

Conference Paper

Technology of Minced Fish Canned Food from Thorny Skate, Enriched with Chondroitin Sulfate

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Abstract

The article presents the results of theoretical and experimental research on the development of technology of functional minced fish canned food. Study of consumer preferences and the market of canned fish in the Murmansk region allowed to determine the range of novelties such as canned fish ("Skate and cod in white sauce" and "Meatballs made from skate and cod in tomato sauce"), enriched with chondroitin sulfate (CS). The use of thorny skate's (a fish that lives in the North Atlantic and the Barents Sea) wings meat for canning purposes enriches the composition of canned food. The content of CS in one can of canned food with net weight of 250 g ranged from 550 to 700 mg. This guarantees the intake of human body from 78 to 100% of the daily rate of this powerful chondroprotector. To remove urea from the skate's meat, the method of infrared blanching is proposed, which ensures the efficiency in removal of urea at over 70% of its initial content in fish. Infrared blanching allows not only saving raw materials from unpleasant smell, but also partially removing water from it (water losses are from 8 to 13%). Partial dehydration of raw materials allows avoiding formation of water sedimentation in ready-made canned goods after sterilization. With the help of the fuzzy logic method, the MatLab program determines the optimal formulations of canned food, which guarantee their best consumer properties. The Ellab device has been used to experimentally select sterilization modes, which guarantee industrial sterility of canned food, hence the actual sterilization effect is higher than the standard one. During the two years of research, experimental studies of organoleptic properties, microbiological and biochemical changes in canned food were carried out, which made it possible to establish the shelf life: one year at a storage temperature not exceeding 20 °C.

Keywords: technology, functional canned food, fish minced meat, thorny skate, chondroitin sulfate, recipe, sterilization mode

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1. Introduction

Currently the thorny skate (*Amblyraja radiata*) is the most promising object of fishing in the Barents Sea according to many experts [1–4]. The main factors that inhibit the

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active fishing of thorny skate nowadays are the insufficiently reliable forecast on the commercial stock of fish and low demand for frozen products from the skate's meat in the domestic market of the Russian Federation. The last of the listed factors is caused by weak development of technologies in processing fish into food, fodder and technical substances and lack of traditions for consumption of this fish in Russia.

The most complete study of the thorny skate is carried out by scientists of the Polar Institute of National Regional Oceanography (PINRO) and the Murmansk State Technical University in the early 90s. The results of the study proved a high protein content in the edible part of fish (wings), a complete amino acid composition of the protein (1992 -- 1996) [5]. Subsequent studies have confirmed the high content of chondroitin sulfate (CS) in the thorny skate, as in other cartilaginous fish [6--9] -- a substance that can have a chondroprotective effect on the human body (2014 -- 2015) [10--12].

Taking this into account, the involvement of the thorny skate in the production of foodstuffs enriched with CS, and the development of technologies of functional products from the thorny skate is an urgent goal of research. In order to achieve this goal, the article solves the problems of substantiation of the method of effective urea removal, development of the recipe, technology and mode of sterilization of minced multi-component canned food, as well as the hygienic justification of the shelf life.

2. Methods and Equipment

2.1. Methods

The work uses modern research methods:

- marketing -- consumer preferences and demands for canned fish were studied by means of anonymous written survey of more than 250 respondents of different sexes, age groups and income levels;

- organoleptic -- the determination of organoleptic properties of canned meat was carried out by means of extended tasting by specialists using the developed scales, the results of tasting after statistical processing were presented in the form of profiling programs;

- physical -- development of modes of sterilization of canned meat with the help of "Ellab" device;

- physic-chemical --

- mass fraction of water, fat -- by weight method;

- mass fraction of total nitrogen (TN) and nonprotein nitrogen (NN) were determined by Kjeldal method on Selecta Bloc Digest apparatus and Pro-Nitro A unit; before mineralization in the sample, trichloroacetic acid (TCA) protein deposition was carried out on NN with subsequent filtration; protein content in fish was found by multiplying the difference between TN and NN by 6.25;

- mass fraction of urea -- spectrophotometric method after color-forming reaction of urea in the water extract from the product (after the deposition of TCA proteins in it), with flame retardant in acidic medium in the presence of diacetylmonooxime;

- the mass fraction of chondroitin sulfate (CX) was determined by the Dichet spectrophotometric method, which is based on the colored reaction of uric acids with carbazole;

- the amino acid composition of the finished product protein is based on high-performance liquid chromatography;

microbiological -- safety indicators (industrial sterility of the canned food) were determined in accordance with the regulatory documents of the Russian Federation (Technical Regulations of the Eurasian Economic Union TR EAES 040/2016) by standard methods; detection of botulinum toxins and *Cl. Botulinum*, *Bacillus cereus*, *Cl. Perfringens* -- standard methods;

mathematical -- the results of the experiments were processed using standard statistical methods via the Excel program, the optimal recipe composition of canned meat from the thorny skate was determined using the Fuzzy Logic Toolbox module included in the MatLab package.

3. Results

It is known that urea easily decomposes at temperatures above 65°C, which leads to the preliminary heat treatment (PHT) of the wings of the thorny skate for its removal. It is possible to perform the fastest heating of the skate's wings to the required temperature using electro-physical methods of heating, among which infrared heating (IR heating) is recognized as the most effective method [13]. Considering this infrared blanching of the wings of the skate can be the best way to reduce the mass fraction of urea.

The task of the research at the initial stage was the development of the design parameters of the IR blancher, namely, the choice of the type of IR-emitter, and the determination of the optimal distance from the radiator to the surface of fish.

To carry out PHT experiments on the wings of the skate, an infrared radiator with following parameters was used: hemispherical infrared lamp with a reflector, power of 1.0 kW, measured heat flux in the focal spot 800 W/m^2 , the maximum wavelength of the radiation of the infrared lamp (calculated on the basis of the value measured by the pyrometer temperature of the radiating surface) 5.63 microns, which corresponds to the maximum absorption of the fish surface.

The experiments were carried out on thorny skate caught in the Barents Sea, homogeneous in chemical composition and dimensional-mass characteristics. The conditions of the experiment are presented in Table 1.

TABLE 1: Characteristics of the thorny skate's wings.

Weight of the whole fish, g	
1112.6 ± 0.9	
Skate's wings, % of the whole fish mass	
28.37 ± 0.67	
Chemical composition of the muscular tissue of the skate's wing, %	
Water	79.20 ± 1.76
Protein	17.63 ± 0.56
Fat	0.38 ± 0.08
Urea	1.2 ... 1.3
Specific surface of the skate's wings, m^2/kg	
0.25 ... 0.50	
Wing thickness, mm	
6 ... 25	

The distance from the IR emitter to the fish surface of 80 mm, established experimentally, allows quickly (within 3 to 10 minutes depending on the color of the wing surface, dark or light side) reaching the temperature of 58...75 °C in the centre of the skate's wing. Short-term heating of the skate's wings facilitates their further processing (skin removal and separation of meat from cartilage). Losses of mass during infrared blanching are ranging from 2 to 8%, which is enough to prevent water settling in canned food after sterilization.

The effectiveness of IR blanching was judged by the change in the urea mass fraction after PHT. The results of the experiments are presented in Table 2.

According to the results of the experimental study of the thermal kinetics of the skate's wings under different modes of IR blanching, the selection and justification of the industrial generator of IR radiation (KGT-220-1000), which meets the requirements of the process of PHT established experimentally, was carried out. Conducted by the

TABLE 2: Results of determining the mass fraction of urea in the semi-finished product before and after PHT.

Object of the study	
Defrosted thorny skate's wings	
Mass fraction of urea, %	
Before IR blanching	1.3
After IR blanching	0.76
Semi-finished product weight loss during infrared blanching, %	
8.0	
Urea removal efficiency, % of the original content regarding mass loss	
82.6	

method of A.S. Ginzburg [13], the calculations allowed accepting the reasonable design parameters of the IR blancher, presented in Table 3.

TABLE 3: Design parameters of the IR blancher.

Operation chamber length, mm	At least 1800
Operation chamber width, mm	At least 600
Operation chamber height, mm	At least 800
Thermal emitter	
Working length of the mesh conveyor for fish transportation inside the oven, mm	At least 1600
Width of the mesh conveyor for fish transportation inside the working chamber, mm	maximum 400
Distance from screen to IR emitters, mm	20

Structurally, the IR blancher is a chamber, inside which there is a meshed (for the removal of moisture from the semi-finished product) conveyor on which the wings of the skate are placed. Above the conveyor, at a height of 100 mm (reasonable height of 80 mm and 20 mm falls on the thickness of the wing) there are IR emitters installed on special holders in a row, at a distance of 100 mm from each other. Above the radiators, there is a reflective screen of oxidized aluminum which allows forming a proper flow of infrared radiation falling on the semi-finished product.

As the main raw material for the production of canned meat from thorny skate, it is proposed to use defrosted wings of the skate, subjected to IR blanching, and chilled or frozen cod. Technological scheme of primary processing of fish raw materials in the manufacture of canned food includes defrosting and sorting of defrosted and chilled fish, washing, infrared blanching of the wings of the skate with subsequent separation

of meat from skin and cartilage, chopping cod on the fillet with the skin and washing, shredding fish, combining minced fish with other components and mixing. Depending on the recipe and the type of canned fish, the minced fish can be packaged in a jar or shaped into meatballs.

The ratio of skate and cod meat in minced meat is a key parameter to determine the nutritional value, functional and consumer properties of new canned foods. This parameter, of course, needs optimization, the main point of which is the achievement of maximum organoleptic evaluation of canned food.

Evaluation of canned food specimens took into account the main quality indicators of minced fish products: taste, smell, color, texture, state; additionally, color and consistency of the tomato sauce were registered.

Percentages of ground skate (X_1) and ground cod (X_2) in the total weight of minced product were taken as the main influencing factors. Changes in the content of fish components of the mince happened by proportional change in the content of other components: sautéed onion, spices, farina.

Recently, more and more works dedicated to mathematical modeling of recipes and food processing modes have been using modern mathematical methods of neural networks and fuzzy logic in addition to traditional regression models [14]. The main advantage of such systems is possibility of fuzzy logic analysis in cases where experimental evaluation cannot be represented in explicit numeric form and has subjective nature. The most typical example is organoleptic evaluation of food products with verbal point-based characteristics.

Let us briefly consider the algorithm of constructing a fuzzy logic derivation aimed at determination of the optimal component ratio for canned minced fish products made of thorny skate and cod, using the Fuzzy Logic Toolbox in the MatLab software package. The system was constructed on the basis of experimental data set and sensory evaluation of mince canned product Skate and Cod Meatballs in Tomato Sauce. The experimental design is given in Table 4.

Processing in MatLab starts with loading the basic fis-editor, and renaming input and output variables. The renamed input variables are X_1 --«skatvfarshe», X_2 -- «treskavfarshe» (Russian for "skate content" and "cod content", respectively). The renamed output variable is Y -- "organoleptika". Then, the ranges of variation were defined for each variable in accordance with Table 4.

Linguistic evaluation of the input variables used 5 terms with symmetric Gauss membership functions: «malo», «neochenmalo», «sredne», «neochenmnogo» и «mnogo» (Russian for "a little", "not quite that little", "average", "not quite that much" and "a

TABLE 4: Experimental design for optimizing the component ratio for Skate and Cod Meatballs in Tomato Sauce".

Organoleptic estimation of ready canned goods Y, points
from 4.4 to 5.0 ¹
Minced skate content X ₁ , % of the total weight of mince
basic level 48.0
variability interval 25.0
top level 71
bottom level 23.0
Minced cod content X ₂ , % of the total weight of mince
basic level 48.0
variability interval 25.0
top level 71
bottom level 23.0
Control (skate-only mince), % of the total weight of mince
83.0
Control (cod-only mince), % of the total weight of mince
83.0
Note: ¹ Subjective range of values corresponding to a relatively high organoleptic evaluation of the ready goods

lot", respectively). Then, membership functions of the «organoleptica» output variable were defined, using 5 terms with Gauss membership functions for linguistic evaluation: «ochenegelatelno», «neohcengelatelno», «ydovletvoritelno», «normalno», «ochenegelatelno» (Russian for "highly undesirable", "somewhat undesirable", "satisfactory", "regular", "highly desirable").

The following screenshots of the user screen show the results of the fuzzy logic modeling in MatLab:

- Renaming the variables of influencing factors X₁ and X₂ (Figures 1-3)

After that, Rule Editor in the knowledge base editor was used to formulate 15 rules reflecting interdependence of the optimization parameter (response function), i.e., organoleptic evaluation of canned goods and the selected influence factors from experimental data and sensor analysis of specimens. Weight coefficients in the range from 0 to 1 were subjectively assigned to each rule. The rules are shown in Figure 4 as a screenshot of the user's screen.

Visualization of the fuzzy derivation for each rule is shown as a sequence of horizontal rectangles (Figure 5). Filling-in shows a degree of correspondence between the input values and the rules being formulated.

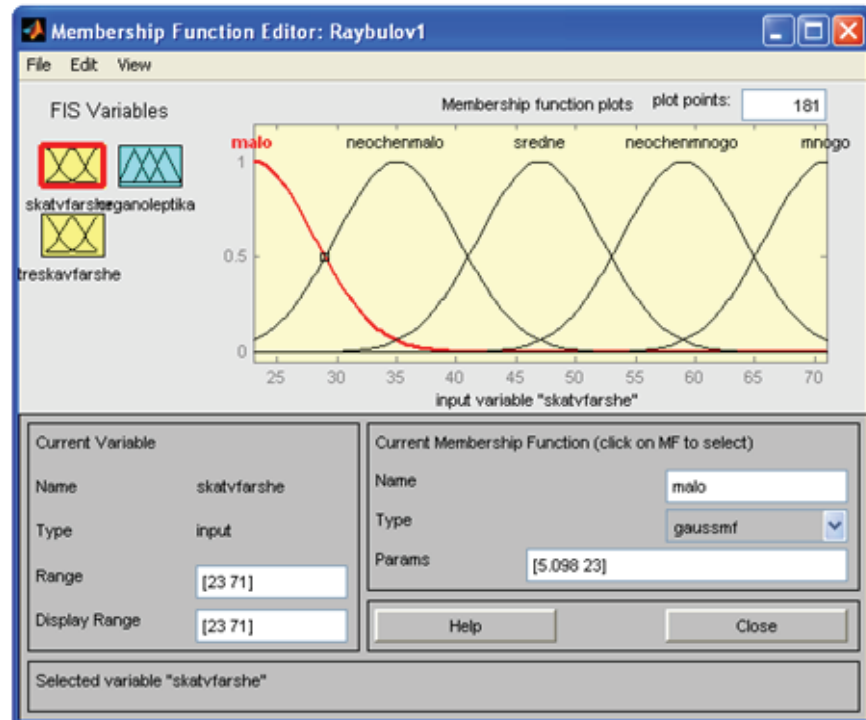


Figure 1: Renaming the X_1 variable (skate content).

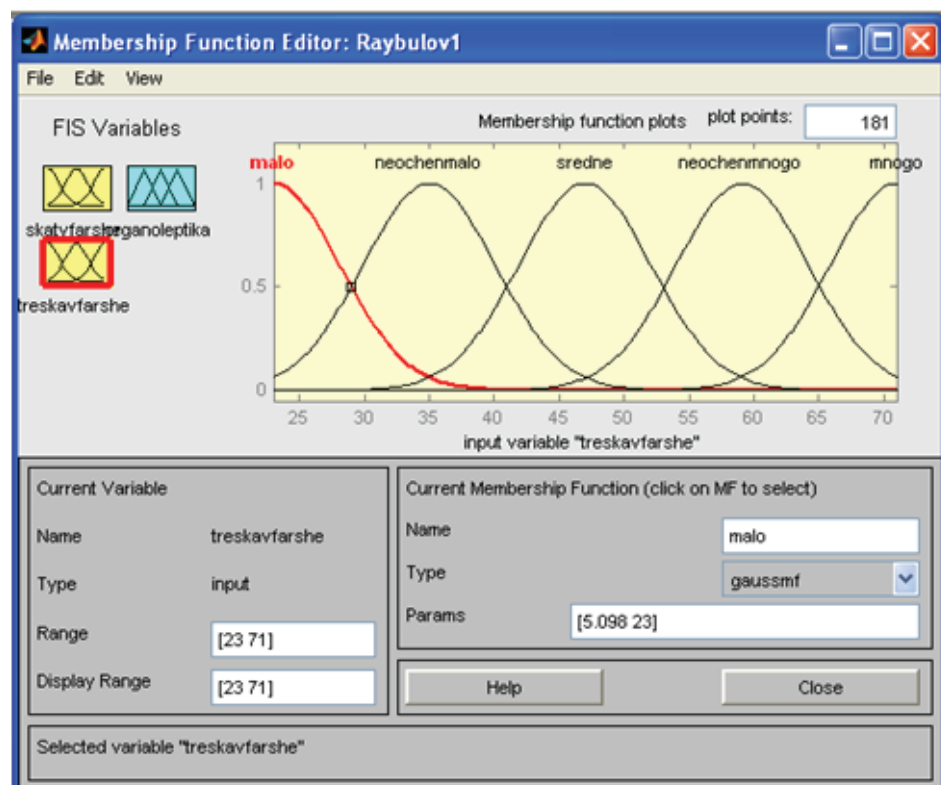


Figure 2: Renaming the X_2 variable (cod content).

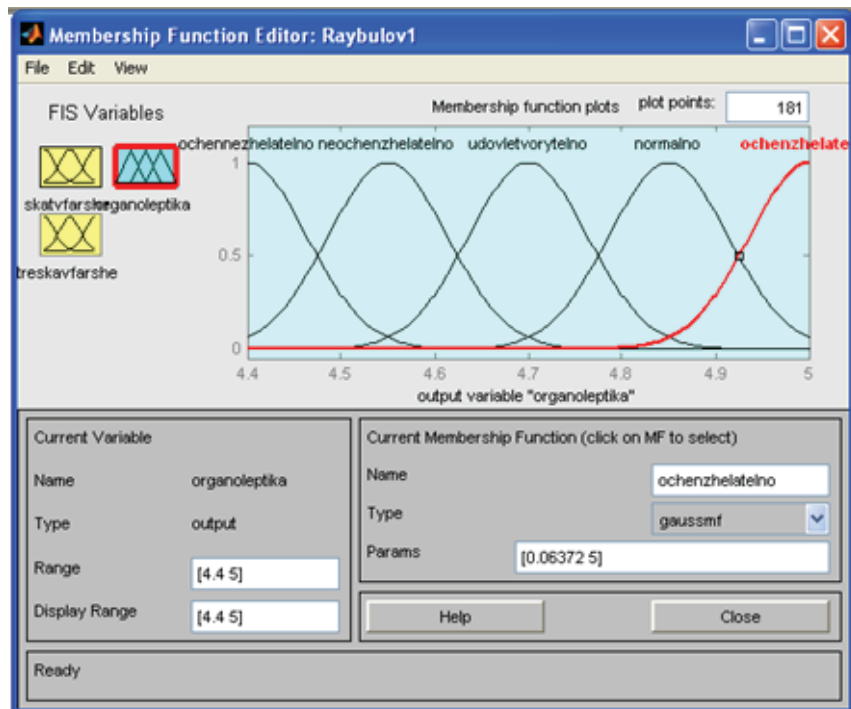


Figure 3: Renaming the output variable (organoleptic data).

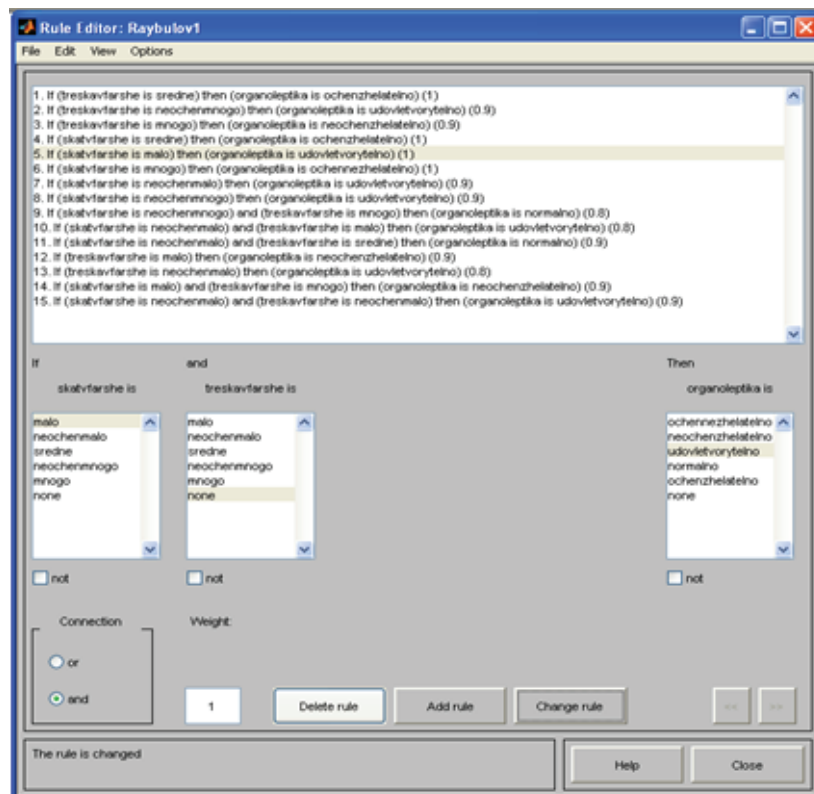


Figure 4: Knowledge base (Rule Editor) for fuzzy derivation.

Filling-in of the output membership function graph is the result of the logic derivation in the form of a fuzzy set for this rule. The resulting fuzzy set corresponding to the

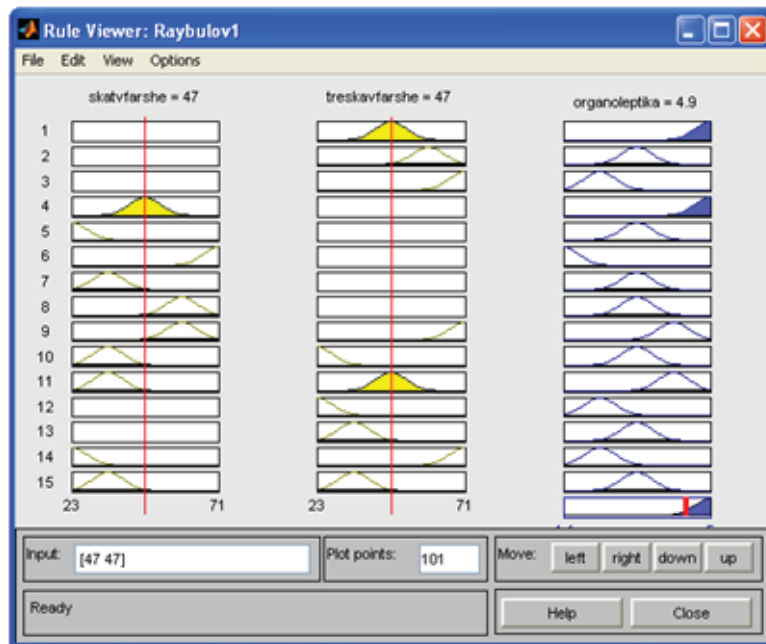


Figure 5: Visualization of fuzzy derivation in MatLab.

logic derivation over the complete set of rules is shown in the bottom rectangle in the last column. The vertical line in the same rectangle shows an exact value of the logic derivation obtained by de-fuzzification

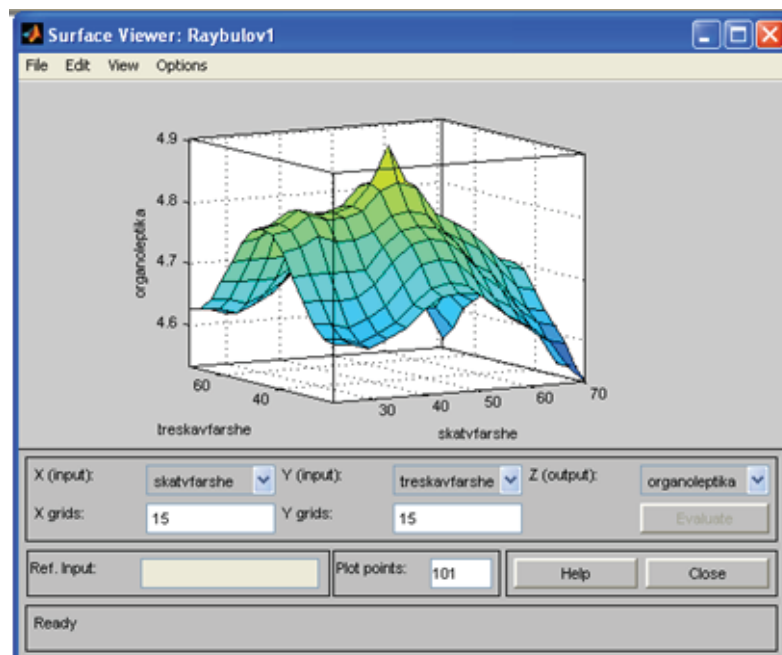


Figure 6: Response surface depending on influencing factors.

The developed model is used to optimize component ratio of mince-based canned foods, as a generator of optimal values for ratios of key components: skate ratio of 47% and cod ratio of 47% of the total weight of the mince. Thus, the non-fish components

shall be under 6% of the total weight. The modeling results are shown graphically in Figure 6. The response surface was obtained with the Surface View module in Matlab. The module visualizes dependence of an output variable on two input variables.

The results of the modeling and recipe optimization were confirmed with the results of expanded sensory analysis of the canned goods, shown in Table 5.

TABLE 5: Results of the expanded sensory analysis of canned Skate and Cod Meatballs in Tomato Sauce.

Organoleptic evaluation of ready canned goods without taking into account the weight coefficients, 5-point scale	
Skate -- 47 %, cod -- 47 % of total mince weight	
Taste	5.00
Smell	5.00
Texture	5.00
State	5.00
Skate -- 73 %, cod -- 23 % of total mince weight	
Taste	4.14
Smell	4.14
Texture	5.00
State	4.57
Skate -- 23 %, cod -- 73 % of total mince weight	
Taste	4.29
Smell	4.14
Texture	4.86
State	4.14
Cod -- 83 % of total mince weight (control)	
Taste	4.71
Smell	5.00
Texture	4.86
State	5.00
Skate -- 83 % of total mince weight (control)	
Taste	3.85
Smell	4.29
Texture	5.00
State	4.00

As it is evident from Table 5, there we have the maximum possible organoleptic evaluation of canned foods produced with the recipe close to the optimal one (as determined by fuzzy logic modeling), thus confirming the adequacy of the model with respect to the actual process. It should be noted, that the control specimens, produced of skate or cod alone (controls) got organoleptic evaluation lower than any combination of cod and skate in the experiment. Optimal recipes for canned food are included in the developed technical documentation.

The next stage of research was the development of sterilization regimes for new canned foods. This stage included:

- Sterilization of canned food according to the modes established in the "Technological instructions for the production of canned food and canned food", with the measurement of temperature and pressure in the autoclave and the temperature of the product in the center of the jar, calculation of the actual mortality rate (F);
- Adjustment of the mode taking into account the required mortality rate and culinary readiness of the product.

Canned food was sterilized in a vertical autoclave of periodic action H2-ITA 602 by steaming and water cooling with backpressure in modes:

- Meatballs from thorny skate and cod meat in tomato sauce: $\frac{5-15-55-20}{115^{\circ}\text{C}}$ 0.16 MPa;
- Thorny skate & cod in white sauce: $\frac{5-15-70-20}{115^{\circ}\text{C}}$ 0.16 MPa.

In the process of sterilization, the temperature of the heating medium in the autoclave was fixed every minute with the help of the system of automatic control of the sterilization process "SAUST-E" (Fig. 2 -- Images *a* and *b*) and, additionally, with the help of the temperature sensor of the device "Ellab" (Fig. 2 -- Images *c* and *d*).

The value of actual lethality was used as a determining indicator when checking the sterilization regime (F), which should be equal to or higher than the normative lethality value (F_H).

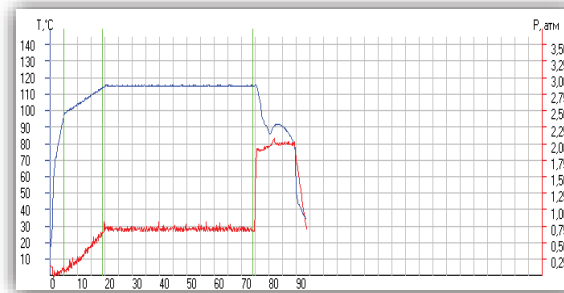
As a result of the experiments it was established that the actual sterilizing effect for canned food was:

- «Meatballs from thorny skate and cod meat in tomato sauce» -- 6.8 probationary minutes;
- «Thorny skate & cod in white sauce» -- 6.5 probationary minutes.

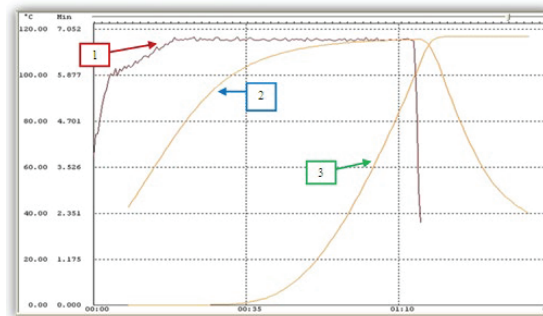
The value of the normative sterilizing effect of canned food in the 'No. 3' marked cans was not experimentally established, it was determined by calculation:

- «Meatballs from thorny skate and cod meat in tomato sauce» -- 4.6 probationary minutes;
- «Thorny skate & cod in white sauce» -- 5,2 probationary minutes.

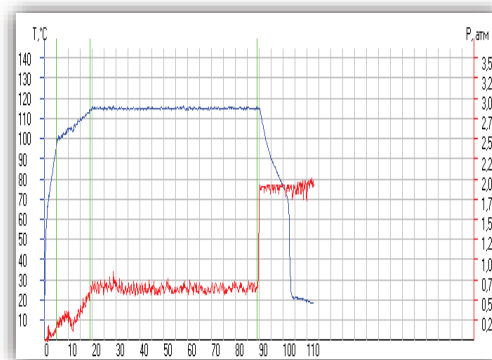
As a result of work, it was found that the sterilization regime for canned food is overestimated (F is significantly higher than F_H). It was also established that at 115 °C «Meatballs from thorny skate and cod meat in tomato sauce» canned products can



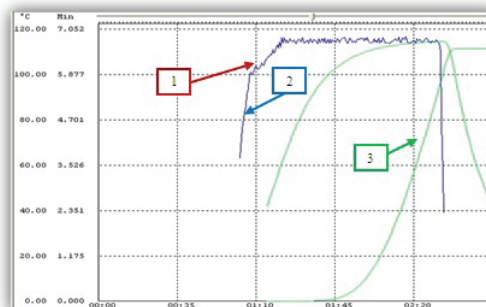
a – thermal barogram of the sterilization process of canned meatballs from thorny skate and cod meat in tomato sauce



b – changes in the temperature of the heating medium (1) and the product (2) and the actual sterilizing effect (3) on the sterilization of canned meatballs from thorny skate and cod meat in tomato sauce



c – thermal barogram of the sterilization process of canned thorny skate & cod in white sauce



r) Changes in the temperature of the heating medium (1) and the product (2) and the actual sterilizing effect (3) on the sterilization of canned thorny skate & cod in white sauce

Figure 7: Results of the experiment on the development of the mode of sterilization of canned products made from meat of cod and thorny skate.

be successfully sterilized within 50 minutes, and «Thorny skate & cod in white sauce» canned products can be successfully sterilized within 65 minutes.

Thus, as a result of the performed research, the sterilization modes of canned food were substantiated as:

- «Meatballs from thorny skate and cod meat in tomato sauce»: $\frac{5-15-50-20}{115^{\circ}\text{C}}$ 0,16 MPa,

$F_f = 5,4$ prob. min.;

- «Thorny skate & cod in white sauce»: $\frac{5-15-65-20}{115^{\circ}\text{C}}$ 0,16 MPa, $F_f = 5.9$ prob. min.

An experimental assessment of the biological value of the new canned food was carried out, which showed that 100 g of the product satisfies the recommended daily level of adequate protein consumption (8.4% of canned food in tomato sauce and 10% of canned food in white sauce). It comprises 3.3 and 12.1% (canned food in tomato sauce and white sauce, respectively) of the recommended daily level of adequate fat consumption, as well as from 39.0 to 50.0% of the recommended daily level of adequate consumption of CS.

Determination of the shelf life of new canned food was carried out according to the research schedule, the duration of which was 18 months, taking into account the reserve coefficient of 1.15 [15]. The results of microbiological studies are given in Table 4 and confirmed the industrial sterility of canned food produced according to the developed sterilization modes.

TABLE 6: Results of microbiological studies of canned skate and cod.

Airtightness
All cans are airtight
Appearance of canned food after thermostatic temperature control at (37±1) °C for 5 days
Appearance hasn't changed
Sporous mesophilic mesophilic aerobic and facultative anaerobic microorganisms of <i>B.subtilis</i> group in 1.0 g of the product
Not found
Sporous mesophilic mesophilic aerobic and facultative anaerobic microorganisms of <i>B.cereus</i> and <i>B. polymyxa</i> group
Not found
<i>Cl. botulinum</i> and <i>Cl. perfringens</i> mesophilic clostridium
Not found
Mesophilic Clostridium in 1.0 g of product
Not found
Sporous mesophilic aerobic and facultative anaerobic microorganisms
Not found

Physicochemical studies have confirmed that the quality of canned food meets the established requirements.

4. Discussion

High content of CS in the canned food makes it possible to classify it as a functional product.

On the basis of the received experimental data it has been concluded that safety indicators are not limiting at definition of shelf life of canned products such as "Meatballs from thorny skate and cod meat in tomato sauce" and "Thorny skate & cod in white sauce" in case of qualitative raw materials in use and observance of all technological requirements while manufacturing the product.

5. Conclusion

A method of removing urea from the wings of the thorny skate via IR blanching has been developed and its high efficiency was experimentally confirmed: more than 82% of the initial urea content in fish is removed. The basic design parameters of the IR blancher of continuous action have been determined.

The technology of manufacturing the assortment of functional canned food enriched with CS from thorny skate is offered.

Optimal formulations of new canned goods with the use of fuzzy logic methods in MatLab software package are developed. The modes of sterilization for state-of-the-art canned food products from thorny skate are scientifically proven: for «Meatballs from thorny skate and cod meat in tomato sauce», sterilization formula is $\frac{5-15-50-20}{115^{\circ}\text{C}}$ 0.16 MPa, and for «Thorny skate & cod in white sauce» it is $\frac{5-15-65-20}{115^{\circ}\text{C}}$ 0.16 MPa (steaming sterilization, backpressure water cooling).

Conflict of Interest

The authors have no conflict of interest to declare.

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