On the issue of studying the forms of moisture coupling in thermolabile heterogeneous products

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Abstract. The article deals with issues related to the study of the connection forms of moisture removed during the drying process of thermolabile heterogeneous products. The difficulties, emerging while developing drying process controlling methods, optimizing energy, material costs, and temperature regimes, necessitate further research. It is shown that the existing methods of studying the forms of moisture connection with the material have significant drawbacks and generally give a qualitative assessment of the state of moisture in the material or are very time-consuming and require long-term laboratory studies. An approach to determining the forms of moisture bond in the material based on graph-analytical analysis of the drying kinetics is proposed, which allows qualitative and quantitative assessment of the state of moisture in the product. With the help of a graphical editor, typical drying kinetics curves were processed and the dependences of the value that characterizes the speed of change in the drying rate on the moisture content of the product were obtained. It is proposed to introduce a new value in the drying theory - drying acceleration. The analysis of the obtained curves testifies to the presence of extremes and inflection points corresponding to the critical moisture content, as well as the presence of areas with slowing or accelerating changes in the drying rate, allowing setting intervals for removing moisture with different binding energy. The approach considered in the article to determining the forms of moisture communication in the material will not only give a qualitative and quantitative assessment of the state of moisture in products, but also reduce the time for analysis and improve the accuracy of the results.

1. Introduction

The drying process is found in almost all food and related industries, especially when processing raw materials of plant origin, and is used to remove moisture from a variety of raw materials and finished products, which makes it an important object for study. At the same time, the drying process itself is one of the most energy-intensive processes in the production of food and other products and is extremely complex due to the many factors that affect it.

During the drying process, thermolabile heterogeneous products can significantly change their physical properties under the influence of heat and moisture. These changes are due to the molecular nature of the moisture-substance bond. The process of removing moisture from products that are colloidal capillary-porous bodies depends on the nature of the molecular bond of the liquid contained...
in the product and is accompanied by a violation of its connection with the dry skeleton of the substance, which requires a certain amount of energy. [1-6].

Each form of moisture connection according to P. Rebinder is characterized by a certain binding energy. When drying food products in the process of their production, physical-mechanical and physical-chemical bound moisture is removed, which by its nature and binding energy is divided into capillary, osmotically bound, adsorptively bound moisture of the polymolecular and monomolecular layers. In order to remove moisture from a product of one form or another, you need to spend a certain amount of energy, depending on the energy of the connection of moisture and the amount of moisture of this form in the product.

The use of modern computer technologies and automation tools allows you to optimize the energy and material costs of the drying process. However, in order to develop a reliable way to control the drying process and optimize temperature conditions and energy costs, it is necessary to know the exact ratio of the various forms of moisture binding in the product and the energy of its binding. The complexity of the problem lies in the fact that for the same products or raw materials, such as wheat, depending on the variety, climatic conditions of cultivation, humidity during harvesting from fields, etc. the moisture ratio of different forms of communication will not be the same. When processing raw materials, the moisture ratios of various forms of bonding can also be influenced by many random factors at the pre-drying production stages.

Therefore, the study of the forms of moisture communication in food products and the development of accurate and accelerated methods for determining the physical state and properties of water in products has important theoretical and practical significance and is an urgent task for many industries.

2. Object and subject of research

The object of the study was the kinetics of the drying process of wet materials: curves of changes in the moisture content of the material during the drying process and curves of the drying speed of various materials. The subject of the study is the forms of moisture bonding in the material that is removed during the drying process.

3. Materials and methods

Over the past decades, a large number of papers have been published on the identification of various methods of forms of moisture binding in the material and their influence on the kinetics of the drying process [1, 2, 4]. Thus, one of the most common methods for determining the physical state and properties of water in a material is the derivatographic method. The advantage of this method in contrast to other thermal methods is the complex nature of obtaining information in the water experiment. This method allows us to conduct a quantitative and qualitative analysis of the forms of moisture bond in the material. However, determining the value of monomolecular adsorption moisture by this method is difficult, since the binding energy of water molecules with the product of the polymolecular adsorption layer continuously increases during the transition from the upper layer to the monolayer [1]. To determine the forms of moisture coupling in the product using the derivatographic method, a long-term qualitative analysis of all the curves obtained as a result of the experiment is required.

In the development of this method by several authors [2] to obtain information about the mechanism of dehumidification is proposed for mathematical processing of the experimental curves obtained on derivatograph and plotting the degree of conversion of a substance from the temperature, where the degree of transformation of the substance α is calculated as $\Delta m / \Delta m_{\text{max}}$ the ratio of the change in mass of the total amount of water contained in the sample:

$$\alpha = \frac{\Delta m}{\Delta m_{\text{max}}}.$$ 

This dependence is recalculated and built in the coordinates “$-\lg \alpha, 10^3/T$”. In this case, the graph shows several linear sections corresponding to a certain temperature range for removing moisture from various forms of binding. We believe that this approach is not entirely correct since it follows that the
removal of water fractions with different binding energies during drying occurs in a strictly defined temperature range. However, it is known from the practice of drying that the associated moisture is removed from the product even at relatively low temperatures, if dry air is used.

A method based on the analysis of material desorption isotherms is also used to determine the qualitative assessment of the moisture bond forms in the material [1, 2]. By isotherms (convexity or concavity), you can judge the nature of the moisture bond in the product. However, the desorption isotherms of most food products are S-shaped smooth curves without the presence of singular points, which indicates that there are no pronounced transitions between individual stages of moisture with the material and, as a result, it is difficult to quantify the forms of moisture communication.

A common drawback of the above methods is the duration of laboratory research and qualitative analysis, which is difficult to carry out in production conditions for each batch of product or raw materials and does not allow you to quickly manage the drying process.

Analysis of drying curves and drying speed also gives only a qualitative picture of the physical state of moisture in the material and does not allow determining with sufficient accuracy the boundaries between the individual stages of binding moisture to the material.

In this regard, the purpose of this work is to justify an approach to determining the qualitative and quantitative evaluation of the forms of moisture-to-material coupling based on graphical processing of the drying kinetics.

On the basis of experimental data, A. Lykov proposed a graphical relationship between the moisture content of the material and the drying time, called the drying curve and having the form of a curve that faces the bulge to the moisture content axis (figure 1) [3]. Based on the nature of changes in the moisture content and temperature of the material during the drying process, the drying process is divided into two periods: constant speed and falling speed.

![Figure 1. Changing the moisture percent in the material during the drying process](image)

The drying rate is understood as the change in moisture percentage per unit of time \( \frac{du}{dt} \). Graphically differentiating the drying curve, you can get a drying rate curve that shows the values of the rate of removal of moisture when the moisture percentage if the product changes. The drying rate is numerically equal to the tangent angle of the tangent to the drying curve \( U = f(\tau) \). Then a graph is built \( \frac{du}{dt} = f(U) \). This method of analysis was first proposed by T. Sherwood [3]. When analyzing drying schedules, it is necessary to read them in reverse order, since the moisture percentage of the material decreases during the drying process. Until now, this method of analysis was not considered accurate and had large errors, since the tangent operation was performed by eye or to improve
accuracy using a special device – a mirror derivator. Therefore, this method was used only for qualitative analysis of the kinetics of the process.

Materials that differ in the nature of the moisture bond give a different shape to the drying speed curve. Lykov gives 6 types of drying speed curves that differ in the behavior of the curve in the falling period of the drying speed [3]. The simplest drying rate curves are 1, 2, and 3 (figure 2).

Figure 2. Typical drying rate curves for wet materials

![Typical drying rate curves](image)

Figure 3. More complex curves for the drying rate of wet materials

Curve 1 is rectilinear and is obtained when drying thin samples of fibrous material, the second one faces the convexity to the ordinate axis and is observed when drying pasta dough, and the third one faces the convexity to the abscissa axis and occurs when drying porous ceramic materials. More complex drying curves include 4, 5, and 6 (figure 3). As in a falling period of the drying curve can be a straight, and then goes into a curve (curve 4) or first drawn convex to the x-axis and then convex to the y-axis (curve 5), this phenomenon is typical when drying bread or in the form of curve 6, that is rare.

Curves of drying speed allows to define a second critical point as a point of inflection or transition direct to a curve that corresponds to the second critical moisture content, which on the curves of
changes of moisture percentage from the time practically non-existent. These curves give a qualitative picture of the drying process.

It is known [1] that the velocity of the second period \( N_2(U) \) can be represented as a calculation:

\[
N_2(U) = N_1 \cdot f(U)
\]

where \( N_1 = f(x_1, x_2, \ldots, x_n) \) is the speed of the first drying period, sec\(^{-1}\);

\( x_1, x_2, \ldots, x_n \) - factor of the process;

\( f(U) \) – some transfer function from the moisture percentage of the product.

If we assume that for a steady-state drying mode with constant parameters, the speed of the first period is a constant value \( N_1 = \text{const} \), as shown in the graphs (figure 2, 3), then the speed of the second drying period depends only on the moisture percentage of the product. Then, for further and deeper analysis of the kinetics of the drying process in the food and related industries, a value that determines the speed of change in the drying speed can be used, that is, the first derivative of the drying speed in terms of moisture percentage or the second derivative of humidity. The term "drying acceleration" can be applied to this value.

The second derivative of the moisture percentage or \( \frac{d^2N}{dU^2} \) represents the rate of change in the slope \( f(U) \) of the curve, and gives an indication of how the curve goes \( N_2(U) = N_1 \cdot f(U) \). A positive or negative sign of the rate of change \( f(U) \) indicates that this function increases or decreases with the change in the moisture content of the material. Since the removal of each water fraction with different binding energies from the product occurs at a rate that varies according to different laws, each fraction will be characterized by its speed of change in the drying rate.

Plotting \( \frac{d^2N}{dU^2} \) the dependence on the moisture content of \( U \) will allow one to determine the inflection points, the intervals of convexity and concavity of the function \( f(U) \). That will give a more complete and accurate idea of the critical moisture content and intervals of moisture removal of a particular form of connection, as well as allow you to quantify the moisture of different fractions. To get a graphical dependence on the moisture percentage \( U \) by \( \frac{d^2N}{dU^2} \), differentiating the graph of the drying speed curve. The value is numerically equal to the tangent angle of the \( \frac{dN}{dU} \) tangent to the drying speed curve.

Modern computer technologies and programs such as Mathcad, MagicPlot, as well as graphic editors such as COMPASS-graph, Autodesk AutoCAD, Autodesk Inventor, and others can be used to process an array of experimental data on drying kinetics, approximate the \( f(U) \) function, and perform this graph-analytical method. These tools allow providing a graphical representation of the data array with high accuracy.

For data processing and graphical differentiation of typical drying speed curves, we used the COMPASS-Graph program. The margin of error of measuring and drawing points on the graph with graphical differentiation was no more than 0.1 mm, and the margin of error of determining the angle of the tangent at a point on the curve is no more than 1'. This suggests that the results obtained from processing the existing sample data presented by A. Lykov are highly accurate. When processing data obtained after conducting an experiment on the drying kinetics of a particular product, the accuracy of the results can be higher due to the use of computer programs for processing experimental data. Based on the results of graphical differentiation of typical drying curves, 6 graphs of "drying accelerations" are constructed (figure 4).

### 4. Results and Discussion

The resulting graphs clearly show periods of increasing and decreasing "drying acceleration". These graphs as well as the drying speed graphs should be read from right to left.

In the first drying period, when the process speed is constant \( N_1 = \text{const} \) on the obtained graphs, the sections have a horizontal rectilinear character, and the function value takes a zero value, that is, the speed of change in the drying speed is zero.
Differences in the curves are observed in the second period of the falling drying rate. Depending on the properties of the dried product, "accelerated drying" can be constant or variable, as seen in figures 4 (a), (b), (c), can go from DC to AC, as in figure 4 (d) and to move out of state variably accelerated in variably slow (e) or vice versa (f).

All graphs (figure 4) clearly show the extremes of the f(U) function and the inflection points corresponding to the first and second $U_{cr1}$ and $U_{cr2}$ critical moisture percentage, while the values of the critical moisture percentage are approximately determined on the drying rate curves.

Analysis of the obtained curves indicates the presence of areas that are not defined on the drying speed curves, with slowing or accelerating changes in the drying speed. Since each water fraction is removed at a rate that varies according to different laws, it is possible to set intervals for removing moisture with different binding energies for these sections. Knowing the exact boundaries of these
intervals, you can quantify the fractional composition of moisture in the product that is removed during drying.

For the practical implementation of the method for determining the forms of connection of moisture with the material, various products should be investigated using this method: colloidal, capillary-porous, and other methods and compare the results obtained with data on the study of moisture bond forms by other methods, for example, thermogravimetric.

5. Conclusion

Existing methods for studying the forms of moisture-to-material communication provide either a qualitative assessment of the state of moisture in it and in most cases have large errors, or are very time-consuming, requiring long-term laboratory studies and further mathematical processing of data.

Using the example of graph-analytical analysis of typical drying rate curves, we propose an approach to determining the forms of moisture connection with the material, which allows not only qualitative, but also quantitative assessment of the state of moisture in the product.

The proposed approach will eliminate the time for conducting laboratory studies to study the forms of connection of moisture with the material and can be used as a basis for controlling and automating the drying process in food enterprises and related industries.

The introduction of such a value as "drying acceleration" into the drying theory will allow us to more fully characterize the period of falling drying speed and opens up additional opportunities for evaluating approaches to its intensification, optimizing energy costs and temperature modes of drying.

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