CryoeXtrusion in technologies for processing aquatic biological resources

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Abstract. The Murmansk region is a coastal region and an integral part of the Arctic economic zone of Russia with its unique geographical location. The development of the regional fishing industry reaches a high level, which makes it possible to fully use the entire range of hydrobionts both for food and forage purposes. Freezing is used as a way to preserve such products in the conditions of fish processing enterprises and fishing vessels in order to improve the safety of proteins, vitamins and minerals in the composition of extracted marine products. To involve in the processing of certain types of raw materials that are difficult to traditional cutting and grinding in thawed form (small fish raw materials, secondary fish raw materials, including waste from cutting fish-heads, gills, vertebrae, trimmings), as well as for algae, it seems rational to carry out technological processes for their processing (including grinding) in conditions of negative temperatures, preventing the phase transition of moisture into a liquid state. Due to grinding in the final product (semi-finished product, minced mass), the availability of nutrients increases. Grinding using the cryoeXtrusion method, that is, pressing frozen raw materials through a die with holes of a certain diameter, which is based on the cutting ability of intracellular and intercellular ice, allows you to eliminate moisture and nutrient losses, reduce the time and energy costs of defrosting. The semi-finished product obtained by cryoeXtrusion can be stored for a long time in a frozen state or used to produce a finished product.

1. Condition

In modern conditions, the Russian Federation is developing the most important areas of state policy in the field of industry and economy, especially the sphere of extraction and processing of aquatic biological resources. In this regard, in the coastal regions of Russia, in particular, in the Murmansk region, the most promising issues for solving are the extraction and processing of aquatic biological resources of the seas of the Northern basin, which is given special attention. There is an increased interest in the expansion of fishing facilities for marine biological resources and the introduction of new advanced, scientifically justified technologies for their processing.

The vector of implementation of a number of modern tasks for the development of the Kola region's fisheries complex as a Arctic component is aimed at expanding the range of hydrobiont production facilities and complex development of new, previously unused fishing facilities. Optimization of various processing industries in this area entails the need to intensify the processing of those fishing objects whose resources are currently not used in full, including in order to reduce the amount of waste generated from processing hydrobionts, as well as the introduction of technologies aimed at the most effective and thorough use of such waste.
Brown seaweed, being a special source of valuable biologically active substances, makes up the vast marine reserves of the basins of the North-Western region of Russia. Algae that can form a large biomass in a short time and synthesize a wide variety of active compounds that have a wide range of effects on the human body and animals. The importance of seaweed is great because of it is a source of scarce organic substances and available raw materials for the production of food and feed products.

Modern research in the field of human and animal health and well-being as an object of obtaining raw materials for food production has revealed the acute problem of lack of nutrition of micro - and macronutrients. One of the most characteristic examples of this deficiency is the iodine deficiency. The lack of this microelement is dangerous for the body, especially the body in a state of pregnancy, for nursing women. Iodine is necessary for the full development and growth of young children and adolescents in active growth phases. The most severe consequences of a lack of iodine in the body can be cretinism, muteness, deafness and other serious pathologies that significantly threaten the body.

The optimal solution of iodine deficiency problems in the body is to take balanced biological supplements, which include a mineral element such as iodine.

*Kelp* is the most famous brown seaweed that contains all trace elements, including iodine, significant amounts of low-molecular carbohydrates, polysaccharides, as well as many vitamins necessary for the normal functioning of a living organism, both human and farm animals and poultry [1]. Kelp is easy to extract, and its reserves in the seas surrounding the territory of the Russian Federation are significant.

*Laminaria saccharifolia* layers are dense, leathery, wrinkled leaf-like plates 20-50 cm long, 5-40 cm wide, without stalks, the edges of the plates are wavy. The layers have a color from light olive to dark olive, a peculiar smell, salty taste. Dry plates are characterized by the presence of a white coating of salts on the outside [2].

Protein and carbohydrates in the composition of kelp under favorable conditions for intensive growth and development of various microorganisms and bacteria in the algae mass. In turn, the use of various conservation technologies is intended not only to slow down the growth of bacteria in algae removed from the environment, but also to help suppress the save the enzymes activity and as a result preserve valuable natural substances in their composition [2].

Freezing is the one of the most common methods of preserving brown algae is, based on artificially lowering the temperature of the raw material below the freezing point of the cell juice. At the same time, the subsequent storage of the frozen product at low temperatures for a long period of time should be provided [2]. Frozen foods have a wide range of uses, in particular, frozen kelp can be used in the food industry, for example, for cooking canned food and culinary products, as well as in modern technologies for preparing food for different types of animals.

Grinding as a process is used widely as the main process in various technologies for processing and production of products of both plant and animal origin, as well as waste products. For feed products, for example, the method they are prepared by plays a significant role in ensuring the subsequent high level of feed consumption by animals. The extent and completeness of the use of nutrients in food and feed also largely depends on the method of their manufacture.

For example, the use of grinding process in the technology of feed products from raw meat and fish contributes to increased availability of nutrients due to the formation of a result of crushing of many particles with high surface area, that helps speed up digestion and improve absorption of nutrients by animals [3].

In addition, the grinding of all types of raw materials with various types of modern equipment allows to process a significant amount of raw materials in a short time, which makes it possible to increase the volume and rate of its processing. The necessary degree of grinding is achieved in different ways on special, different in design, machines-shredders, but such equipment as a rule is not suitable for grinding raw materials in a frozen state [4].

However, subsequent defrosting can negatively affect the structure of tissues and cells. For example, kelp cells frozen at a temperature of minus 18 °C are significantly deformed after thawing and lose water irrevocably [2].
Thus, it is possible to prevent negative changes in the cellular structure of laminaria tissues and cells by preserving the physical condition of raw materials during the process of its grinding. In other words, the processing should involve raw materials that have not been previously defrosted, namely, frozen kelp in blocks. As a result, the removal the stage of their defrosting from the processing brown algae allows you to preserve the properties of processed raw materials and prevent loss of nutrients in the final product. This becomes possible when using the cryoextrusion method for the purpose of grinding raw materials from kelp [3].

Cryoextrusion called the process of punching the product frozen sample through a cooled die. In turn, the die must have a certain diameter of holes [3]. In this method, grinding occurs by cutting the raw material tissue exposed to low temperatures (minus 180 °C and below) with crystals of intracellular and intercellular ice, which is always formed inside the frozen product due to the presence of intracellular and intercellular fluid in the tissues. For raw material processing method of cryoextraction prior thawing (defrosting) is not required.

The relevance of studying this method and the products obtained as a result of its application (grinded raw materials of plant and animal origin) is justified by the possibility of obtaining products from hydrobionts with high quality characteristics. The cryoextrusion method can become part of a comprehensive industrial technology for harvesting, processing and storing marine brown algae directly in the areas of their production, which will certainly contribute to the development of the fish processing industry in the coastal “fish” regions of Russia.

The ways of industrial application of the semi-finished product obtained in this way are quite diverse – the semi-finished product can be used for further processing, including for the production of dried kelp, and also become the basis for the production cycle of full-grain granulated feed. One of the promising directions of the developed technology, especially in the situation that has developed in the Russian Federation with the need for import substitution (which concerns, first of all, the import of a significant amount of raw materials for the production of feed and feed additives), is the addition of vegetable raw materials, namely, brown seaweed (laminaria, fucus) to fish feed mince. As a result, combining the useful properties of such fish feed mince with vegetable components leads to a significant improvement in the nutritional properties of feed [1].

Thus, the aim of this work is the development of rational modes of grinding of aquatic biological resources with the use of cryoextrusion. The results obtained can be recommended for use in food and feed production technologies.

2. Materials and methods
The method of Latin (least) squares was chosen by us as the main one when planning an experimental study of the process of grinding raw materials of plant and animal origin. The use of this method helped to minimize the number of experiments performed. It should be noted that in some cases, the use of a full factorial experiment or rotatable planning is not effective. This happens when there are a lot of factors that are identified as essential for the experiment. In turn, an increase in the number of factors to implement invariably leads to the need for a large number of experiments.

We chose a two-factor method for planning the experiment on matrices with holes with a diameter of 7.0 mm and 4.5 mm the chosen shape of the holes is "hourglass".

The study of the method for obtaining a crushed product (semi-finished laminaria sugar ice cream, cryofarsh putassu), which is based on the cryoextrusion process, was carried out using a utility model of a piston-type extrusion plant with cooled working bodies.

The unit is used for grinding various types of raw materials of plant and animal origin in a frozen condition.

The installation diagram is shown in figures 1 and 2.
The design features of the installation are as follows. Hydraulic drive 2 is installed on a U-shaped carrier frame 3. The supporting frame 3 is attached to the base plate 4. In turn, the base plate is a flat plate that consists of two stages. In the upper stage of the base plate, through-threaded holes are provided for fixing the supporting frame 3, which consists of two side racks and a horizontal support beam.

Hydraulic drive 2 drives the working part of the unit 1. The working part of the unit consists of a working chamber and a cooling jacket. The height of the working part is not fixed and can be changed depending on the need. The cooled working bodies are located inside the working chamber. They are presented in the form of a moving piston (plunger) and a replaceable grinding grade (matrix). The matrix must be installed in a groove in the glass, the purpose of which is to receive the already crushed semi-finished product.

The design of the unit also provides for the use of a thermocouple for periodic temperature control of the resulting semi-finished product. There is a hole in the glass to install the thermocouple. Temperature control by means of a thermocouple must be performed in order to monitor compliance with the appropriate technological modes during the grinding process. The grinding system itself consists of a die with holes of a certain specified diameter and shape, and a plunger pair.

Before the plant starts working, the temperature of the working bodies is lowered to minus 18 °C and must be maintained in this state until the grinding process is completed. For this purpose, a circulating refrigerating agent or coolant is fed into the cooling jacket.

Together with the movement of the piston (plunger) up, the loading window of the working chamber opens, which is necessary for loading raw materials intended for grinding into the unit. When the upper "dead" point is reached, the piston stops, after which the direction of its movement changes, and the piston begins to move in the opposite direction.

When the piston starts to move down, the loading window closes. In this case, the hydraulic drive creates pressure by pushing the raw material through a replaceable grinding grate (matrix). The pressing cycle is completed after the crushed semi-finished product enters the glass. Reaching its lower point (the product has passed through the matrix), the hydraulic drive returns the piston back to the upper position [5].

To conduct the experiment, it was decided to use a grinding grate (matrix) with holes of the "hourglass" type, since the resistance is minimal when using this type of holes. The quality of grinding and reduction of energy consumption are achieved by using the grate shown in figure 3.
The experiment was carried out using blocks of Laminaria saccharifolia frozen (GOST 31583-2012 "Frozen sea Cabbage. Technical conditions") and blue whiting frozen (GOST 32366-2013 "Frozen Fish. Technical conditions").

In detail, the preparation process and methods of research of raw materials are presented in [6, 7], the characteristics of matrices in [8, 9].

The data obtained as a result of the experiment was processed using linear regression using the DataFit program (V 9.1.32). The adequacy of the obtained mathematical models was determined by the Fisher criterion (F-criterion) and the coefficient of determination [10]. The significance of each regression coefficient was determined by the student's criterion (t-criterion). The smallest values of the functions are determined by the differentiation method.

3. Results and discussion.

As a result of mathematical data processing, the response surfaces of the factor space were constructed. Figures 4 and 5 show the response surfaces of the factor space for matrices with the smallest diameter of holes of complex shape equal to 7 mm. In addition, a mathematical model is obtained—equations of the form (1).

\[ y = a + bx_1 + cx_1^2 + dx_2, \]  

where \( x_1 \) – the coefficient of the geometric shape of the hole, \( \text{cm}^3 \); \( x_2 \) – the degree of grinding of raw materials, dimensionless value.
For grinding frozen sugar laminaria by co-extrusion using a matrix with the smallest diameter of holes of complex shape equal to 4.5 mm, equation (1) will have the form:

\[ y = 11,509 - 227,246 x_1 + 2197,824 x_1^2 + 0,689 x_2, \]  

(2)

On set of values of the Fisher criterion (F-criterion) and coefficients of determination \( R^2 = 0.881 \) model should recognize adequate, all factors need to be considered as significant.

It should be noted that for matrices with a diameter of 4.5 mm holes, the degree of grinding varied from 9.65 to 14.36.

As the matrix with the calculated coefficient of the hole shape in general was not constructive, we adopted the nearest, constructive matrix with the shape of the hole of the "hourglass" type and the coefficient of the hole shape, which was 0.062.

Then, at a grinding degree of 9.65, the minimum grinding pressure respectively is 12.55 MPa, and at a grinding degree of 14.36 - 15.79 MPa.

For grinding Laminaria saccharifolia by cryoextrusion for a matrix with the smallest diameter of holes of complex shape equal to 7 mm, equation (1) will have the following form:

\[ y = 16,384 - 39,618 \cdot x_1 + 68,926 \cdot x_1^2 + 0,478 \cdot x_2. \]  

(3)

According to the set of values of the Fisher criterion (F-criterion) and the coefficients of determination \( R^2 = 0.963 \), the models were also found to be adequate, and all the coefficients of the equations were significant.

Based on the results obtained, we also concluded that the least pressure is observed by the matrix with holes of the 'hourglass' type with a hole shape coefficient of 0.32.

Then at the degree of grinding 5.13 the minimum pressure is 13.23 MPa at the same time as at the degree of grinding 8.46 the minimum pressure is 14.82 MPa respectively.

Thus, in accordance with the developed technology for obtaining crushed semi-finished laminaria, based on the use of the cryoextrusion method, we have determined the following rational modes of grinding frozen laminaria, which correspond to the matrix with holes of the "hourglass" type:

- for a hole diameter of 4.5 mm, the minimum working pressure is 12.55 MPa and the grinding degree is 9.65;
- for a hole diameter of 7 mm, the minimum working pressure is 13.23 MPa and the grinding degree is 5.13.

Taking into account the above, it is recommended to use a matrix with holes of the "hourglass" type and a working diameter of 7 mm for the semi-finished product output from 98 to 99 %.

As a result of the implementation of the experiment plan and processing of the obtained data to determine the rational modes of grinding blue whiting, matrices with the smallest working diameter of the hole 7 mm were selected. In order to create a universal regression equation that adequately describes the effect of the hole shape coefficient of the working matrix and the degree of grinding on the punching force, the previously developed mathematical model for whiting was converted to the form (4)

\[ y = 15,522 - 56,513 x_1 + 89,806 x_1^2 + 2,624 x_2, \]  

(4)

where \( x_1 \) is the coefficient of the geometric shape of the hole, cm\(^3\);
\( x_2 \) – the degree of raw material grinding, dimensionless value.

According to the set of values of the Fisher criterion (F-criterion) and the coefficient of determination \( R^2 = 0.965 \), the model is also considered adequate, and all the coefficients of the equation are significant.

The minimum grinding pressure corresponds to a matrix with a coefficient of the geometric shape of the hole of 0.32 cm\(^3\) (an "hourglass" type hole with a diameter of 7 mm) and the degree of grinding of 1.3 and is 10 MPa. The highest degree of grinding is 2.25 at a pressure of 12.54 MPa.
Based on the results of granulometric analysis, a diagram of the distribution of particles of semi-finished laminaria during grinding on an matrix with holes of the "hourglass" type with a hole diameter of 7 mm was constructed, shown in figure 6.

![Diagram of particle distribution](image)

**Figure 6.** Diagram of particle distribution according to the data of granulometric analysis of kelp during grinding on an matrix with holes of the "hourglass" type with a hole diameter of 7 mm.

### 4. Conclusion

Based on the above, it should be concluded that the "hourglass" matrix with a hole diameter of 7 mm is preferable. Since the size of the holes of the die used for punching does not fundamentally affect the change in the organoleptic properties of the final crushed product, this allows you to increase the productivity of the grinding process by using dies with larger holes.

The results of granulometric analysis confirm the organoleptic evaluation of the resulting semi-finished product from frozen sugar kelp, which has a fairly uniform structure: large fractions (from 4 to 7 mm) make up 94.8 %, and small fractions (from 1 to 3.5 mm) - 5.18% of the total mass of the semi-finished product.

Comparing the results of granulometric analysis of crushed frozen kelp and whiting on the same matrix, we can conclude about the uniformity of the resulting semi-finished product in the case of grinding raw materials of both vegetable and animal origin.

This property of the resulting semi-finished products will ensure a uniform drying speed during further processing.

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