main task of optimization, as a rule, consists in obtaining full-value formulations in terms of the amino acid composition; that is, no amino acid should be limiting regarding the reference — the «ideal protein» according to the FAO/WHO scale.

Moreover, to develop a protein ingredient, it is necessary to detect its constituent fractions, their percent ratio in a formulation, an amino acid composition, a proportion of a formulation and its effect upon adding into forcemeat systems of meat products. It is also necessary to study properties and indicators of the meat formulation system and products made with its use.

Objects and methods

The formulation of the protein ingredient contained dry blood plasma (Veos, Belgium) and dry hydrolysates of beef hide spit [6], pork skin [7], obtained in the laboratory conditions by nonenzymatic hydrolysis with the protein mass fraction of 97.2 % and moisture of 2.8 %. Hydrolysates were dried in a drying unit with counter-swirling flows of inert bodies [8]. After preparation and comminution of meat raw materials, the protein ingredient (instead of the main raw material — beef) and additional water were introduced during forcemeat mixing. Prepared forcemeat was supplied to the forming equipment and formed patties were frozen to the end medium-volume temperature of –18 °C. Frozen patties were fried and the functional-technological and organoleptic indicators were determined in the finished product after thermal treatment. The protein ingredient with an improved amino acid composition and minced semi-prepared products were produced and the finished product was analyzed in the pilot production shop of the technological center of KT «OOO Stern Ingredients».

The amino acid content in the hydrolyzed split and pork skin was determined after specific sample preparation [9] by the method of reversed-phase HPLC using a liquid chromatograph Shimadsu LC–20 Prominence (Japan) with UV detection (254 nm). The chromatographic column 250x4.6 mm, Supelco C18 5 μm (USA) was used. In calculation of the content of essential amino acids in dry blood plasma and its amino acid score, the data on the amino acid content (in %) to blood protein were used.

The mass fraction of moisture in raw materials and finished products was determined by the method of drying to constant mass [10].

The mass fraction of protein was measured by the Kjeldahl method [11].

The mass fraction of fat in forcemeat was measured by the reflectometric method with α- monobromnaphtalin by the method of VNIITeK, a branch of the Gorbatov Research Center for Food Systems [12].

Moisture holding and moisture binding capacities were determined by the centrifugation method [13].

Organoleptic assessment of the minced semi-prepared product made with different proportions (10, 15, 20 %) of beef replacement with the protein ingredient was carried out by the profile method and assessed by 5-point scale [14]. Twenty respondents took part in the assessment, among them were 12 males and 8 females at the age of 20 to 35 years. All respondents had the technological education and possessed knowledge of meat and meat product technology.

Ultimate strength was measured on the apparatus of the Valenta type by rupturing the surface of the minced semi-prepared products with changing masses of weights. The parameter was calculated taking into account half of the mass of the total load and a table, g/cm^2:

The modulus of elasticity was determined using the consistometer and calculated by the equation:

$$E = \frac{(M_{gr} + M_{st})g}{S \cdot E},$$

where, M_{gr} — critical mass of the load determining rupture, kg; M_{st} — mass of a table, on which a sample was placed, kg; g — free fall acceleration, m/s^2; S — area of a sample, m^2; $S = \Pi D^2/4$, where D — a diameter of a sample, mm; E — relative deformation; $E = \sigma/H$, where σ — readings of the indicator, mm; H — thickness of a sample, mm. M_{gr} =0.1 kg; M_{st} = 0.027 kg; G = 9.81 m/s^2.

Shear force was measured in a product sample that had a shape of a rectangular parallelepiped 10x10x40 mm. A sample was placed on the platform of the instrument with the long side along the string. The string fixed on the carriage was placed on the product surface (longitudinally). After that, the platform of the carriage was gradually loaded with weights. The mass of weights, at which the string began to cut a product, was fixed. The mass of the carriage (52 g) and a diameter of the cutting string (1 mm) were taken into account upon calculation.

Shear force P (Pa) was determined by the equation:

$$P = \frac{(M + 0.052) \cdot g}{L \cdot D},$$

where, L = 0.05 m — the length of the wire; D = 0.01 m — the diameter of the wire; g = 9,8 м/с^2 — free fall acceleration; M — mass of weights, kg.

Results and discussion

The strong covalent bond is observed in the primary and quaternary structures of collagen. The secondary and tertiary structures are linked by the non-covalent interactions, which are much weaker. In the tissues, collagen fibrils achieve the large size forming collagen fibers, for example in tendons and derma, or homogeneous mass of their microfibrils as in cartilages [4,15]. This peculiarity of collagen structure is necessary to take into account when developing methods for deep processing of secondary raw materials to obtain ingredients with a given composition and properties [6].

The amino acid composition of secondary products is presented by amino acid oxiproline, which is characteristic for the connective tissue, while tryptophan and cystine, which are characteristic of any muscle tissue, are absent. The average content of amino acids in the hydrolysates of secondary products (per 100 g total protein) is shown in Table 1.

It can be seen from the analysis of the values presented in Table 1 that the essential amino acid (EAA) content in pork skin was 14.00 g/100 g protein. This was 1.32 lower than the EAA content in beef split.

Table 1. Amino acid composition of collagen in beef split and pork skin

Amino acid	Content g/100 g protein in pork skin	Content g/100 g protein in beef hide split
Essential amino acids (EAAs):		
Isoleucine	1.46	1.88
Leucine	2.80	3.73
Lysine	2.40	3.95
Methionine + cysteine	1.24	0.97
Phenylalanine + tyrosine	2.40	3.34
Threonine	2.00	2.26
Valine	1.70	2.47
Total:	14.00	18.60
Nonessential amino acids:		
Alanine	4.10	10.32
Arginine	3.88	8.22
Aspartic acid	3.90	6.95
Histidine	1.15	0.70
Glycine	16.71	26.57
Glutamic acid	6.58	11.16
Serine	2.15	4.27
Proline	5.50	12.8
Oxyproline	11.43	12.81
Total:	55.4	93.80

It is also important to note that collagen of beef hide has the high content of proline and hydroxyproline. Hydroxyproline is not found in such high amounts in any other protein except elastin. Proline occurs in collagen, largely, in the sequence glycine-proline-X, where X is often presented by alanine or hydroxyproline. Collagen does not contain cystine or tryptophan, and the presence of oxyproline and oxylysine noticeably differentiates it from other proteins in living organisms (these amino acids do not occur in the composition of other proteins). The role of these amino acids is exceptionally important in stabilization of the triple-helical conformation of the collagen molecules [4,16].

The sum of essential amino acids is about 22 % of all collagen amino acids. However, the mass fraction of methionine, tyrosine and histidine is very low, while tryptophan, cystine and cysteine are absent; therefore, the nutritional value of collagen of surface covering is low as well as of collagens that are constituents of other organs and tissues.

The unique properties of collagen allow developing highly functional protein ingredients that begin to gain the largest popularity in meat product manufacture as protein ingredients of animal origin have high values of moisture holding and fat holding capacities, moisture binding capacity and functions of emulsifying agents, which is very important for production of high quality foods [5] with high indicators of both technological and consumer properties of the finished products.

Each year, the question is raised regarding effective processing of secondary raw materials of the meat processing and agricultural industries, which is directed towards solving the ecological tasks, extending food assortment and increasing the production volumes of domestic protein ingredients and their advancement on the Russian market of additives with the aim of active competition with import production. It is important to note that secondary products (beef tendons, beef hide split and pork skin), which are rich in collagen, are the main source for commercial production of protein ingredients of animal origin. For example, by the end of 2016, the volume of pig husbandry products was about 4,500 thousand tones, and if we consider the yield of skins of about 8% of carcass weight, then the secondary resources will be 360 thousand tones, which should be a driving force for their processing and a new stage in production of domestic stabilizing protein systems for products of economy, middle and premium segments [3].

In designing a fractional composition of the protein ingredient, different ratios of hydrolysates of beef split and pork skin were used. The best variants of ratios were determined by the value of ultimate strength of the forcemeat system, which showed that the maximum values were achieved at a ratio of the hydrolysate formulation from beef split and pork skin of 1:1.

The content of essential amino acids in the hydrolysate formulation and the calculated amino acid score are presented in Table 2.

Table 2. The content of essential amino acids (mg/g protein) in the hydrolysate formulation of beef split and pork skin and its amino acid score

Amino acid	EAA content, m/g protein	FAO/WHO	Amino acid score
Leucine	32.6	70	0.46
Lysine	65.4	55	1.18
Methionine + cystine	23.4	35	0.66
Phenylalanine + tyrosine	33.1	60	0.55
Threonine	21.9	40	0.54
Valine	34.9	50	0.69
Isoleucine	19.3	40	0.48
Tryptophan	—	10	—

However, in the mixture of hydrolysates with the composite ratio of 1:1, the low content of isoleucine, leucine and threonine, and complete absence of cystine and tryptophan was noticed. Therefore, taking into consideration the values of amino acids and their amino acid score, for creation of a protein ingredient, it is necessary to compensate its composition with additional components (for example, dry blood plasma) to increase its biological value.

Based on the amount of essential amino acids (in %) with respect to blood protein [13], their content in dry blood plasma and amino acid score were calculated, which is shown in Table 3.

It can be seen from the analysis of table 3 that dry blood plasma is a source of essential amino acids and their content is higher than the norms for «reference» protein, which are specified by the requirements of FAO/WHO. Therefore, blood plasma can be used for enrichment of the biological value in a formulation with hydrolisates of hide split and pork skin.

Table 3. Content of essential amino acids (mg/g) in dry blood plasma and their amino acid score

Amino acid	Content of EAAs, mg/g protein formed from the sum of albumins, globulins and fibrinogen	Amino acid score
Teucine	108.4	1.54
Lysine	98.8	1.79
Methionine + cystine	52.1	1.49
Phenylalanine + tyrosine	114.3	1.91
Threonine	67.5	1.69
Valine	73.8	1.47
Isoleucine	25.7	0.64
Tryptophan	19.1	1.91

The calculated content of essential amino acids of the protein ingredient and its amino acid score are presented in Table 4.

It can be seen from the data in Table 4, than upon addition of 50 % of dry blood plasma, it was possible to approximate the amino acid content to the «reference» protein and partly compensate for the absence of tryptophan

Table 4. Content of essential amino acids and amino acid score of the protein ingredient of different formulations

Amino acid	Protein ingredient composed of 90 % of hydrolysate mixture and 10 % of dry blood plasma		Protein ingredient composed of 80 % of hydrolysate mixture and 20% of dry blood plasma		Protein ingredient composed of 50 % of hydrolysate mixture and 50 % of dry blood plasma	
	EAA content, m/g protein	Amino acid score	EAA content, m/g protein	Amino acid score	EAA content, m/g protein	Amino acid score
Leucine	40.18	0.57	47.76	0.68	70.50	1.00
Lysine	68.74	1.25	71.08	1.29	82.10	1.49
Methionine + cystine	26.27	0.75	29.14	0.83	37.75	1.08
Phenylalanine + tyrosine	41.22	0.68	49.34	0.82	73.7	1.23
Threonine	26.46	0.66	31.02	0.78	44.7	1.11
Valine	39.79	0.79	42.68	0.85	54.35	1.08
Isoleucine	19.94	0.50	20.58	0.51	22.5	0.56
Tryptophan	1.91	0.19	3.82	0.38	9.55	0.95

and low content of isoleucine, leucine and cysteine in the mixture of the protein ingredient. The further increase in the proportion of dry blood plasma will lead to a significant increase in prime cost of the protein ingredient and finished product.

At the second stage, the functional-technological indicators and structural-mechanical characteristics were studied in the minced semi-prepared products made with addition of the protein ingredient into the forcemeat system to replace 10, 15 and 20 % of meat raw material (beef). The protein ingredient contained meat hydrolysate from beef split, pork skin and blood plasma in a ratio of 45:45:10. A sample that did not contain the protein ingredient was used as the control.

The main raw materials for preparation of the minced semi-prepared product were chilled beef of the first grade under GOST R 52601–2006; chilled trimmed semi-fat pork under GOST R 53221–2008; protein-fat emulsion in a ratio of 1:10:15 (1 — an emulsifying agent, 10 — pork speck and 15 parts of water). Edible salt, edible chicken eggs, black powdered pepper, powdered allspice, rusk flour and food grade phosphates Carnal 2110 (Budenheim) were used as food ingredients. The recipe of the control sample of the semi-prepared products is presented in table 5.

Table 5. Recipe of the semi-prepared product

Raw materials	Amount, kg/100 kg:
Beef of the first grade	40.00
Semi-fat pork (80/20)	25.00
Protein-fat emulsion 1:10:15	12.00
Chicken eggs	1.20
Chopped onion	4.70
Edible salt	1.20
Black powdered pepper	0.15
Powdered allspice	0.05
Rusk flour	3.70
Water/ice	12.00

Investigation of the properties of raw forcemeat for minced semi-prepared products with the added composite mixture was carried out at a temperature of 4°C. The data on the composition, moisture holding capacity (MHC) and forcemeat strength are presented in Table 6.

Table 6. Properties of raw forcemeat for minced semi-prepared products at a temperature of 4 °C

Proportion of replacement of meat raw materials with the composition mixture,%	Components, %			MHC, %	Strength, g/cm²
	moisture	protein	fat		
0 %	71.5	12.5	17.1	63.1	53.0
10 %	70.8	11.7	16.3	64.9	57.5
15 %	70.5	11.5	15.9	65.8	58.4
20 %	69.3	11.0	15.7	67.2	59.1

Analysis of the values of the presented indicators of the control and the experimental samples of the minced semi-prepared products shows that MHC and the forcemeat strength increased correspondingly to a proportion of protein ingredient addition. Due to the higher MHC in the forcemeat samples with replacement of part of meat raw materials, the finished (thermally treated) semi-prepared products had lower frying losses. An increase in moisture of the fried samples of the minced semi-prepared products led to the juicier product.

After thermal treatment, ultimate strength, modulus of elasticity and shear force depending on an amount of meat raw materials replaced with the protein ingredient were measured in the samples of the minced semi-prepared products. The data are presented in Figure 1, Figure 2 and Figure 3.

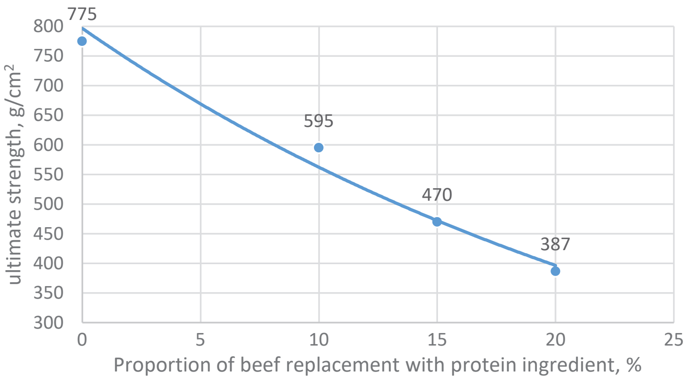

Figure 1. Dependence of ultimate strength in the minced semi-prepared product on the level of beef replacement with the protein ingredient

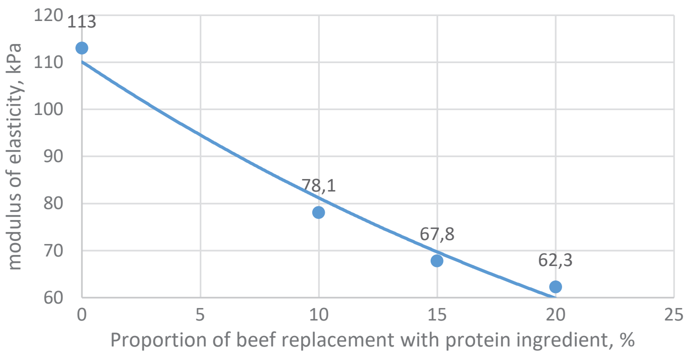

Figure 2. Dependence of modulus of elasticity in the minced semi-prepared product on the level of beef replacement with the protein ingredient

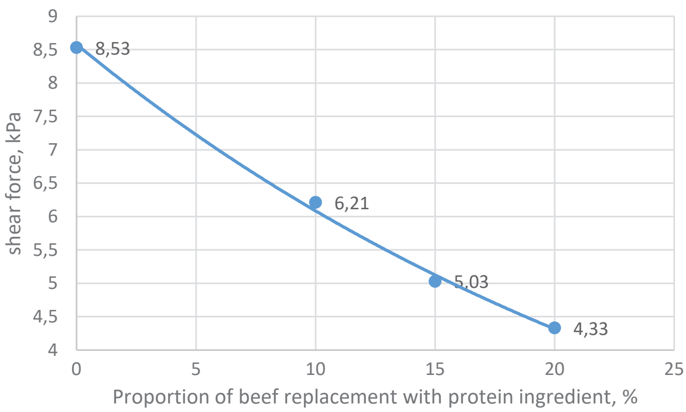

Figure 3. Dependence of shear force in the minced semi-prepared product on the level of beef replacement with the composite mixture

Modulus of elasticity and ultimate strength of the patty samples decreased with an increase in the dose of the added protein ingredient. This is indicative of an increase in tenderness and juiciness of the finished product. However, upon addition of more than 15% of the ingredient instead of beef, the values of modulus of elasticity in the finished product significantly decreased regarding the values of the control samples. A significant increase in looseness and deterioration of patty quality were noticed. When a dose of addition of the protein ingredient increased, the shear force values in the finished product samples reduced; that is, the product became more tender and softer. Upon replacement of more than 15 % of beef with the protein ingredient, the values of shear force in the experimental samples decreased with regard to the values of the control sample; with that, the patties had the crumbly texture.

Organoleptic investigations of the samples are presented in Figure 4. It was also noticed that all samples of the semi-prepared products had odor that was characteristic of the high quality raw materials, an oval shape, a surface without irregular and ruptured edges and homogeneously breaded with wheat rusk flour. On the cut surface of the finished product samples, the homogeneous distribution of well mixed forcemeat and the absence of any lumps of dry carriers were observed; it was noticed that all samples had pleasant aroma of spices. Upon increasing a percent of protein ingredient replacement, consistency of the finished product became crumbly and spreading. The best samples were the finished products with the mass fraction of replacement equal to 15 %. An increase in addition of up to more than 15 % can be considered inexpedient.

Reduction of price of the control recipe for a meat semi-prepared product with maintenance of its functional properties is a priority for a producer.

Figure 5 presents the data on prime costs of the recipes under investigation

Reduction of the recipe price by 7–12 % was achieved upon replacement of 10–20 % of meat raw materials, respectively. This also reduced prime cost of the finished product.

Conclusion

The performed investigations showed that in the protein ingredient with the complex formulation, which con-

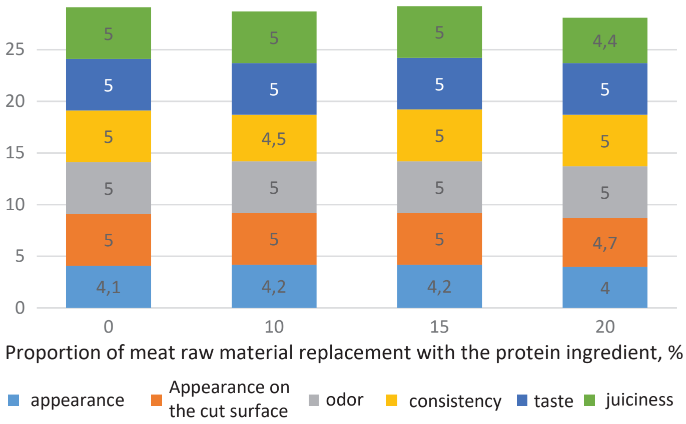

Figure 4. Organoleptic assessment of the minced semi-prepared products with different replacement of meat raw materials with the composite mixture

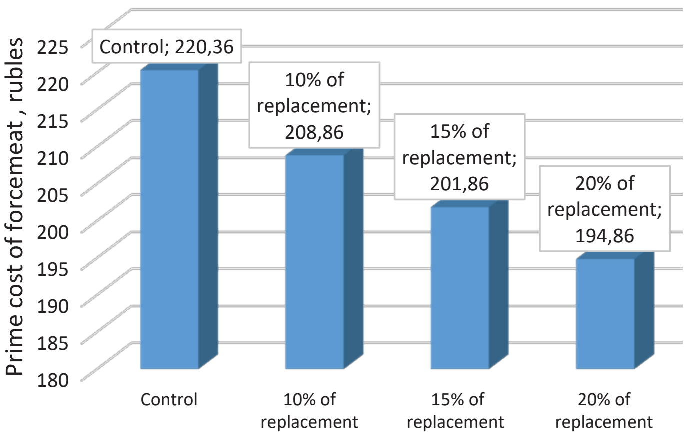

Figure 5. Prime cost of the recipes for patty production with replacement of the main raw materials with the protein ingredient

tained hydrolysates of beef hide split, pork skin and dry blood plasma in the percent ratio of 45:45:10, an amount of essential amino acids approximated the «reference protein» according to the FAO/WHO norms. This composition has the high biological value and emulsifying abilities due to blood plasma proteins, mainly albumins, and high functional-technological properties and rheological characteristics due to hydrolysates of the mixture.

Analysis of the quality indicators of the minced semi-prepared products made with the use of the composite mixture showed that replacement of 15 % of meat raw materials with the composite mixture was the best; product consistency became more tender and juicier and at the same time less loose compared to the control sample.

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