Conference Paper

Improving the Processing of Dried Brown Algae of the Northern Basin Seas

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Abstract
Dried brown algae, abundant in the seas of the Northern basin, are additional sources of iodine, the lack of which affects more than two thirds of Russians. Brown algae of the Northern basin seas: sugar wrack and baddy wrack, harvested in the Barents Sea were chosen as the object of the study. The use of cryoextrusion and freeze-drying will allow expanding the possibilities of brown algae processing. The use of frozen raw material allows processing it industrially far from the harvesting areas. The results presented in the paper confirm the possibility and expediency of applying cryoextrusion and freeze drying since they are advanced methods of resource-saving technology for the processing of the North basin brown algae. The modes for grinding of the frozen brown algae were developed on the basis of cryoextrusion with the use of dies with holes of "cone-cone" type; the design of the unit is protected by a patent. The yield of ground semi-finished product obtained at different modes varies from 98.57 to 99.80 % from the weight of the raw material. The resulting semi-finished product is of homogeneous structure. The use of freeze-drying, depending on the type, allows achieving the final content of product moisture from 5,24 to 10, 6 %.

Keywords: brown algae, cryoextrusion, freeze drying

1. Introduction

According to the Research Center of Endocrinology of Ministry of Health of the Russian Federation, more than two thirds of inhabitants of our country suffer from iodine deficiency, resulting in memory loss, fatigue, frequent depression [1]. Dried algae, the Northern basin seas are rich in, can be used as an additional source of iodine. In the far North algae are often the only natural source of vitamins and minerals. Algae are superior to terrestrial plants in the content of some trace elements. Brown algae are often dried naturally or using freeze dryers. However, drying in natural conditions is long-term and directly depends on weather conditions. The freeze-drying of fresh seaweed is possible only for several months after harvesting. To increase the opportunities of processing the brown algae all year round it is advisable to utilize frozen raw material.
This paper presents the results of improving the processing of dried brown algae, obtained using freeze-drying of the frozen raw material ground by cryoextrusion.

2. Materials and Methods

2.1. The object of and preparation

The brown algae of the Northern basin seas were chosen as the object of study: sugar wrack according to GOST 31583-2012 "Frozen seaweed. Technical Specifications" and bady wrack caught in the Barents Sea.

The beneficial effect of algae has been appreciated since the ancient times. In the 13th century, in China there were decrees obliging people to use seaweed in food to prevent a number of diseases. Brown algae contain a complete set of minerals and more than forty micro- and macroelements [2-4].

Before the experiments began, the raw material was evaluated organoleptically, bady wrack was frozen in the unit EQTA BC05 Benefit of 5 levels 265025. The frozen raw material was cut into rectangular pieces, their linear dimensions were determined using a measuring ruler.

2.2. Experimental equipment

The experimental study was carried out in several stages. At the first stage, pre-prepared frozen raw material was ground by cryoextrusion in an extruder-grinder. A detailed description of the extruder-grinder is presented in [5]. Grinding dies are shown in Figure 1. The parameters and calculation of dies are presented in detail in [6].

Figure 1: Grinding dies.
At the second stage, the ground raw material was dried by two methods: vacuum freeze-drying and freeze-drying at atmospheric pressure. The thickness of the raw material's layer being dried was 10 mm.

**Figure 2**: Freeze dryer FreeZone 1L.

**Table 1**: Experimental conditions.

| Parameter                                           | Raw material -- frozen sugar wrack, Frozen bady wrack |
|-----------------------------------------------------|------------------------------------------------------|
| **Grinding of raw material**                         |                                                       |
| Sample volume, cm$^3$                                | 77.00 $\div$ 160.8                                   |
| Equivalent diameter, mm                             | 35.91 $\div$ 64.60                                   |
| Specific surface m$^2$ / kg                          | 0.1990 $\div$ 0.4864                                 |
| Mass of raw materials loaded into the working chamber, g | 31.48 $\div$ 83.50                                   |
| Temperature of the extrusion chamber, °C             | minus 18                                             |
| Temperature of the raw material, °C                 | minus 18                                             |
| Temperature of the ground semi-finished product, °C | minus 18                                             |
| The coefficient of the geometric shape of the holes of the grinding die, cm$^3$ | 0.100694 $\div$ 0.534748 |
| **Freeze-drying of the ground semi-finished product** |                                                       |
| **Vacuum**                                           |                                                       |
| Collectortemperature, °C                             | minus 50                                             |
| The initial temperature of the crushed semi-finished product, °C | minus 18 |
| The duration of the process, h                       | 1 $\div$ 6                                           |
| **At atmospheric pressure**                          |                                                       |
| Air temperature, °C                                  | minus 18                                             |
| The initial temperature of the ground semi-finished product, °C | minus 18 |
| The duration of the process, day                     | 43 $\div$ 65                                         |
The process of vacuum freeze drying was performed on the freeze dryer - FreeZone 1L, with a condenser capacity of 1 l and a collector temperature of "minus" 50 °C, shown in Figure 2.

Freeze-drying at atmospheric pressure was done using a shock freezer EQTA BC05 Benefit of 5 levels 265025 at temperature "minus" 18 °C.

The initial and residual moisture content of the dried product using the moisture analyzer (VCHM, Chizhova’s device).

The conditions of the experimental stages are presented in table 1.

2.3. Research Methods

The technique of the experiments on grinding the raw material and the mathematical processing of the data obtained at this stage are described in [5].

When determining the initial moisture content of the raw material and the residual moisture content of the dried product, the sample was dehydrated applying evaporation by heating at the required temperature for a certain time.

Mass fraction of water in the ground raw material before and after drying was calculated by formula 1:

\[ X = \frac{(m_1 - m_2) \cdot 100}{m_1 - m} \quad (1) \]

where \( m \) is the mass of an empty bag, g; \( m_1 \) is the mass of the bag with a sample before dehydration, g; \( m_2 \) is the mass of the bag with the sample after dehydration, g. The reliability of the results obtained is ensured by triplicate experiments.

During the process of drying, the temperature and pressure in the apparatus were controlled, and the process time was recorded.

2.4. Experiment Planning and Data Processing

The smallest number of experiments was achieved by planning the experiments using the method of Latin squares [7].

The search for a rational grinding regime was carried out by linear regression using the program DataFit version 9.1.32. The adequacy of the developed mathematical models was determined according to the Fisher criterion (F-criterion) and the determination coefficient, the significance of each regression coefficient was determined by the Student criterion (t-criterion) [8]. The smallest function values are determined by differentiation.
Microsoft Office Excel software was also used for graphical presentation of the obtained results with subsequent analysis

3. Results and Discussion

In grinding of the frozen brown algae, the degree of the raw material grinding varied from 5.13 to 13.97, driving pressure from 12.26 to 19.12 MPa (from 125 to 195 (kgf / cm²)), the duration of the process was from 15 to 60 s. The yield of semi-finished product ranged from 98.57 to 99.80% of the raw material mass.

Figure 3 shows frozen sugar wrack, ground by cryoextrusion.

As a result of processing the experimental data, equations were obtained that adequately describe the dependence of the grinding pressure of frozen brown algae (y) on the coefficient of the geometric shape of the die hole (x₁) and the degree of grinding of raw materials (x₂). Equation (2) corresponds to dies with the smallest diameter of complex shaped hole, 4.5 mm

\[ y = 11.509 - 227.246x_1 + 2197.824x_1^2 + 0.689x_2, \]  

(2)

where \( x_1 \) is the coefficient of the geometric shape of the hole, cm³; \( x_2 \) - the degree of grinding of raw materials, dimensionless quantity.

By the combination of the Fisher criterion (F-criterion) values and the coefficient of determination \( R^2 = 0.881 \), the model is recognized as adequate and all the coefficients of the equation are significant.

The response surface of the factor space corresponding to Equation (2) is shown in Figure 4. The smallest grinding pressure is 12.55 MPa and corresponds to the dies with holes of "cone" - "cone" type with grinding ratio 9.65.
Figure 4: Response surface of factor space of cryoextruded frozen brown algae grinding pressure for the dies of 4.5 mm - the minimal diameter of complex shaped holes.

The chemical composition of the ground semi-finished product from sugar wrack is presented in table 2.

| Parameter                     | Value |
|-------------------------------|-------|
| Mass fraction of protein, percent | 6,25  |
| Mass fraction of ash, percent  | 26,02 |
| Mass fraction of moisture, percent | 76,4  |

The generalization of the results of the particle size analysis, presented in Figure 5 suggests a fairly uniform structure of the obtained semi-finished product: large fractions (from 3.5 to 7 mm) make up 87.47 %, and small fractions (from 1 to 3 mm) - 12.53 % of the total mass.

The results of freeze-drying of ground frozen brown algae are presented in figures 6 and 7.

The use of vacuum freeze drying allowed obtaining sugar wrack with a final moisture content of 5.24 and 5.46 % for the diameters of the holes of the grinding dies 7 and 4.5 mm, respectively. Freeze-drying at atmospheric pressure made it possible to achieve the final moisture content 7.6 and 7.8 % for bady wrack, and 10.6 % for sugar wrack, in both cases die openings are of the same diameter.

4. Conclusion

The presented results confirm the possibility and expediency of applying cryoextrusion and freeze drying since they are advanced methods of resource-saving technology for processing the brown algae of the North basin.
Figure 5: Distribution of the particles of frozen brown algae ground by "cone - cone" type die (5.5 \ 4.5 \ 5.5).

Figure 6: Change in moisture of ground frozen sugar wrack during vacuum freeze-drying, depending on the duration of the process.

Figure 7: Change in moisture of ground frozen brown algae in the process of freeze-drying at atmospheric pressure depending on its duration, for bady wrack (a), for sugar wrack(b).

The modes of grinding the frozen brown algae based on cryoextrusion using dies of "cone-cone" type (8 \ 7 \ 8 and 5.5 \ 4.5 \ 5.5) have been developed. The smallest grinding pressure, for example, for a die with holes 5.5 \ 4.5 \ 5.5, is 12.55 MPa at grinding ratio 9.65. The yield of the ground semi-finished product in various modes ranges from 98.57 to 99.80 % from the weight of the raw material.
The use of freeze-drying, depending on its type, allows achieving the final moisture content of the product from 5.24 to 10.6 %.

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**Conflict of Interest**

The authors have no conflict of interest to declare.

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