Extrusion as an element of resource and energy saving technologies for processing of underutilised cartilage fish of the Northern Basin

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Abstract. Currently one of the main objectives of the domestic fishery complex development is to increase the efficiency of aquatic biological resources (ABR) extraction and optimize their processing. Accelerating rate of ABR processing is associated with the search and implementation of energy-saving, low-waste and waste-free technologies to increase the number and expand the diversity of feed and food products. Starry ray (Raja radiata) is a valuable raw material containing significant amount of high-quality protein, as well as a number of important trace elements for nutrition, such as cobalt, nickel, fluorine, chromium, copper, iodine, iron, sulfur, chlorine, phosphorus, potassium, magnesium, sodium, vitamin PP and others. High content of chondroitin sulfate in starry ray meat makes it an indispensable component of functional nutrition, as well as in the production of special feeds. The study of grinding process of frozen raw material from starry ray on a piston-type extrusion unit with cooled working bodies allowed to determine rational grinding regimes with the lowest possible energy costs. The subsequent organoleptic evaluation of the obtained minced meat confirmed that the product has homogeneous structure and crumbly, juicy texture. In order to establish the shelf life of the semi-finished product produced, standard tests were carried out to determine the quality and safety parameters during its storage. To do this, organoleptic indicators were monitored, and the dynamics of fluctuations of nitrogen content of volatile bases being the indicator of the prevailing type of damage to this product. The determination of nitrogen in volatile bases was carried out using titrimetry. The results of the study can be used in the development of feed mixtures.

1. Introduction
The main goal of the national fisheries complex (NFC) development provides for the implementation of numerous urgent tasks. By 2020 it is supposed to achieve the level of economic and social development of the NFC corresponding to the status of the Russian Federation as one of the leading countries in the modern world, occupying leading positions in the global economy market, as well as to expand the extraction of aquatic biological resources (ABR) and optimize various industries processing aquatic products [1]. Accelerating rate of ABR processing is associated with the search and implementation of new technologies in order to increase the number and expand the diversity of feed and food products made from hydrobionts.

By the Decree of the President of the Russian Federation of August 6, 2014 No. 540, in the consequences of a troublesome economic situation, the tasks of ensuring rapid import substitution for agro-industrial complex, including the supply of raw materials for the food and feed industry, were
assigned [2]. The action of the mentioned subordinate act was prolonged by a number of decrees of the President of the Russian Federation. Thus, the “pivot” of the state policy towards import substitution is a long-term and strategic activity and is firmly bound in the current regulatory and legal framework. In this reality, the tasks of obtaining high-quality and inexpensive raw material for the production of protein-rich food and feed are of particular relevance. These tasks can be solved only comprehensively, using various resources, utilising local raw material of the Arctic zone of our country [3].

For the Murmansk region, the most topical ones are the issues of developing the newest low-waste and waste-free integrated technologies for ABR processing for the complete development of low-value, non-harvested or underutilized fishing objects and fish processing wastes.

Currently, products from raw material of marine origin are of great popularity among food manufacturers and their consumers. One of the most popular products of this kind are minced fish. Today, the market offers a wide range of minced fish made of raw material of marine origin, but, unfortunately, not all types of marine resources are fully utilized. Some ABR species are underutilized or not commercially harvested at all, although this raw material is caught as by-catch.

Currently there is an increased demand for feed products from raw materials of marine origin, as feed made of fish is distinguished by particularly high levels of protein as an essential and most expensive part of the diets for agricultural and other animal species and poultry [4].

The most well-known and common method for the manufacture of feed products based on ABR is the production of feed fish meal and fish hydrolysates [5]. Meanwhile, the new technologies for the production of feed products based on fish mince, mechanically ground mass of fish with improved nutritional properties, are not considered to be less promising [6].

The innovative solution of the tasks assigned could be replacing the traditional approaches to the production of food and feed minced fish from the raw material of marine origin with advanced technology based on the application of cryo-extrusion method, which allows to eliminate redundant operations, preserve the level of nutrients in the final product more effectively, and significantly reduce the economic costs of its processing [7].

A significant contribution to the development of new technologies for cryoprocessing of raw materials was made by scientists: Babakin B.S., Belova Z.I., Ilyukhin V.V., Kaukhcheshvili E.A., Kasyanov G.I., Rogov I.A., Semenov B .N., Shazzo R.I., Shlyakhovetsky V.M., Fatykhov Yu.A., Erlikhman and others. However, fish raw material harvested in the Northern Basin in the recent years is hardly the subject of many research, and there are no extrusion units of the piston type in technological lines for the production of food and feed minced fish.

2. Materials and methods
2.1. The object of research and preparation
In some countries, taste properties of starry ray meat are highly valued and considered a delicacy. For example, in Portugal, starry ray wings rank prominently in the national culinary tradition [8]. At the same time, starry ray meat is rich in trace elements, such as: cobalt, nickel, fluorine, chromium, copper, iodine, iron, sulfur, chlorine, phosphorus, potassium, magnesium, sodium, vitamin PP and others. Starry ray is a high-protein fish. 100 grams of the product contain 24 g of protein, 1.6 g of fat and do not contain carbohydrates. Caloric value of starry ray is on average 110 kcal per 100 grams of the product [9].

Frozen starry ray wing (according to full product specifications 9261-028-00038155-02 “Skate frozen semi-finished product for industrial processing”) was chosen as the object of research.

Prior to conducting experimental studies, the raw material was subjected to organoleptic evaluation.

To determine the adequate mode of grinding the raw material was cut into pieces of approximately the same volume and size, making a batch. Five samples were taken from each batch. The volume was
determined by Archimedes method. The average volume of the batch sample was calculated as the arithmetic average of the volumes of 5 selected samples.

2.2. Research methods
The mass of each sample and raw material loaded into the working chamber of the experimental unit was determined by the method of periodic weighing.

The density of the raw material was calculated using the formula

\[ \rho_i = \frac{m_i}{V_i}, \]

where \( \rho_i \) - the density of the raw material, kg/m³; \( m_i \) - sample mass, kg; \( V_i \) - sample volume, m³.

The total surface of each sample was determined by the standard method. The specific surface was calculated as the ratio of the total surface area of the sample to its mass.

The equivalent diameter of a piece was determined by the formula

\[ d_{\text{equ}i} = 2 \cdot \sqrt[3]{\frac{3 \cdot V_i}{4 \cdot \pi}}, \]

where \( d_{\text{equ}i} \) - the equivalent diameter of the piece, mm; \( V_i \) - sample volume, mm³.

The degree of grinding was determined by the ratio

\[ i = \frac{d_{\text{equ}i}}{d_{\text{hole}i}}, \]

where \( d_{\text{hole}i} \) - the functional diameter of the die hole, m.

During the experiment the temperature of the raw material, minced fish, initial and final temperatures of the extrusion chamber, grinding pressure, duration of the process, the mass of the raw material, semi-finished product and waste were measured.

The validity of the results obtained is ensured by the triple repetition of the experiment.

At the end of the grinding process, a particle size analysis was performed on a sieve column consisting of sieves with the hole diameter of 7.0; 5.0; 4.5; 3.5; 3.0; 2.0; 1.0 mm. By the beginning of the experiment, the sieve column was cooled to the temperature “minus” 18 °C.

For establishing the shelf life of the ground semi-finished product, standard tests on changing the quality and safety during its storage at the temperature “minus” 18 °C were carried out. To do this, organoleptic indicators, as well as the dynamics of fluctuations in the nitrogen content of volatile bases as an indicator of the prevailing type of damage to this product were monitored. Determination of the nitrogen of volatile bases was performed by the titrimetric method according to All-Union State Standard (GOST) 7636-85. Experiments were conducted taking into account the reserve ratio of 1.2.

2.3. Experimental unit
The method of producing minced meat by extrusion was implemented and examined in the piston-type experimental extruder-grinder, developed at the Department of Processing and Refrigerating Equipment of the Murmansk State Technical University, and can be used for grinding frozen, thawed and blanched raw material [10,11]. The technical result achieved with the help of this unit “consists in simplifying the kinematic scheme of the mechanism, improving the quality of the obtained semi-finished product by eliminating the process of heating the raw material and enriching it with microelements at the expense of grinding without prior cutting, as well as more appropriate use of raw materials” [12]. The block diagram of the unit is shown in Figure 1, the general view of the extruder-grinder is shown in Figure 2, and the driven elements of the extrusion unit are shown in Figure 3.
Figure 1. Structural scheme of the extrusion unit: 1 - plunger; 2 - replaceable extrusion matrix

Figure 2. General view of extruder-grinder of piston type: 1 - working part; 2 - hydraulic drive; 3 - bearing frame; 4 - base plate

Figure 3 - The main driven elements of the extrusion unit

The experimental extrusion unit is extensively described in the study [13]. The ratio of the diameter of the extrusion chamber to the stroke of the plunger is 1:2, the capacity of the extrusion chamber is 185 cm³. The plunger is driven by a 1.6 kW hydraulic drive.

Experimental studies were conducted using matrices, their characteristics are presented in Table 1. It is impractical to use holes of a larger diameter for grinding matrices, since the structure of the minced meat is characterized by considerable heterogeneity. When using holes of smaller diameter, the matrix is destroyed under the influence of grinding pressure. The conditions of the experiments are presented in table 2.

Table 1 - Characteristics of the grinding matrices
Hole type and quantity | The ratio of hole diameters, mm | Geometry coefficient, cm³ |
---|---|---|
Cone cylinder, 19pcs | 8\7\7 | 0,534748 |
Cone-cone, 19pcs | 8\6\8 | 0,323057 |
Cone, 19pcs | 9\7 | 0,100694 |

* «The height of each part of the hole is ¼ of the matrix thickness, the tangent of the inclination angle of the side surface of the matrix holes to the horizontal surface is constant and equal to 6» [12]

| Parameter | Type of raw material - frozen starry ray |
|---|---|
| Sample volume, cm³ | 4,20 ÷ 30,20 |
| Equivalent diameter, mm | 20,00 ÷ 38,79 |
| Specific surface, m² / kg | 0,4100 ÷ 2,2690 |
| Mass of the raw material loaded into the working chamber, g | 31,07 ÷ 76,40 |
| Temperature of the main driven elements of the extrusion unit, °C | minus 18 |
| Raw material temperature, °C | minus 18 |
| Mincemeat temperature, °C | minus 18 |
| Index of the geometric shape of the grinding matrix hole, cm³ | 0,100694 ÷ 0,534748 |

2.4. Experiment Planning and Data Processing

The minimization of the number of experiments was ensured by planning an experimental study using the combinatorial squares method [14].

The search for the adequate mode of grinding was performed by non-linear regression using DataFit version 9.1.32. The validity of the obtained mathematical models was determined by Fisher criterion (F-criterion) and the coefficient of determination. [15].

For graphical representation of the results obtained, Microsoft Office Excel software was also applied and the subsequent analysis was performed.

3. Results and discussion

Alteration of the parameters of the frozen starry ray grinding during the experimental studies is shown in Table 3.

| Parameter | Value |
|---|---|
| Grinding degree | 2,85 ÷ 5,55 |
| Working grinding pressure, MPa (kgf / cm²) | 10,8 ÷ 15,7 (110 ÷ 160) |
| Duration of grinding, with | 50,99 ÷ 210 |
| Index of the geometric shape of the grinding matrix hole, cm³ | 0,100694 - 0,534748 |

The resulting equation (4) properly describes the dependence of pressure for the frozen starry ray grinding (y) on the index of the geometric shape of the die (x₁) and the degree of raw material grinding (x₂)

\[
y = 3.55 + 4.53 \ x₁ + 7.02 \ x₁^2 + 1.70 \ x₂ + 0.20 \ x₂^2. \tag{4}
\]
where \( x_1 \) is the index of the geometric shape of the hole, cm\(^3\); \( x_2 \) - the degree of raw material grinding, a dimensionless value.

For the aggregate values of the Fisher criterion (F-criterion) and the index of determination \( R^2 = 0.877 \) the model is recognized as valid, all the indexes of the equation are significant.

Figure 4. The response surface of the factor space for frozen starry ray grinding pressure: \( y \) – grinding pressure, MPa; \( x_1 \) is the index of the geometric shape of the hole, cm\(^3\); \( x_2 \) - the degree of raw material grinding, a dimensionless value.

According to Figure 4, the minimum grinding pressure of starry ray is 10.8 MPa, which corresponds to the index of the geometric shape of the die hole 0.32 cm\(^3\) (hourglass-like hole) and the degree of grinding 2.85.

The analysis of the bar chart presented in Figure 5 and made on the results of the sieve analysis of mince fish obtained from the frozen raw material using an hourglass-like matrix (8 \( \times \) 7 \( \times \) 8), makes it possible to conclude that the structure of the mince fish is quite homogeneous: large fractions (from 4.5 up to 7 mm) account for 85.75 %, and small fractions (from 1 to 4 mm) – 14.25 % of the total mass of mince fish.
Figure 5. The bar chart of the distribution of the particles of mincemeat obtained from frozen raw material using an hourglass-like matrix (8 \ 7 \ 8)

The subsequent organoleptic evaluation of the obtained mince confirmed that the product has homogeneous structure and crumbly, juicy texture.

Based on the nitrogen content of volatile bases (Figure 6) in the mince obtained, its shelf life was established, it equals 6 months.

Figure 6. The nitrogen content of volatile bases in the mincemeat obtained from frozen raw material using an hourglass-like die (8 \ 7 \ 8)

4. Conclusion
The obtained results confirm the possibility and feasibility of using cryo-extrusion method to create resource and energy-saving technologies for processing underutilised cartilage fish of the Northern Basin.
For the production of feed mince fish made of frozen starry ray, a grinding mode based on cryo-extrusion using an hourglass-like matrix (8 \ 7 \ 8) has been developed. The minimum grinding pressure is 10.8 MPa when the degree of grinding 2.85. An increase in the degree in grinding on the recommended matrix 1.95 times causes a 1.15 times increase in grinding pressure. The output of the finished product on the recommended matrix amounted to 93.81 - 97.95% of the initial mass of the raw material.

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