В.Э. Поликарпова [V.E. Polikarpova][1],
И.Ю. Алексанян [I.Yu.Aleksanyan][1],
З.М. Арабова [Z.M. Arabova][2],
А.Х.-Х.Нугманов [A.Kh.-Kh.Nugmanov][1],
Е.Ю.Запорожец [E.Yu.Zaporozhets] [1]

УДК [536.712: 664.955]

DOI: 10.37493/2307-910X.2022.3.8

ГИГРОСКОПИЧЕСКИЕ ПАРАМЕТРЫ САЗАНЬЕЙ ИКРЫ, КАК ИСТОЧНИКА ЛЕЦИТИНА И ОБЪЕКТА СУШКИ, И ТЕРМОДИНАМИЧЕСКИЙ АНАЛИЗ СТАТИЧЕСКИХ ЗАКОНОМЕРНОСТЕЙ ЕЕ ВЗАИМОДЕЙСТВИЯ С ВОДОЙ

HYGROSCOPIC PARAMETERS OF SAZAN CAVIAR AS A SOURCE OF LECITHIN AND A DRYING OBJECT AND THERMODYNAMIC ANALYSIS OF THE STATIC REGULARITIES OF ITS INTERACTION WITH WATER

[1]ФГБОУ ВО «Астраханский государственный технический университет»
[2] Институт геохимии и аналитической химии им. В. И. Вернадского
/ [1] FSBEI HE «Astrakhan State Technical University»
[2] Vernadsky Institute of Geochemistry and Analytical Chemistry

Аннотация

Повышение эффективности глубокой переработки сырья товарного рыбоводства, в том числе мало востребованной на российском рынке икры пресноводных рыб семейства карповых, В качестве объекта исследования использована икра из сазана, которая является перспективным источником для выработки природных эмульгаторов высокого качества, к примеру, лецитина. Известно, что самым распространенным способом консервации биополимеров является сушка исходного сырья. Анализ способов обезвоживания продуктов, подобных сазаньей икре, показал, что наиболее рациональным из них для этой цели является конвективный при возможной комбинации с кондуктивным энергоподвод, что предопределяет контакт объекта изучения с паровоздушной средой и обусловливает целесообразность определения его гигроскопических параметров для рациональной организации процесса сушки и хранения высушенного продукта с целью максимального сохранения в продукте комплекса фосфолипидов, состоящих из ненасыщенных и насыщенных жирных кислот, фосфорной кислоты, глицерина и холина, в целом представляющий собой лецитин. Целью исследования послужило определение гигроскопических и термодинамических параметров взаимодействия сазаньей икры с водой для применения при рациональной реализации технологии ее сушки и получения лецитина из сазаньей икры с целью выявления условия максимальной сохранности в ней необходимого целевого компонента. В рамках данного исследования для икорного продукта определялась его гигроскопичность, характеризующая равновесную влажность продукта, посредством тензометрического метода. Полученные функциональные зависимости гигроскопических параметров от влияющих факторов позволяют определить численные значения удельной тепловой энергии испарения для подстановки их в дифференциальное уравнение теплопереноса при моделировании процессов сушки икорного продукта. В результате, можно сделать вывод о том, что полученные гигроскопические и термодинамические параметры икорного продукта могут успешно использоваться при рациональной организации и реализации технологии и техники его сушки.

Ключевые слова: *икра сазана, сушка, внутренний тепломассоперенос, гигроскопические параметры, статика процесса сушки, термодинамический анализ, конечная влажность.*

Abstract

Increasing the efficiency of deep processing of raw materials for commercial fish farming, including caviar of freshwater fish of the carp family, which is little in demand on the Russian market. As an object of study, carp caviar was used, which is a promising source for the production of high quality natural emulsifiers, for example, lecithin. It is known that the most common method of conservation of biopolymers is the drying of raw materials. An analysis of the methods for dehydrating products like carp caviar showed that the most rational of them for this purpose is convective, with a possible combination with conductive energy supply, which predetermines the contact of the object of study with the steam-air medium and determines the expediency of determining its hygroscopic parameters for the *rational organization of the drying and storage process. dried product in order to maximize the preservation of the complex of phospholipids in the product, consisting of unsaturated and saturated fatty acids, phosphoric acid, glycerol and choline, which in general is lecithin. The aim of the study was to determine the hygroscopic and thermodynamic parameters of the interaction of carp caviar with water for use in the rational implementation of the technology for its drying and obtaining lecithin from carp caviar in order to identify the conditions for maximum preservation of the necessary target component in it. Within the framework of this study, for the caviar product, its hygroscopicity, which characterizes the equilibrium moisture content of the product, was determined using the tensometric method. The obtained functional dependences of hygroscopic parameters on the influencing factors make it possible to determine the numerical values of the specific thermal energy of evaporation for their substitution into the differential heat transfer equation when modeling the drying processes of the caviar product. As a result, it can be concluded that the obtained hygroscopic and thermodynamic parameters of the caviar product can be successfully used in the rational organization and implementation of the drying technology and technique.*

Keywords: carp caviar, drying, internal heat and mass transfer, hygroscopic parameters, statics of the drying process, thermodynamic analysis, final moisture content.

Introduction

Increasing the efficiency of deep processing of raw materials for commercial fish farming, including caviar of freshwater fish of the carp family , which is little in demand on the Russian market [1, 2], is an important and urgent task.

In modern conditions, the food industry of the Russian Federation needs high quality natural emulsifiers, for example, lecithins. It should be noted that carp caviar, in particular carp caviar, contains a large amount of lecithin [3, 4], about 10,000 mg per 100 g of the product [5]. According to the data of the European Association of Lecithin Manufacturers (ELMA), its world production is currently more than 250 thousand tons per year, and the need is more than 400 thousand tons per year [6]. With the increasing demand for lecithin, the question arises of identifying a new raw material base for its production.

It is known that lecithin parameters are significantly affected by the source of its production [7, 8, 9, 10], in which it is necessary to preserve its target properties as much as possible during its conservation until the moment of direct use in the selected technology, while the most common methods of conservation are drying and freezing of raw materials.

An analysis of the methods for dehydrating products like carp caviar showed that the most rational of them for this purpose is convective, with a possible combination with conductive energy supply, which predetermines the contact of the object of study with the steam-air medium and determines the expediency of determining its hygroscopic parameters for the rational organization of the drying and storage process. dried product in order to maximize the preservation of the complex of phospholipids in the product, consisting of unsaturated and saturated fatty acids, phosphoric acid, glycerol and choline, which in general is lecithin.

Purpose of the study

Determination of hygroscopic and thermodynamic parameters of the interaction of carp caviar with water for use in the rational implementation of the technology of its drying and obtaining lecithin from carp caviar in order to identify the conditions for maximum preservation of the necessary target component in it.

Objects and methods of research

The object of the study was carp caviar,

As part of this study of the hygroscopic characteristics of the caviar product, its hygroscopicity, which characterizes the equilibrium moisture content of the product, was determined using the Van Bamelen tensometric method. According to this static method, samples of the test product with a predetermined moisture content were kept in desiccators with a solution of sulfuric acid of various concentrations. At the same time, a certain partial pressure of water vapor corresponds to a certain concentration of the solution at a given temperature, i.e. a certain value of relative air humidity φ[11, 12]. A certain amount of the test material is weighed on an analytical balance with an accuracy of 0.001 g after reaching a constant mass, at which its moisture content corresponds to equilibrium.

Equilibrium humidity W_p, which was obtained during the experiments, is determined by the formula:

$$W_p = \frac{G_2 - G_1(1 - W_{обр})}{G_2}, \quad (1)$$

where $W_{обр}$ is the initial moisture content of the sample, kg/kg; G_1 is the initial mass of the test sample, kg; G_2 is the mass of the sample upon reaching hygrothermal equilibrium, kg;

The experimental study of the hygroscopic properties is intended to characterize the dry product under study and give recommendations on the choice of the final moisture content of the material, which is the most appropriate for the storage process. When constructing sorption curves, it was assumed [12] that the numerical values of the water activity indicator A_w and the relative air humidity φ coincide, due to the equality of the vapor pressure above the surface of the material under study and its pressure in the desiccator medium.

Research results and discussion

After a series of experiments on a desiccator pilot plant, moisture sorption isotherms of the dehydrated caviar product were obtained at air temperatures of 25°C and 40°C, which are presented below (Fig. 1).

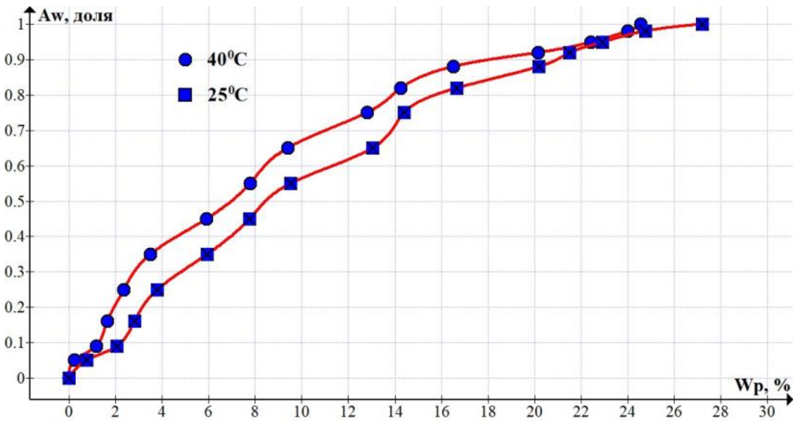

Figure 1. Equilibrium curves for moisture sorption by a dry product

The resulting sorption isotherms can be conditionally divided into three sections, which is especially clearly seen when they are plotted in a semilogarithmic modification (Fig. 2).

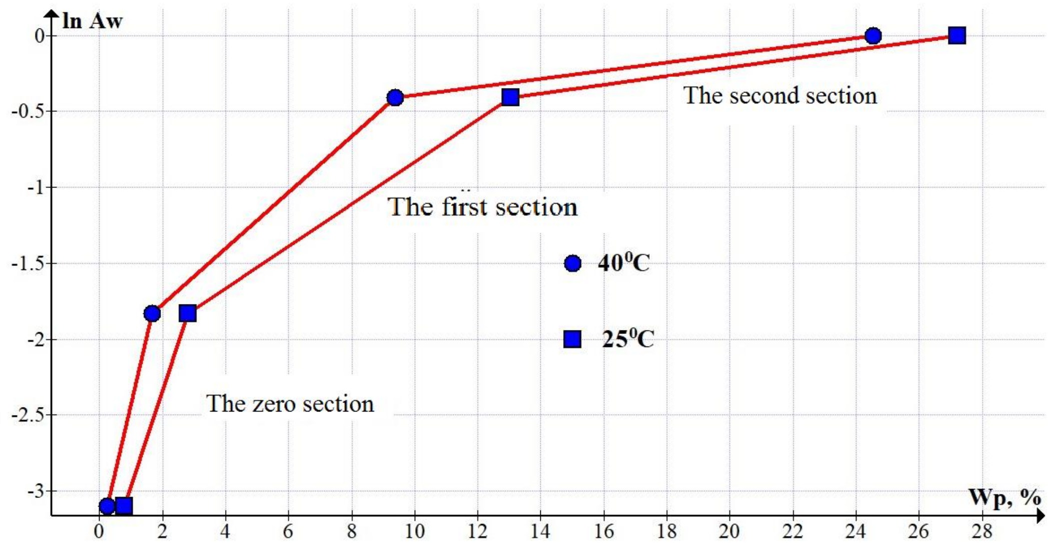

Figure 2. Equilibrium curves plotted in semi-logarithmic coordinates

According to A.V. Lykov [13], all wet materials are divided into several main groups depending on their colloid-physical properties: capillary-porous, colloidal and capillary-porous colloidal, occupying an intermediate position between the first and second. This classification is widely used in generalizing the results obtained. The dry structure of carp caviar is a capillary-mesoporous body with a large number of pores and capillaries through which water vapor can penetrate or be removed. The characterization of the state of moisture in the material and the corresponding parameters of moisture transfer is given on the basis of an analysis of the adsorption phenomena developing on the phase interface (moist air - solid). A generalization of knowledge in this area is currently the theory of polymolecular adsorption developed by S. Brunauer, L. Deming, W. Deming, R. Emmett and B. Teller [12], who proposed a classification based on the identification of five types of isotherms.

The resulting isotherms can be attributed to type I– V , and if the adsorption of gas by a solid body is described by an isotherm of this type, then this indicates that the dry skeleton of dried caviar is characterized as a mesoporous body, i.e. is a porous material, the structure of which is characterized by the presence of cavities or channels with a diameter in the range from 2 to 50 nm [14]. The type IV isotherm also describes physisorption and multilayer processes, resembling the type II isotherm, but now in porous or mesoporous solids, where condensation of gas particles in small volumes of liquid is possible, and therefore, until the pores are “clogged” with liquid, the monolayer is not complete .

Type IV isotherms have a hysteresis loop, the lower branch of which is obtained by measuring adsorption with the sequential addition of gas to the system, and the upper branch is obtained with its sequential decrease (desorption). Effects associated with hysteresis are also possible for other types of isotherms [14].

G.K. Filonenko proposed a mathematical description of isotherms to be carried out by two equations. To do this, you need to divide the curve (Fig. 2) into two sections: the first - from W_0 to W_m; the second - from W_m and above. The point W_0 on the isotherm characterizes the transition from monomolecular to polymolecular adsorption and is obtained by crossing the normal from the first singular point on the isotherm to the abscissa axis. Usually, during actual drying of materials, moisture bound by monomolecular adsorption is not removed, so the isotherm section from 0 to W_0 is not described by the isotherm equation. The point W_m characterizes the transition from moisture bound by polymolecular adsorption to capillary- and osmotically-bound moisture and is obtained by crossing the normal from the second singular point on the isotherm to the abscissa axis. Starting from the values W_m, the isotherm curve sharply goes to the right. Figure 3 below shows a breakdown of the obtained sorption isotherm at 25°C into 2 sections.

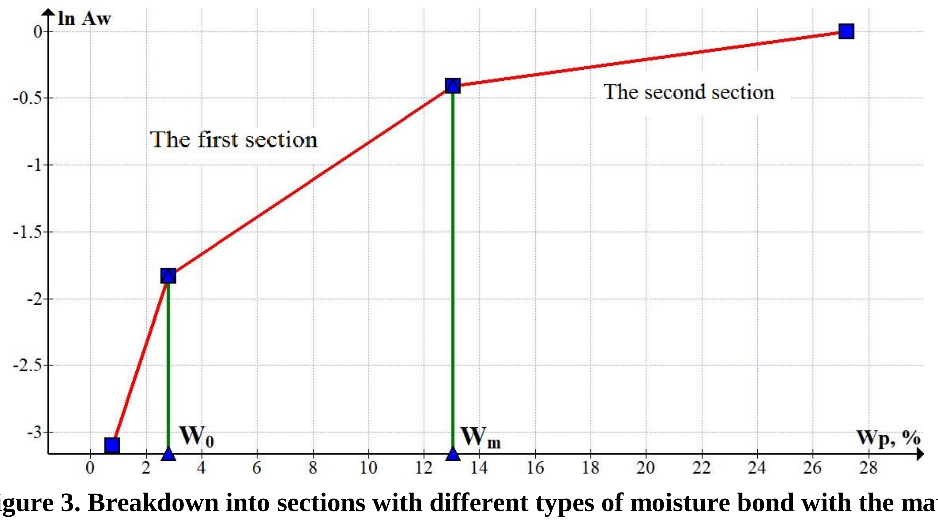

Figure 3. Breakdown into sections with different types of moisture bond with the material: from 0 to W_0 - chemical bond prevails; from W_0 to W_m – adsorption bound moisture prevails; from W_m and above - capillary bound and osmotic moisture

Following the approach described above, on the moisture sorption isotherm of the studied caviar product (Fig. 3), these areas are distinguished: the area from W_0 to W_m characterizes adsorption-bound moisture and the area from W_m and above characterizes capillary-bound and osmotic moisture.

Thus, two sections are distinguished from the empirically obtained sorption isotherms, the reason for the appearance of which is analytically substantiated. It should be noted that the first section starts from the moment where the monomolecular adsorption zone ends, in which moisture is quite strongly bound to the product, therefore, for the dried polymer material, the most appropriate final moisture content is the one that borders on the adsorption-bound interval: $0{,}03 \leq W_p \leq 0{,}13$, i.e. the most rational final moisture for the investigated product is the range from 10 to 12%.

Carrying out the logarithm facilitates the mathematical processing and interpretation of the obtained isotherms (Fig. 2), which, for convenience, are divided into 2 sections (Fig. 3) and approximated by the equations presented below. The calculated error between the approximated and empirically obtained values is no more than 2%.

Approximate Equations 2 and 3 for the sorption isotherm plotted at 40°C.

Plot 1: $0{,}03 \leq W_p \leq 0{,}13$:

$$\ln A_W = 13{,}142W_p - 2{,}141. \quad (2)$$

Plot 2: $0{,}13 \leq W_p \leq 0{,}27$:

$$\ln A_W = 3{,}04W_p - 0{,}828. \quad (3)$$

Approximate Equations 4 and 5 for the sorption isotherm plotted at 25° C .

Plot 1: $0{,}03 \leq W_p \leq 0{,}13$:

$$\ln A_W = 9{,}179W_p - 1{,}47. \quad (4)$$

Plot 2: $0{,}13 \leq W_p \leq 0{,}27$:

$$\ln A_W = 2{,}386W_p - 0{,}587. \quad (5)$$

Due to the fact that the process of drying the caviar product under study proceeds, including in the hygroscopic region, a thermodynamic analysis of the static laws of heat and mass transfer is necessary to identify the influence of the nature of moisture binding with the dry residue on the quality of the resulting dry semi-finished product. In addition, the result obtained must be taken into account when making design decisions for the rational implementation of the processes under study.

On the basis of the obtained equations, graphic dependences of energy changes on the moisture content of the material are constructed, which are shown in Figure 4.

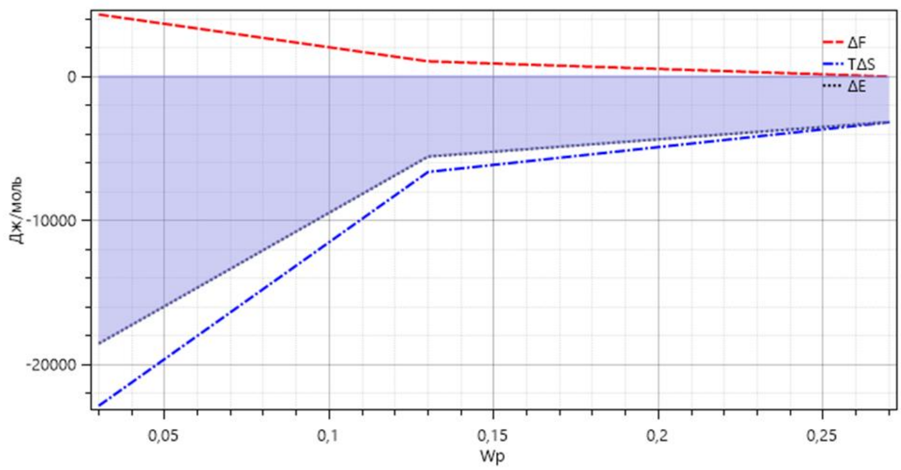

Figure 4. Change in free $\frac{\partial \Delta F}{\partial W_p}$, bound $T\frac{\partial \Delta S}{\partial W_P}$ and internal $\frac{\partial \Delta E}{\partial W_P}$ energy depending on the moisture content of the material

The graphic dependences presented in Figure 4 show that the statics of the processes of interaction with water and the analysis of sorption isotherms allows us to establish and quantify the nature of the change in the thermodynamic components of the Gibbs-Helmholtz equation for an isobaric-isothermal process:

$$\Delta F = \Delta E - T\Delta S, \quad (6)$$

where $\Delta F, \Delta E, \Delta S$ are, respectively, changes in free, internal energy (enthalpy) and entropy, according to moisture content W_p at $P, T = const$.

Equation 6 in differentiated form looks like this:

$$\left(\frac{\partial \Delta F}{\partial W_P}\right)_{T,P} = \left(\frac{\partial \Delta E}{\partial W_P}\right)_{T,P} - T \cdot \left(\frac{\partial \Delta S}{\partial W_P}\right)_{T,P}, \quad (7)$$

where the entropy component of the free energy $T \cdot \left(\frac{\partial \Delta S}{\partial W_P}\right)_{T,P}$ plays a significant role for most products.

The calculation of differential changes in the bound sorption energy for different temperatures is necessary in order to determine the value of the specific heat of vapor formation r, (J/kg) under different technological conditions of the drying process. Figure 5 graphically shows the dependence of the specific thermal energy of evaporation on the equilibrium humidity in the process of sorption of water vapor by dry caviar product for two sections in the interval: $0{,}03 \le W_p \le 0{,}27$.

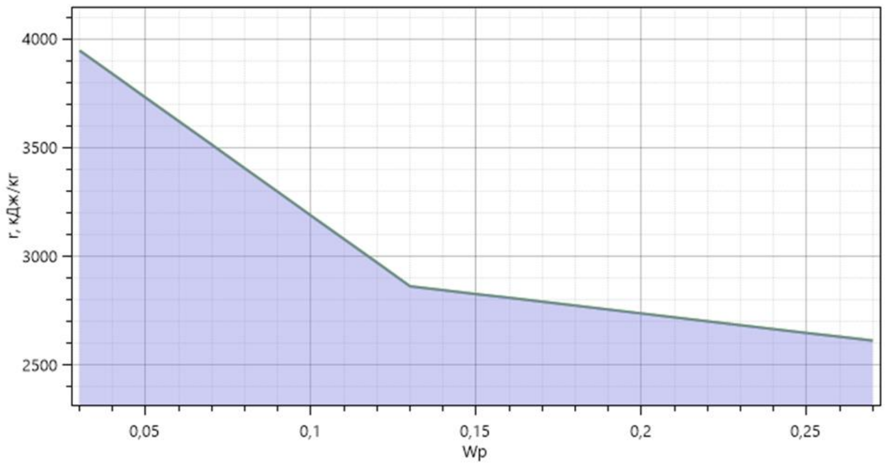

Figure 5 - Graphical dependence of the specific thermal energy of evaporation on the equilibrium humidity in the process of reducing the humidity of the material under study.

It should be noted that the nature of the dependence $r = f(W_p)$ for the product under study is typical for most food materials, and is due to various energy forms of the relationship between the moisture in the sample and its dry residue.

Heat of vaporization associated with the material for 1 section:

$$r = 2437230 + |294724 - 1808985W_p| + |9028799W_p - 1541193|. \quad (8)$$

The heat of vaporization associated with the material for section 2:

$$r = 2437230 + |113953 - 418438W_p| + |1371267W_p - 545714|. \quad (9)$$

Functional dependencies (8 and 9) make it possible to determine the numerical values of the specific thermal energy of evaporation for their substitution into the differential heat transfer equation when modeling heat and mass transfer processes of caviar product drying.

Conclusions

As a result, it can be concluded that the obtained hygroscopic and thermodynamic parameters of the caviar product can be successfully used in the rational organization and implementation of the technology and technique for drying it and obtaining lecithin from carp caviar, because make it possible to determine the conditions for the preservation of the necessary target component in it.

ЛИТЕРАТУРА

1. Добрецкая Е.И. Рынок рыбной продукции в Российской Федерации // Молодой ученый. 2022. № 13 (408). С. 44-47.
2. Беляева Д.С. Проблемы развития рыбной отрасли России / Д.С. Беляева // Современные проблемы менеджмента: Электронный сборник научных работ. – Белгород: ИД Белгород, 2016 – 192 с. – URL: http://dspace.bsu.edu.ru/handle/123456789/16101.
3. Карповая икра [Электронный ресурс]. Режим доступа: https://food.ru/products/19274-karpovaja-ikra (Дата обращения: 02.07.2022).
4. Сазан [Электронный ресурс]. Режим доступа: https://foodandhealth.ru/ryba/sazan/ (Дата обращения: 02.07.2022).
5. В каких продуктах содержится лецитин? [Электронный ресурс]. Режим доступа: https://herbalsale.by/v-kakih-produktah-soderzhitsya-letsitin/ (Дата обращения: 02.07.2022).
6. Лисовая Е.В., Викторова Е.П., Лисовой В.В. Анализ ассортимента лецитинов, представленных на российском рынке // Технологии пищевой и перерабатывающей промышленности АПК – продукты здорового питания. 2019. № 2(28). С. 51-55.
7. Бутина Е.А., Герасименко Е.О., Пащенко В.Н. Обоснование необходимости разработки технологии получения подсолнечных жидких лецитинов // Новые технологии. 2012. № 2. С.30-32.
8. Жаркова И.М., Рудаков О.Б., Полянский К.К., Росляков Ю.Ф. Лецитины в технологиях продуктов питания: монография. Воронеж: ВГУИТ, 2015. 256 с.
9. Белина Н.Н., Герасименко Е.О., Бутина Е.А., Воронцова О.С., Спильник Е.П. Разработка технологии получения модифицированных лецитинов // Политематический сетевой электронный научный журнал Кубанского государственного аграрного университета. 2013. №. 91. С. 802-811.
10. Нечаев А.П., Траубенберг С.Е., Кочеткова А.А., Колпакова В.В., Витол И.С., Кобелева И.Б. Пищевая химия: учебное пособие. Санкт-Петербург: ООО «Издательство ГИОРД». 672 с.
11. Гинзбург А.С., Савина И.М. Массовлагообменные характеристики пищевых продуктов. М.: Легкая и пищевая промышленность, 1982. 280 с.
12. Никитина Л.М. Гигроскопические параметры и коэффициенты массопереноса во влажных материалах. Москва: Энергия, 1967. 499 с.
13. Лыков А.В. Теория сушки. М.: Энергия, 1968. 471 с.
14. Адамова Л.В., Сафронов А.П. Сорбционный метод исследования пористой структуры наноматериалов и удельной поверхности наноразмерных систем: учебное пособие. Екатеринбург. 2008. 62 с.

REFERENCES

1. Dobretskaya E.I. Rynok rybnoi produktsii v Rossiiskoi Federatsii // Molodoi uchenyi. 2022. № 13 (408). S. 44-47.
2. Belyaeva D.S. Problemy razvitiya rybnoi otrasli Rossii / D.S. Belyaeva // So-vremennye problemy menedzhmenta: Ehlektronnyi sbornik nauchnykh rabot. – Belgorod: ID Belgorod, 2016 – 192 s. – URL: http://dspace.bsu.edu.ru/handle/123456789/16101.
3. Karpovaya ikra [Ehlektronnyi resurs]. Rezhim dostupa: https://food.ru/products/19274-karpovaja-ikra (Data obrashcheniya: 02.07.2022).
4. Sazan [Ehlektronnyi resurs]. Rezhim dostupa: https://foodandhealth.ru/ryba/sazan/ (Data obrashcheniya: 02.07.2022).
5. V kakikh produktakh soderzhitsya letsitin? [Ehlektronnyi resurs]. Rezhim do-stupa: https://herbalsale.by/v-kakih-produktah-soderzhitsya-letsitin/ (Data obrashcheniya: 02.07.2022).

6. Lisovaya E.V., Viktorova E.P., Lisovoi V.V. Analiz assortimenta letsiti-nov, predstavlennykh na rossiiskom rynke // Tekhnologii pishchevoi i pererabatyvayushchei promyshlennosti APK – produkty zdorovogo pitaniya. 2019. № 2(28). S. 51-55.

7. Butina E.A., Gerasimenko E.O., Pashchenko V.N. Obosnovanie neobkhodimosti razrabotki tekhnologii polucheniya podsolnechnykh zhidkikh letsitinov // Novye tekhnologii. 2012. № 2. S.30-32.

8. Zharkova I.M., Rudakov O.B., Polyanskii K.K., Roslyakov YU.F. Letsitiny v tekhnologiyakh produktov pitaniya: monografiya. Voronezh: VGUIT, 2015. 256 s.

9. Belina N.N., Gerasimenko E.O., Butina E.A., Vorontsova O.S., Spil'nik E.P. Razrabotka tekhnologii polucheniya modifitsirovannykh letsitinov // Politematicheskii se-tevoi ehlektronnyi nauchnyi zhurnal Kubanskogo gosudarstvennogo agrarnogo universite-ta. 2013. №. 91. S. 802-811.

10. Nechaev A.P., Traubenberg S.E., Kochetkova A.A., Kolpakova V.V., Vitol I.S., Kobeleva I.B. Pishchevaya khimiya: uchebnoe posobie. Sankt-Peterburg: OOO «Izdatel'stvo GIORD». 672 s.

11. Ginzburg A.S., Savina I.M. Massovlagoobmennye kharakteristiki pishchevykh produktov. M.: Legkaya i pishchevaya promyshlennost', 1982. 280 s.

12. Nikitina L.M. Gigroskopicheskie parametry i koehffitsienty massopereno-sa vo vlazhnykh materialakh. Moskva: Ehnergiya, 1967. 499 s.

13. Lykov A.B. Teoriya sushki. M.: Ehnergiya, 1968. 471 s.

14. Adamova L.V., Safronov A.P. Sorbtsionnyi metod issledovaniya poristoi struktury nanomaterialov i udel'noi poverkhnosti nanorazmernykh sistem: uchebnoe poso-bie. Ekaterinburg. 2008. 62 s.

ОБ АВТОРАХ / ABOUT THE AUTHORS

Поликарпова Виолетта Эдуардовна, аспирант ФГБОУ ВО «Астраханский государственный технически университет», кафедра «Технологические машины и оборудование», e-mail: albert909@yandex.ru, 8-927-282-43-07.

Polikarpova Violetta Eduardovna, Graduate student, FSBEI HE Astrakhan State Technical University, Department of Technological Machines and Machinery, e-mail: albert909@yandex.ru, 8-927-282-43-07

Алексанян Игорь Юрьевич, Д.т.н., Профессор, ФГБОУ ВО «Астраханский государственный технически университет», кафедра «Технологические машины и оборудование», 16081960igor@gmail.com, 8-960-863-26-04, https://orcid.org/0000-0001-5494-1226

Aleksanian Igor Yurievich, Doctor of Technical Sciences, Professor, FSBEI HE Astrakhan State Technical University, Department of Technological Machines and Machinery, 16081960igor@gmail.com, 8-960-863-26-04, https://orcid.org/0000-0001-5494-1226

Арабова Зарема Михайловна, кандидат технических наук, Научный сотрудник, Институт геохимии и аналитической химии им. В. И. Вернадского, zarema.polymer@gmail.com, https://orcid.org/0000-0002-6787-7697

Arabova Zarema Mikhailovna, Candidate of Technical Sciences, Researcher, Vernadsky Institute of Geochemistry and Analytical Chemistry, zarema.polymer@gmail.com, https://orcid.org/0000-0002-6787-7697

Нугманов Альберт Хамед-Харисович, доктор технических наук, профессор, ФГБОУ ВО «Астраханский государственный технически университет», кафедра «Технологические машины и оборудование», albert909@yandex.ru, 8-927-282-43-07, https://orcid.org/0000-0002-4093-9982.

Nugmanov Albert Khamed-Kharisovich, doctor of technical sciences, professor, FSBEI HE Astrakhan State Technical University, Department of Technological Machines and Machinery, albert909@yandex.ru, 8-927-282-43-07, https://orcid.org/0000-0002-4093-9982

Запорожец Екатерина Юрьевна, заведующий редакцией, ФГБОУ ВО «Астраханский государственный технически университет»

Zaporozhets Ekaterina Yurievna, Editorial manager, FSBEI HE Astrakhan State Technical University

Дата поступления в редакцию: 12.07.2022
После рецензирования:18.08.2022
Дата принятия к публикации:19.09.2022