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# THERMOGRAVIMETRIC RESEARCH INTO FISH AND PLANT SEMIFINISHED PRODUCTS MADE OF RAW AND BLANCHED TISSUES OF AZOV GOBY AND WHEAT BRAN

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*Проведено визначення термогравіметричних показників та диференційно-термічний аналіз нативних та відновлених рибо-рослинних напівфабрикатів на основі бичка азовського. Здійснено порівняльну характеристику кількості адсорбційно та капілярно зв'язаної вологи досліджуваних зразків. Вивчено вплив рослинної сировини, гіротермічної обробки та процесу дегідратації рибо-рослинних напівфабрикатів на форми та енергію зв'язку вологи*

*Ключові слова: термогравіметричний аналіз, рибо-рослинні напівфабрикати, бичок азовський, дегідратація, капілярна і адсорбована волога, енергія активації*

*Определены термогравиметрические показатели и осуществлен дифференциально-термический анализ натуральных и восстановленных рыбо-растительных полуфабрикатов на основе бычка азовского. Осуществлена сравнительная характеристика количества адсорбционно и капиллярно связанной влаги исследуемых образцов. Изучено влияние растительного сырья, гигротермической обработки рыбного сырья и процесса дегидратации рыбо-растительных полуфабрикатов на формы и энергию связи влаги*

*Ключевые слова: термогравиметрический анализ, рыбо-растительные полуфабрикаты, бычок азовский, дегидратация, капиллярная и адсорбированная влага, энергия активации*

## 1. Introduction

Modern trends of improvement of food product technologies are oriented at creating balanced products by their nutritional value enriched by biologically valuable nutrients. It is known that among the nutrients needed to satisfy physiological needs of the human body, the most valuable is protein. A promising direction in the creation of protein-containing products of a new generation is a target combination of hydrobionts and vegetable raw materials. Hydrobionts occupy an important place in human nutrition due to the high content of easily digestible valuable proteins with a balanced amino acid composition.

Problems of creating balanced fast food and semifinished products with a high degree of readiness need a solution. Further improvement of technologies and properties of health food based on fish and plant raw materials, in particular dry polyfunctional semifinished products of long storage, is an actual issue. They can be used in the technologies of a wide assortment of culinary products, bakery products

as protein-mineral enrichers, in the technologies of snack products, sauce concentrates, dry breakfasts, concentrates of lunch products, dry molded products for special purposes (soldiers nutrition, tourists, etc.).

Considering that the traditional ways of drying of food raw materials are very energy-intensive, long-lasting and do not allow obtaining a homogeneous quality product, searching for new and improvement of existing methods of drying is rather actual. Herewith the priorities are determined in the direction of reducing the duration of drying process, reducing specific energy consumption, improving quality of the finished fish and plant products.

The process of dehydration of fish and plant semifinished products is one of the important stages that characterizes quality of the finished product and economic efficiency of its production. Defining the peculiarities of the state of moisture in fish and plant semifinished products based on raw and blanched Azov goby (guttated headless) using plant ingredients by the method of thermogravimetric analysis will make it possible to substantiate the structural changes of water.

## 2. Literature review and problem statement

The technologies of complex and low-waste processing of available fish raw materials, especially small Azov goby, gain an important value for food security of the country. Today this type of fish raw materials is one of the most representative and affordable by its price objects of the marine fisheries in Ukraine. Azov Goby *Neogobius melanostomus* is a source of valuable and easily digestible protein and its bone tissue is a source of bioavailable calcium, which determines the expediency of its complex processing for the production of food products in the segment of social nutrition [1, 2]. Implementation of resource-saving technologies, in a simultaneous reduction of dependence on the foreign market, will allow reducing the waste, using local fish resources more efficiently, reducing the cost and increasing the efficiency of production of fish products.

Significant contribution to the solution of the fundamental problems of creating the technologies of dry products with plant and fish raw materials was achieved by studies of many scientists [3–10]. Many of them continue to deal with this problem, because it has not lost its relevance today.

The known technologies of dry fish and plant products [11–13], in our opinion, have some faults related with those that do not take into account the bioavailability of fish protein that is introduced. In addition, the use of powdered sugar and sacchariferous plant raw materials in the production of developed dry foods may adversely affect their organoleptic characteristics and the process of digestion in the gastrointestinal tract of humans. It is generally known that at temperatures from 40–60 to 100 °C, the interaction of proteins with renewable sugars occurs at considerable speed, accompanied by the formation of carbonyl compounds and dark colored products – melanoidins (Mayar reaction). Sugar amine reaction is the cause not only of food darkening but also the loss of essential amino acids (lysine, threonine). Melanoidins reduce the biological value of products, as the digestibility of amino acids is reduced because the sugar amine complexes are not amenable to hydrolysis by enzymes of the digestive tract.

In recent years, an increase has been observed in the interest of scientists to the creation of new technologies of food-stuffs with fish, enriched by dietary fibers. While the authors pay special attention to the research into scientific aspects of using insoluble forms of dietary fibers in the composition of fish products, in particular, vegetable fibers [14–16].

The use of vegetable fiber in the composition of fish products gives them healthful properties, enabling to reduce the energy value, the content of cholesterol and fats. Vegetable fiber in technologies of fish products also can solve certain technological challenge for moisture and fat retention, regulation of hydration, viscous and plastic, adhesive properties, texture and sensory characteristics, parameters of quality during storage [17, 18].

Researchers confirmed the technological and physiological efficiency of using vegetable fiber, such as wheat bran, in the technologies of combined and restructured fish products. Technological effect from the use of wheat bran as part of fish mince from muscle tissue of hake, horse mackerel and other species is to raise moisture viscous properties and improvement of structural and mechanical characteristics of minces [19, 20].

Authors defined the efficiency of hydrobionts use (fish oil, fish protein, biologically active peptides, seaweed, micro

seaweed) as functional ingredients for making bakery and pasta products of high biological value [21].

A production technology is known of making cookies using 12 % paste from hygro-thermic treated fish bones of tilapia and flax seed from the mass of wheat flour [22]. It gave the possibility to enrich the cookies with Omega-3 fatty acids, protein and mineral substances, including Calcium, Phosphorus and Iron.

A certain number of studies are devoted to the study of the thermophysical properties of fish raw materials and hydrobionts. A large part of such studies covers the problem of moisture condition and thermal conversion in structures based on muscle tissue, collagenous – with skin and scales of fish raw materials and chitosan – from the shells of molluscs [23, 24]. However, the thermographic studies of the combined fish and plant systems on the basis of muscle, bone and connective tissue of fish raw materials and wheat bran are absent.

Despite the significant amount of scientific data, the aspect of the problem concerning the rational and complex processing of small Azov goby remains explored insufficiently. However, this type of fishery resources is the largest and the cheapest way of fishing industry in Ukraine. The complex use of muscle, connective and bone tissue of Azov goby has scientific and practical interest for the production of poly functional dry fish and plant semifinished products on the principles of complexity of processing and energy efficiency. It should be noted also the insufficiency of study of technological and thermophysical properties of dehydrated combined food systems of multifunctional purpose based on fish and plant raw materials that, depending on the technological tasks, fulfill different functions in nutrition systems.

According to the results of complex of the conducted studies, we developed an ingredient formulation of dry concentrates of the multifunctional purpose based on fish and plant food compositions with a determined complex of indicators of nutritional value. Developed products are dried minces (moisture content is 10–12 %) from the preliminary thermally treated fishing raw materials with the use of enriched mixtures. Wheat and oat bran, kelp powder, seed of flax, sunflower and pumpkin, carrot and pumpkin puree, a wide assortment of spicy-aromatic raw materials and spices are selected as the raw material for the developing of enriched mixtures. Dry concentrated products of multifunctional purpose, optimized for biologically valuable nutrients, may be recommended for health food of different population groups as snack foods, in the composition of soups-puree or cereals of instant cooking, as well as protein-mineral supplements for a wide range of food products.

A special feature of the used scientific approach to the development methodology is a consideration of the influence of different technological factors and complex of physical and chemical and functional technological properties of raw materials on the regularities of formation of the developed capillary-porous structure of dry polyfunctional fish and plant semifinished products to ensure their quality and safety, minimize the losses of the labile food nutrients and increasing the efficiency of the technological process. Increasing the complex of processing of fishing raw materials, the use of plant ingredients and ways of preliminary preparation allow reducing the resource capacity of the production of fish and plant semifinished products, the duration of the process of dehydration.

Scientific justification of the method of drying of food products during production of the dry fish and plant semifinished products requires a depth study of effectiveness of the process of drying. The effect of plant ingredients and preliminary hydrothermic treatment of fishing raw materials on patterns changes of moisture in terms of thermal heating of native and recovered fish and plant semifinished products based on mince made from muscle, connective and bone tissue of Azov goby is studied unsufficiently. This causes the need for research in this direction.

The moisture in the developed fish and plant semifinished products based on mince from Azov goby is found in different states, the degree of its connectivity with the protein and carbohydrate components of the semifinished products will affect the duration of dehydration and play a significant role in forming the structural and mechanical properties of semifinished products, as well as to exert influence on the behavior of the food systems during storage.

Research and detailed analysis of the thermographic data of native and recovered fish and plant semifinished products based on Azov goby covers the main aspects of the forms of moisture binding in them and the structural changes that take place under the influence of thermal treatment.

### 3. The aim and tasks of the study

The aim of present work is the study of features of moisture state in fish and plant semifinished products based on the raw and blanched Azov goby, whole and gutted, headless, using plant ingredients (wheat bran) and its structural changes that occur under thermal treatment.

To achieve this aim, the following problems were to be solved:

- to determine thermogravimetric indicators and conduct differential thermal analysis of the experimental samples of fish and plant semifinished products based on raw and blanched Azov goby, whole, gutted, headless, using plant ingredients;

- based on data analysis, to conduct a comparative characteristic of the amount of adsorption and capillary bound moisture in the experimental samples of semifinished products on the basis of complex processed raw, blanched Azov goby and the recovered dry fish and plant semifinished product with blanched Azov goby;

- to explore the effect of plant raw materials, hygrothermal treatment of Azov goby on the forms of moisture bonds, change in moisture retaining ability and the nature of activation energy in the fish and plant semifinished products.

### 4. Materials and methods of the research into thermophysical processes of fish and plant semifinished products

As objects of study, we used freshly prepared (native) model minces based on raw and blanched Azov goby, whole, gutted, headless, using functional plant ingredients, as well as model minces from the recovered dry fish and plant semifinished products (powders) (Fig. 1).

Detailed methods of research into thermal-physical processes of the fish and plant semifinished products are given in paper [25].

Activation energies ( $E$ ), calculated by the represented method, and pre-exponential factor ( $k_0$ ) of the experimental samples are given in Table 3.

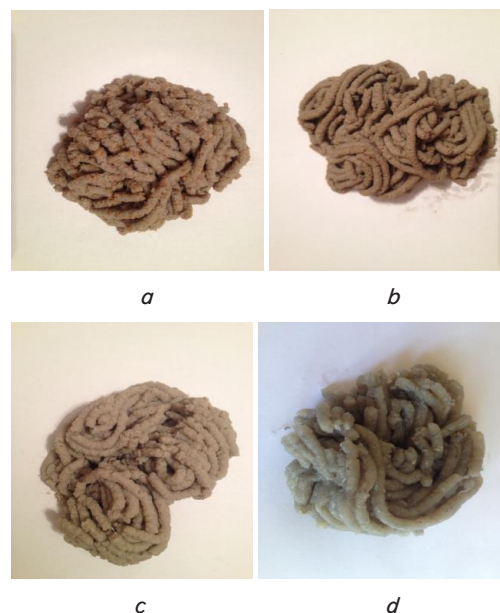


Fig. 1. Experimental samples of fish and plant semifinished products: *a* – control 1 (C1), model mince from whole gutted headless Azov goby blanched, crushed twice on a mincer with a diameter of holes 5 and 2 mm; *b* – control 2 (C2), model mince from the whole gutted headless raw Azov goby, crushed twice on a mincer with a diameter of holes 5 and 2 mm; *c* – experiment 1 (E1), model mince from the whole gutted headless Azov goby, blanched, crushed twice on a mincer with the addition of 15 % wheat bran; *d* – experiment 2 (E2), model mince on the base of dry fish and plant semifinished product, recovered (hydro module 1:3) – from whole gutted headless Azov goby, blanched, crushed twice on a mincer with the addition of 15 % wheat bran

### 5. Results of thermogravimetric research into fish and plant semifinished products from native and blanched tissues of Azov Goby and wheat bran

Drying is a complicated thermal process of moisture removal, which occurs as a result of its evaporation and diffusion. Wet fish and plant minces are the colloid dispersion systems. According to the classification of A. V. Lykov, such systems during dehydration are considered as capillary-porous colloidal bodies where moisture is combined with the skeleton of the body by forces different in their physical nature. Moisture transfer mechanism is determined by the form of bonds of moisture with wet body, features of its structure and thermodynamic conditions of the body's interaction with the environment. Wall porous skeleton body (capillaries) absorbs water, as a result, the bodies become swollen at wetting. Capillaries of porous body are rather elastic, and at drying they give shrinkage and become brittle. In capillary-porous body, moisture is mostly held by adsorption and osmotic diffuse forces. The transfer of liquid-like moisture occurs by the diffuse way by the type of selective diffusion, which is caused by the difference in osmotic pressures. Moisture transfer (moisture diffusion)

in the experimental samples is described by the gradients of moisture content and temperature.

According to the scheme of M. F. Kazanskiy, all moisture in colloidal capillary-porous bodies, that are the samples of minces, based on fish and plant raw materials, is divided into moisture of physical-mechanical and physical-chemical bonds. Moisture of physical and mechanical bond includes three types of capillary moisture, two of which represent water, that differ from each other by the feature of states (capillar and joint) in the gross macropores of the body, and the third is the capillary moisture of micropores. All the moisture of physical and chemical bonds may consist of osmotic moisture and two types of adsorbed moisture, such as moisture of poly-molecular and mono-molecular layers at the internal and external surfaces of the capillary-porous body.

We obtained dependences of relative change in mass  $\Delta m/m_0$  (Fig. 2, 3) and derivative of the change in mass DTG (Fig. 4, 5) on the temperature for different samples of the fish and plant semifinished products.

Weight loss by the experimental samples is related to the evaporation of moisture; in this case, the use of plant raw materials slows down the process of moisture evaporation. The curve T shows the gradual increase of temperature inside the sample in any moment of heating. For all of the samples we observe a bend of slowing the heat inside at the temperature range from 110 to 140 °C that can be accounted for by the endothermic transformations in samples, which are associated with the processes of evaporation of moisture, and is confirmed by the presence of endopeak in the specified temperature range on the DTA curve. In this period, molecular diffusion of osmotic-related and capillary moisture wetting is also reduced due to the amplification of thermal gradient, which reduces the speed of drying.

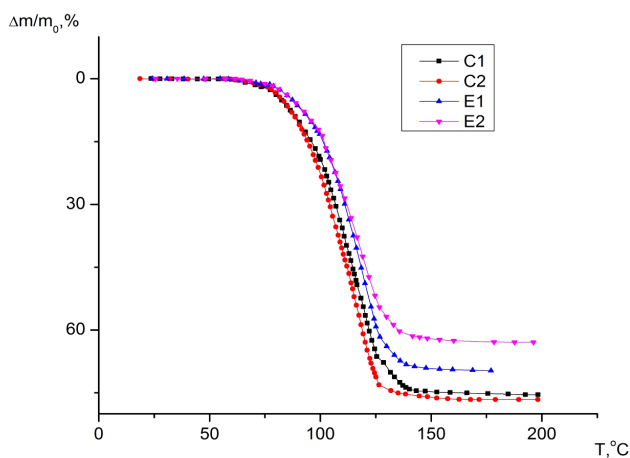


Fig. 2. Temperature dependence of relative changes in the mass of fish and plant semifinished products based on model minces  $F=\Delta m/m_0$

The curve TG that describes the reduction in the mass of the sample for the control sample (C1 and C2) begins to come down slowly at temperature above 57 °C, for the experimental samples of minces (E1, E2) – at temperatures 80 and 93 °C, respectively. However, there is also a bend on the curve, which coincides with the temperature of the end of endothermic process – about 150 °C.

DTG dependence, which characterizes the speed of mass change in the experimental samples, is divided into peaks with the help of Gauss distribution (Table 1). DTG depen-

dence for each of the experimental sample optimally can be described by the presence of four peaks with maximum in temperature ranges:  $T_{m1}$  – from 57 to 63 °C,  $T_{m2}$  – from 102 to 110 °C,  $T_{m3}$  – from 119 to 122 °C,  $T_{m4}$  – from 132 to 136 °C (Table 1).

Table 1

Analysis of DTG peaks of the fish and plant semifinished products

Name of the sample	I ( $f_1$ )		II ( $f_2$ )		III ( $f_3$ )		IV ( $f_4$ )	
	$T_{m, °C}$	w, %	$T_{m, °C}$	w, %	$T_{m, °C}$	w, %	$T_{m, °C}$	w, %
Control 1	63	5	102	44	122	41	136	10
Control 2	61	4	108	67	119	25	132	4
Experiment 1	57	3	107	43	120	38	135	15
Experiment 2	61	3	110	69	122	20	133	8

According to the results of DTG peaks analysis of the fish and plant semifinished products, it is determined that the largest number of capillary bound moisture of micropores is in the control sample C2, made from the raw mince of Azov Goby as well as in the experiment sample E2, made from the recovered dry fish and plant semifinished product. The loss of moisture by them in  $f_2$  is the highest and reached 67 and 69 %, respectively. The largest number of osmotic and adsorption bound moisture is seen in the control sample C1 and experiment sample E1, the loss of moisture by them in  $f_3$  reached 41 and 38 %, respectively.

Results of analysis of the peaks  $f_3$  that describe the process of removing of the osmotic and adsorption bound moisture of the fish and plant semifinished products are presented in Fig. 3.

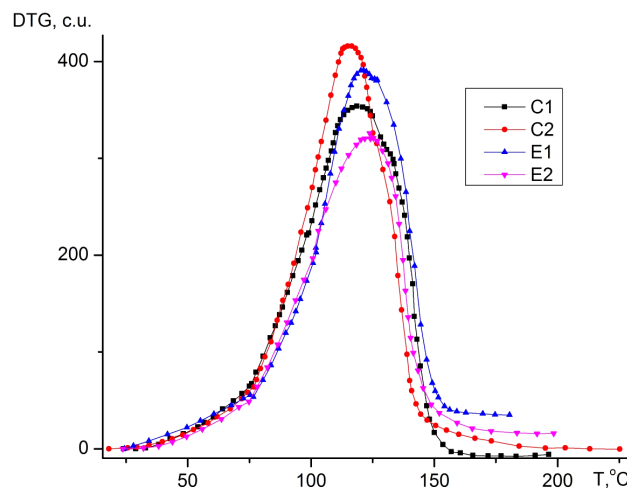


Fig. 3. Temperature dependence of derivative of mass change  $f_3=dF/dT$  of control (C1 and C2) and experimental (E1, E2) samples of the fish and plant semifinished products

There is a pronounced thermal effect on DTA curve associated with the processes that occur with the heat absorption. It is observed for all experimental samples (Fig. 4).

The temperature interval of endopeak is in the range from 50 to 80 °C (process start) through 110...130 °C (endopeak maximum) to 140...175 °C (process finish). The area of the endopeak characterizes energy consumption for the implementation of processes that occur in the specified tem-

perature interval. They are caused by thermal destruction of the samples and release of gas-like phase. In this case, the most energy consuming process of dehydration is observed in the control sample C2, which is made from raw fish mince.

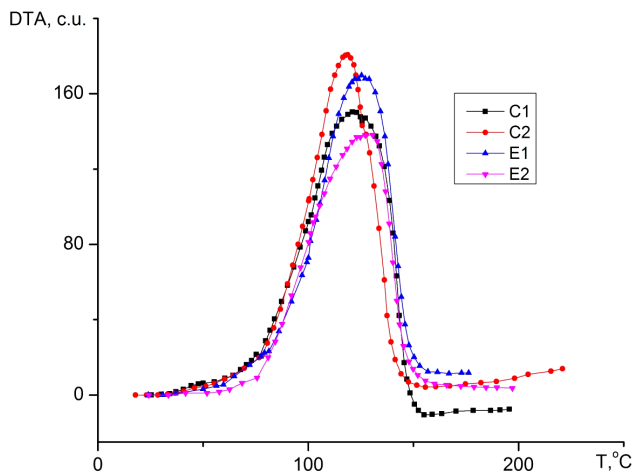


Fig. 4. Peaks of DTA dependence of control (C1 and C2) and experimental (E1, E2) samples of the fish and plant semifinished products

According to the derivatograms, we defined the amount of water which is lost by the samples at different temperature intervals. Results of the calculations are presented in Table 2.

Table 2

Analysis of derivatographic curves of the fish and plant semifinished products

Name of the sample	Water which is lost by samples according to zones, mg			
	25–75 °C	76–100 °C	101–125 °C	126–150 °C
Control 1, mg	3,68	39,17	134,72	151,87
Control 2, mg	4,03	46,86	142,45	152,48
Experiment 1	3,19	26,53	118,37	138,73
Experiment 2	2,44	27,62	110,80	126,47

It is found that at temperature 25–75 °C, it is removed from 1.20 % (experiment 2) to 1.81 % (control 1) of free moisture from the experimental samples of control and model minces, which is kept in the rough macropores of the body and mechanically held in the joints of macropores (Table 2). Besides, the largest amount of free moisture is released from the control samples that may indicate a higher content of free moisture in them.

At temperature 76–100 °C, physical-mechanical moisture of macropores continues to release, as well as micro capillary moisture. Its amount, lost by the control samples, is significantly larger by the table data than experimental mince samples. Besides, the largest amount of mechanically-bound capillary moisture is released from the control samples that may indicate a higher content of free moisture in them and their better developed capillary-porous structure in size, amount and total area.

It is found that experimental samples of model minces lose less amount of water over temperature period 76–100 °C, unlike the control ones (Table 2). The share of water losses by the experimental samples of native and recovered fish minces has approximately the same values – 11.67 and 12.41 %,

respectively experiment samples E1 and E2, which may indicate their certain identity in size, amount and total area of macro and micro capillaries.

The degree of water binding in the fish and plant semifinished products may be characterized by the speed of moisture loss. At the same time, the amount of water, that is actually removed, will be different. According to the results of calculations of TG data curve and change in the mass of water for each experimental, sample histograms are built, which allow identifying the intensity of moisture release at different temperature intervals (Fig. 5).

Histograms are characterized by the presence of four periods, which correspond to the zones of samples heating. The share of water removal from areas of free and capillary moisture (the first and second periods) is lower than from the area of water binding zone (the third period).

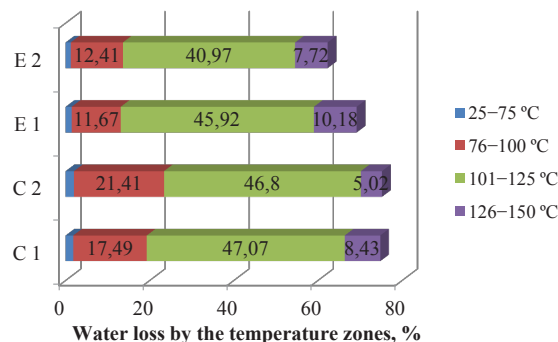


Fig. 5. Dynamics of water loss by the fish and plant semifinished products by the temperature zones during heating, %

It is found that the largest loss of mass by the samples (over 40 %) occurs in the third temperature period – 101–125 °C. During this period, the osmotic and adsorption bound moisture is removed, which is bound with colloid more strongly (proteins, polysaccharides) and diffuses in the form of steam. Experimental samples over this period lose a lower share of water – 45.92 and 40.97 %, respectively for samples E1 and E2, which indicates a higher content of bound water in their composition (Fig. 5).

Traditionally it was believed that the growth of energy consumption during drying is due to the removal of more tightly bound water and reducing the amount of bound water that is possible only after the removal of all free water. But today there are a number of experimental papers, from where it follows that it is not always so. There is a considerable amount of scientific data about the removal of free and bound water from plant and animal materials during drying. In this case, specific content of bound water under conditions of drying is determined by the hydration capacity of components of dry material substances and their change under conditions of drying.

There are a variety of known mechanisms of water binding by the organic and mineral substances of animal and plant tissues:

- ionic hydration of soluble salts;
- hydration of ordinary soluble carbohydrates with the formation of water clathrates;
- hydration of complex insoluble carbohydrates of the cellulose type, between molecules of which water is held with the help of two hydrogen bonds;
- hydration of gelling polysaccharides and starch;

– complex mechanism of hydrophilic and hydrophobic hydration of protein and fats molecules. All these types of interaction of chemicals, animal and plant tissues with water differ in energy bonds and a number of bound molecules.

In connection with the stated above, of specific scientific interest is the study of conditional activation energy of experimental systems from native and preliminary thermally treated fish raw material, separately and in combination with plant raw materials at different temperatures of moisture removal.

According to data of thermograms of the conducted differential-thermal analysis and the methods proposed in present work, we calculated conditional activation energy ( $E$ ) and pre-exponential factor ( $k_0$ ) of removal of bound moisture at different temperatures – for endothermal peaks  $f_2$  and  $f_3$ , which are listed in Table 3.

Table 3

Characteristics of conditional activation energy of the fish and plant semifinished products

Name of sample	Moisture content ( $w^0$ ), %	Conditional activation energy ( $E$ ), kJ/mol		Pre-exponential factor ( $k_0$ ), units	
		$f_2$	$f_3$	$f_2$	$f_3$
Control 1	74,5	152	223	44	63
Control 2	77,0	143	280	41	81
Experiment 1	69,6	124	263	34	76
Experiment 2	63,0	121	282	34	82

Calculated for peak  $f_2$ , whose characteristic is the removal of low bound moisture – capillary and, partly, osmotic bound moisture, the experimental mince samples with plant raw material had low values of conditional activation energy, which are lower than the correspondent values for minces without plant additives. Indeed, for peak  $f_2$ , conditional activation energy and pre-exponential factor of the control samples exceeds the experimental ones by 20.4 % on average (Table 3). A higher value of conditional energy of activation of the control sample from thermally treated mince compared to the native (by 6.3 %) in  $f_2$  may be caused by changing in the hydration capacity of the components of dry substances in the samples under conditions of drying and requires additional research.

However, in the next endothermal peak  $f_3$ , conditional activation energy and pre-exponential factor of control sample C1 have the lowest value among all experimental samples – 223 kJ/mol and 63 units respectively. At this temperature peak, a significant share of water is removed from the hydration shells of soluble substances, which has higher values of bound energy with the product. Higher values of activation energy of the molecules of water in  $f_3$  are displayed by control sample C2 (280 kJ/mol), made from raw fish material, that is by 25.56 % larger than the corresponding values of C1 compared to control sample C2, which is made from blanched fish mince (Table 3).

Table 3 displays that the activation energy (263 kJ/mol), and pre-exponential factor (76 units) in  $f_3$  for experimental sample E1 using wheat bran, by 17.94 % and 20.63 %, respectively, higher than the values of these indicators for control sample C1 (223 kJ/mol and 63 units), indicating the larger amount of bound water. It may be related to the decrease in

the degree of hydration of soluble polysaccharides of plant component on the experimental samples over this period.

Conditional activation energy and pre-exponential factor for experimental sample E2, made from the recovered fish and plant semifinished product, in  $f_3$ , have the highest values among all experimental samples – 282 kJ/mol and 82 units, respectively.

## 6. Discussion of research results into thermal-physical processes of the fish and plant semifinished products

According to the calculation of conditional activation energy of model fish and plant minces, the existence of differences is found in its values for some objects at different temperatures of bound moisture removal, which is explained both by the processes of tissues deformation, proteins denaturation, which lead to the change in the quantity of active centers, and by the decrease in the degree of polar, non polar and volumetric hydration of protein molecules of minces and soluble polysaccharides of wheat bran – cellulose, hemicellulose, pectin substances.

It is found that conditional activation energy for the mince made from thermally pre-treated mince at temperature 102 °C ( $f_2$ ) exceeded by 6.3 % the corresponding value for the mince from the native fish raw material. Binding energy in  $f_2$  for the sample from blanched fish raw material is higher in comparison with the sample from native mince as a result of a more complicated process of releasing the molecules of bound moisture of volumetric hydration of proteins (first of all, capillary-bound moisture of micropores and osmotic-bound moisture) from the ordered structures of denatured protein molecules. Thus, hygrothermic pre-treatment of fish raw materials leads to a partial loss of free moisture and a certain increase in weakly bound moisture as a result of watering of proteins in fish, first of all myofibrillar muscle proteins of fish, and also as a result of glutenization of collagen connective tissue and ossein, bone tissue of fish raw material.

However, in the next endothermal peak  $f_3$  (at 119 °C), conditional activation energy of mince sample made from the native fish raw material exceeded the value for the thermally treated mince significantly, by 25.6 %. It confirms a larger share of the bound water in the mince samples from native fish. This can be explained by the presence of active phase of the conformation process of protein denaturation of complex of raw tissues of Azov goby in temperature peak  $f_3$ , accompanied by a significant decrease in their hydration degree and release of a significant part of bound moisture. It is known that thermal efficiency of convectional-conductive drying of animal and plant tissues increases according to the reduction in the amount of water that they are able to bind. The presence of exothermal denaturation process may affect the reduction in thermal efficiency of drying of native tissue of fish raw materials due to possible reduction in their thermal-physical properties and the intensity of their heat moisture exchange, which requires conducting additional research into determining specific heat capacity of tissues and heat of water evaporation.

It is determined experimentally that experimental samples of model minces lose less amount of water by the temperature zones, in contrast to the control samples, which indicates the lower content of free moisture in them. Such

a difference in the loss of water mass by the mince samples over this period can be explained by the difference in the amount of previously absorbed water by them (moisture content in the beginning of the process), as well as the influence of plant components, due to high moisture binding properties (content of the hydrophilic functional groups) and large specific surface increase the energy of moisture binding in a product.

It is possible to predict that the introduction of powdered dispersions ( $50 < r < 500$ ) to the composition of fish mince that have large specific surface and, consequently, high capacity to absorb moisture leads to the transition of moisture, contained by the fish mince without additives in free state (bound by physical-mechanical forms of bonds), into the bound state, which should objectively lead to the increase in bond heat, increase in the viscosity of cells of dispersion medium and, accordingly, to the strengthening of product structure.

Experimental data regarding conditional activation energy of experimental samples allow confirming this assumption. Indeed, for peak  $f_3$ , characterized by the removal of large portion of water from the hydration shells of dissolved substances, experimental samples of minces made from plant raw material have high values of conditional energy of activation, which exceeded the corresponding values for the control thermally pre-treated mince without plant additives. It can be associated with a decrease in the degree of hydration of soluble polysaccharides of plant component of the experimental samples over this period as a result of partial removal of water from the hydrate shells.

Taking into account the given results, it would be correctly to argue about increasing the amount of bound water and maintaining larger amount of bound water by the system in the experimental samples E1 and E2 due to the increase in specific surface of its disperse structure when using powder-like plant raw materials, as well as the formation of hydration bonds by bran polysaccharides which include hemicellulose, cellulose, lignin, pectin substances in its composition. Probably, when introducing powder-like dispersion into the composition of fish mince, such as wheat bran, the increase in moistening heat occurs, which leads to the fact that a part of physical-mechanical moisture passes into physical-chemical; on average 6.9 % of free moisture of the control fish mince (C1) is bound by the additive in experimental sample E1 and 13.5 % – by the complex of plant components in experimental sample E2. Such a system will require more energy or higher temperatures to remove water, which is confirmed by experimental data of conditional activation energy of the given samples for peak  $f_3$ .

For peak  $f_2$ , which is characterized by a removal of moisture, that is, capillary and, partially, osmotic-bound moisture, the experimental mince samples with plant raw material had low values of conditional energy of activation, which are lower than the corresponding values for the minces without plant additives.

The obtained experimental data indicate that the experimental samples of fish minces with plant raw material have retained less mechanically bound moisture, which is retained by osmotic-diffusion forces of capillary-porous body of the fish and plant semifinished products, and by larger bound moisture of hydrate layers around the molecules of bran polysaccharides. In this case, the humidity of the experimental systems is reduced, as well as the content of free moisture in them, and the moisture content of hydra-

tion and wetting is increased. Thus, the use of bran slightly increases the amount of bound moisture in the structure of fish minces as a result of increasing the amount of available hydroxyl groups and the formation of macroporous structure, which causes the increase in its hydrophilicity. Such fish and plant semifinished products will easily absorb or release capillary-bound moisture depending on the changes in environmental conditions.

It is found experimentally that the influence of plant raw materials on increasing the activation energy of the molecules of water for the experimental fish and plant semifinished products is less significant than the use of native fish raw material. Data of experiments confirm that hydrothermic pre-treatment of muscle, connective and skeletal tissue complex of Azov goby leads to the reduction in the amount of adsorption-bound moisture.

The stated hypotheses concerning the mechanism of influence of plant raw materials on the properties of fish and plant semifinished products based on raw and blanched muscle, connective and skeletal tissue of Azov goby with wheat bran might be substantiated quantitatively when comparing the research into energy of bound-moisture with a product, obtained by the isotherms of sorption-desorption, and general and differential porosity of the control and experimental samples. This will need conducting additional studies.

The obtained results allow better understanding of the structural changes that occur in the process of drying fish and plant semifinished products. They may be applied for the optimization of process of drying of fish and plant semifinished products and for the prediction of their technological behavior in various food systems and during storage. To solve optimization problem on the fish and plant semifinished products drying, it is necessary to determine the Rehbinder and Kosovich criteria according to the results of differential microcalorimetry, which is the next stage of scientific research.

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## 6. Conclusions

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1. We defined thermal-gravimetric indicators and performed differential-thermal analysis of experimental samples of the fish and plant semifinished products based on raw and blanched Azov goby, whole, gutted headless, using plant ingredients such as wheat bran.

2. According to results of analysis of DTG peaks of the fish and plant semifinished products, it was determined that the largest amount of capillary-bound moisture, as well as osmotic-bound moisture, was contained in the control sample, made from the thermally pre-treated fish mince. The largest amount of osmotic- and adsorption-bound moisture was observed in the samples made on the base of raw mince from Azov goby. The obtained experimental data indicate that the experimental samples of fish minces made from plant raw material retained less mechanically-bound moisture that is retained by osmotic-diffusion forces of capillary-porous body of the fish and plant semifinished products, and more of the bound moisture of hydrate layers around the molecules of bran polysaccharides. Thus, the use of wheat bran somewhat increases the amount of bound moisture in the fish minces structure as a result of increase in the number of available hydroxyl groups and the formation of macroporous structure, which causes an increase in its hydrophilicity.

3. According to results of the conducted thermographic and differential-thermal studies, the activation energy

value was determined of the molecules of water at different temperatures of moisture removal in the samples of fish and plant semifinished products. It is established that the binding energy of adsorption-bound moisture in the fish and plant semifinished products depends on the hydrothermal pre-treatment of fish and plant raw materials and the use of plant raw materials.

According to the calculated data of conditional activation energy of fish, as well as fish and plant minces, the existence of differences is found in the values for some of the objects at different temperatures of bound-moisture removal, which is explained both by the processes of tissues deformation, dena-

turation of proteins, which lead to a change in the number of active centers, and by the decrease in the degree of polar, non-polar and volumetric hydration of protein molecules of minces and soluble polysaccharides of wheat bran, such as cellulose, hemicellulose, pectin substances. It is established experimentally that the influence of plant raw materials on the increase in the activation energy of water molecules for experimental fish and plant semifinished products is less significant than the use of native fish raw material. Experiments data confirm that hydrothermal pre-treatment of muscle, connective and skeletal tissue complex of Azov goby leads to the reduction in the amount of adsorption-bound moisture.

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*Досліджено процес механічної обробки цибулі ріпчастої під час її очищення комбінованим способом. Визначено раціональні параметри проведення комбінованого процесу очищення цибулі ріпчастої. Отримано величину необхідного коефіцієнта заповнення робочої камери апарата для очищення цибулі ріпчастої. Запропоновано математичну модель процесу механічної обробки цибулі ріпчастої під час її очищення. Розраховано мінімальну частоту обертання робочої камери апарата*

*Ключові слова: цибуля ріпчаста, комбінований процес, параметри очищення, попереднє проварювання, механічна обробка*

*Исследован процесс механической обработки лука репчатого во время его очистки комбинированным способом. Определены рациональные параметры проведения комбинированного процесса очистки лука репчатого. Получена величина необходимого коэффициента заполнения рабочей камеры аппарата для очистки лука репчатого. Предложена математическая модель процесса механической обработки лука репчатого во время его очистки. Рассчитана минимальная частота вращения рабочей камеры аппарата*

*Ключевые слова: лук репчатый, комбинированный процесс, параметры очистки, предварительный провар, механическая обработка*

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## MODELING OF MECHANICAL TREATMENT OF NAPIFORM ONION TO DETERMINE THE RATIONAL PARAMETERS OF ITS CLEANING

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### 1. Introduction

Under conditions of modern economic development, there is a need to create new resource-saving processes and equipment that meet all international requirements. In this case, such indicators should be strictly monitored as quality of the manufactured product and ecological safety of conducting production processes.

Manufacturing food products from vegetable raw materials has important economic and social significance. Vegetables play an important role in the nutrition of all categories of population, which necessitates their presence in people's daily diet. Therefore, safety and quality of such food, the absence of physical, chemical and microbiological contamination should be warranted by manufacturers and processors. To guarantee the safety, producers should apply control

measures along the entire chain of the production process – obtaining, processing and preservation of vegetables. These requirements imply high quality and ecological cleanliness of the products, as well as maximum mechanization and automation of the processes [1]. One of the main tasks for the vegetable-processing industry is to use modern advanced technology during production [2]. But the intensity of the pace of development is reduced due to the low degree of mechanization of most of the processes in the processing of vegetable raw materials, a high degree of manual work. As a result, it is impossible to manufacture the products that would meet European and world requirements [3].

One of the ways to ensure the chosen direction on resource- and energy-saving is the development and implementation into production of new technologies and equipment for cleaning vegetable raw materials. Despite the fact that at