Improving the heat treatment process of the underutilized fish raw materials of the Northern Basin

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Abstract. The extent of dehydration of raw fish being blanched depends on the method and the mode of blanching and determines the area of their application. Stingray stellate meat is a valuable raw material for the fish foods production, since its protein contains all essential amino acids not synthesized in the human body. The main obstacle to the intensive industrial use of stingray stellate meat is the necessity to remove urea. The removal of uric acid is only possible in its thermal decomposition at temperatures above 60 °C. Mixed blanching (water-steam) can significantly expand the range of the loss of the raw material mass from 11 to 30 % compared to blanching with steam or water when removing the urea. The developed mathematical models for determining the basic parameters of the process of mixed blanching of stingray stellate are adequate and can be used for the predictive calculations. The developed modes of mixed blanching of stingray stellate are experimentally confirmed and can be recommended for the industrial use.

1. Introduction
Preliminary heat treatment of fish raw materials is widely used in the production of various types of canned foods and cooking. The relevance of the research issue is determined by the main areas of implementing the Strategy for the development of food and processing industry of the Russian Federation for the period until 2020. According to the document, one of the most promising areas of the fish processing industry development is the expansion and the improvement of processing methods used for under-utilized fish resources [1].

A significant number of hydrobiont species of the Northern Basin are yet to be properly utilized for both food and feed purposes. One of the most prominent representatives of the underutilized fish species in the Northern Basin is stingray stellate - Raja radiata [2]. “The protein of stingray is complete; it contains all essential amino acids that are not synthesized in the human body” [2]. Stingray stellate meat contains lots of microelements, but its main value is due to the presence of chondroitin sulfate, “which makes it possible to characterize it as enriched with a component which is proved to be of preventive and curative effects — antitumor and anti-inflammatory” [3]. One of the problems preventing the extensive industrial processing of such valuable raw material for food purposes is urea that must be removed but proteins should be ultimately preserved. Urea easily undergoes thermal decomposition at temperatures above 60 °C. This feature of uric acid was used in the development of a preliminary heat treatment method (PHT) - blanching of stingray stellate with water, and made it possible to abandon the lengthy operation of soaking. However, the developed method is limited by a narrow water temperature
range (from 95 to 98 °C) and allows to get the loss of the raw material mass during pre-heat treatment (blanching) limited to 14 %. [4].

Based on the analysis of the data derived from the literature, the method was proposed and the development of mixed blanching modes (water-steam) of stingray stellate was carried out, aiming to expand the range of the raw material mass loss when preliminary heat treatment (blanching) with simultaneous removal of uric acid was performed.

2. Materials and methods

2.1. Object of study
The object of the study were the wings of frozen stingray stellate according to the technical specifications -TU 9261-028-00038155-02 “stingray stellate semi-finished product for industrial processing” harvested in the period from autumn 2016 to autumn 2018. The raw material was previously air-defrosted for the period of 24 hours at temperature “plus” 4 ° C in the defrosting chamber. The quality of the raw material was visually assessed, then it was washed and drained.

For the experiment, the wings of stingray stellate with a specific surface area (0.2560 ± 0.05) m²/kg were selected, which accounted for 75 % of the total number of samples in a block of the raw material weighing 10 kg. The average weight of the selected samples was 161.33 g [5].

2.2. Research methods
The samples mass was determined by the method of periodic weighing before and after blanching. The specific surface was found by dividing the total surface of the wing by its mass.

The urea content was determined by a modified photocolorimetric method according to the standard-GOST R 50032-92 "Feed meal from fish, marine mammals, crustaceans and invertebrates. Methods for determining the mass fraction of urea and calculating the crude protein taking into account the mass fraction of urea and considering the characteristics of the product under study [6]. The efficiency of the urea removal was confirmed by comparing its mass fraction in stingray stellate muscle tissue before and after blanching. To reduce the number of the experiments, test planning was carried out based on the method of Latin squares [7]. The results of the experiment were processed using linear regression using DataFit version 9.1.32. The adequacy of the obtained mathematical models was determined by F-test and the determination coefficient. The significance of each regression coefficient was determined by T-test [8]. The largest and the smallest values of the functions are determined by differentiation.

2.3. Experimental setup and experiment conditions
The method of mixed blanching of stingray stellate was proposed and studied using an experimental unit for mixed blanching of raw materials developed at the Department of Technological and Refrigeration Equipment of the Murmansk State Technical University and protected by patent [9].

"The technical result, aimed to by the claimed invention, consists in providing the method of mixed blanching or carrying out the process in each of the processing media separately, reducing time and labor costs to conduct the experimental studies determining the optimal mode of blanching the raw materials" [9]. The experimental setup is described in detail in the source of literature [5].

The conditions of the experiments are presented in table 1.

| Parameter                        | Value       |
|----------------------------------|-------------|
| Specific surface of the sample, m²/kg | 0.2560 ± 0.05 |
| Average sample weight, g         | 161.33      |
| Average sample weight, g          | 1.9         |
| Water temperature, °C             | 70 ± 95     |
| Water temperature variation span, °C | 5          |
3. Results and discussion

Mixed blanching (water - steam) is a complex two-step process, therefore it seems advisable to consider changing the process parameters in stages.

The temperature of the sample center after the treatment with water can be adequately described by the equation (1) depending on the water temperature ($x_1$) and the duration of water treatment ($x_2$), taking into account the Fisher criterion (F-criterion) and the determination coefficient ($R^2 = 0.811$). All the coefficients of the equation are significant.

$$y_1 = -32.049 + 0.674x_1 + 0.0687x_2,$$

(1)

The variation interval $x_1$ for the equation (1) ranged from 70 to 95 °C with a span of 5 °C. The parameter $x_2$ for all mathematical models was changed in 60 s span in the range from 60 to 300 s.

The response surface of the factor space in figure 1 shows that the temperature of the sample's center increases with the increasing water temperature and the duration of water treatment.

![Figure 1. The response surface of the factor space temperature of stingray stellate sample's center after blanching with water: $x_1$ - water temperature, °C; $x_2$ — the duration of the raw material treatment with water, c.](image)

The largest and the smallest values of the sample's center temperature calculated using the equation (1), are experimentally confirmed and presented in table 2.

| Water temperature, °C | Duration of water treatment, c | Estimated value, °C | Experimental value, °C | Relative error, percentage |
|-----------------------|-------------------------------|---------------------|------------------------|---------------------------|
| 70                    | 60                            | 20                  | 21                     | 4.76                       |
| 90                    | 300                           | 49                  | 50                     | 2.00                       |

Initially, during processing of the experimental data, a generalized mathematical model was developed, which allows to determine both maximum and minimum mass losses in the process of stingray stellate blanching. However, the practical application has proved the model obtained to be much complicated.

As a result, there was made a decision to develop two mathematical models which could separately determine the minimum and maximum mass losses in the process of stingray stellate blanching.

The equation (2) adequately describes the dependence of the maximum ($y_2$), and equation (3) - the minimum ($y_3$) mass loss in the process of stingray stellate blanching on water temperature ($x_1$) and on the duration of treatment with water ($x_2$)

$$y_2 = -1010.508 + 2.473x_1 - 0.143x_1^2 - 0.120x_2 + 0.000325x_2^2,$$

(2)
\[ y_3 = 187.730 - 4.020 x_1 + 0.0238 x_1^2 - 0.0795 x_2 + 0.0002 x_2^2, \]  
\hspace{1cm} (3)

The variation interval \( x_1 \) for the equation (2) is from 80 to 90 °C with a span of 5 °C, since at lower water temperatures the maximum loss of the raw material mass was not observed.

For the equation (3), the parameter \( x_1 \) changed from 70 to 90 °C with a span of 5 °C.

Taking into account the values of F-test and the determination coefficients (\( R^2 = 0.969 \) and \( R^2 = 0.998 \), respectively), the models were considered adequate, all the coefficients of the equations are significant.

Figure 2 shows the response surface of the factor space for the maximum and minimum mass loss of the blanched raw material.

\[ y_3 = -21216.854 + 481.516 x_1 - 2.719 x_1^2 + 9.594 x_2 - 0.00781 x_2^2 - 0.0724 x_1 x_2, \]
\hspace{1cm} (4)

where \( x_1 \) - is the water temperature, °C; \( x_2 \) - the duration of treatment of the raw material with water, c.

The variation interval \( x_1 \) for the equation (4) ranged from 80 to 95 °C.

Considering the value of F-test and the determination coefficient (\( R^2 = 0.851 \)), the model is admitted adequate, all coefficients are significant.

Figure 3 shows the response surface of the factor space for the total duration of the blanching process.

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**Figure 2.** The response surfaces of the factor space of the maximum (a) and the minimum (b) stingray stellate losses in blanching: \( x_1 \) — water temperature, °C; \( x_2 \) - the duration of water treatment of the raw material, c.

The design modes corresponding to the largest and the smallest losses of stingray stellate in mixed blanching are obtained using mathematical models and are presented in table 3.

**Table 3.** Design modes of mixed blanching for obtaining maximum and minimum losses.

| Water treatment mode | Mass loss, percent |
|----------------------|--------------------|
| temperature, °C | treatment time, c | maximum loss | minimal loss |
| 86 | 60 | 30,51 | - |
| 90 | 198 | - | 11 |

The total duration of stingray stellate blanching (\( y_4 \)) is adequately described by the equation (4)
The longest duration of the mixed blanching process corresponds to the water temperature of 86 °C and the duration of treatment with water of 217 s and is 447 s.

**Figure 3.** The factor space response surface of the total duration of stingray stellate blanching: $x_1$ - water temperature, °C; $x_2$ - the duration of water treatment of the raw material, c.

Considering the equation (4), the duration of steam treatment can be determined by the equation (5)

$$y_4 = y_3 - x_1,$$

(5)

The calculated blanching modes for maximum and minimum losses are verified experimentally.

For the selected modes, the efficiency of urea removal is also confirmed, which corresponds to the efficiency of the removal when blanching with live steam, water (fish: water ratio 1:1) and IR blanching with the treatment time of 12 minutes [6].

The modes of stellate stratum mixed blanching recommended for the industrial use are presented in table 4.

| Duration of treatment (s) | Heat carrier temperature (°C) | Weight loss (percent) | Semi-finished product output (percent) | Efficiency of urea removal in PHT (water-steam blanching) considering the weight loss of the semi-finished product (percent) |
|---------------------------|-------------------------------|-----------------------|----------------------------------------|--------------------------------------------------------------------------------|
| 60                        | 194 ± 4                       | 85 ± 1                | 100                                    | 30.04 ± 0.4                                                                 |
| 189 ± 9                   | 209 ± 8                       | 90                    | 100                                    | 11.1 ± 0.1                                                                 |

### 4. Conclusion

The improvement of PHT of the underutilized fish raw materials of the Northern Basin helps to overcome the problem of obsolescence and physical deterioration of technological equipment and expand the possibilities of its use for food processing purposes.

The proposed method of mixed blanching allows to get safe semi-finished foods from stingray stellate, suitable for further processing and production, including functional properties, which confirms the relevance of this study issue and the areas of the research.

The developed modes of stingray stellate mixed blanching are experimentally confirmed and can be recommended for the industrial use.
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