THERMOGRAVIMETRIC STUDY OF THE FORMS OF MOISTURE BONDS IN KNEADING FLOUR SEMI-FINISHED PRODUCTS WITH THE ADDITION OF CRICKET FLOUR

Abstract

Thermal analysis methods, primarily thermogravimetric analysis (TGA), play an important role in the study of phase transitions and degradation of active food components and auxiliary substances during heating or cooling. The most important areas of application of TGA in the food industry include the analysis of patterns of changes in the mass of the studied system during its heating or cooling due to the presence of phase transitions of the first kind and chemical reactions. In this work, a study of the change in mass of biscuit products during heating was carried out. The effect of replacing wheat flour with cricket flour in the amount of 5.0% on the structure of the resulting biscuit product compared to the control was determined. This study showed a change in the distribution of forms of connection of system water with dry substances of the system and, as a result, an expansion of the range of temperatures at which water evaporation from this sample took place. However, with a further increase in the amount of cricket flour in the recipe, which has an increased protein content, an increase in the part of the system water associated with the proteins of this raw material was observed. As a result, the range of temperatures at which water evaporation occurred from biscuit products with cricket flour in the amount of 10.0% and 15.0% decreased. It was noted in the work that the most acceptable functional and technological property of biscuit products is a wider range of forms of connection of system water with dry substances of such food products, since the presence of different forms of connection of water significantly determines the organoleptic indicators of finished products, terms and conditions its storage. The results obtained by the method of thermogravimetric analysis showed that, from the point of view of expanding the spectrum of forms of connection of system water with dry substances of the studied samples, the sample with the replacement of wheat flour with flour from crickets in the amount of 5.0% should be considered more acceptable.

Key words. derivatives, whipped flour semi-finished product, thermogravimetric analysis, biscuit product, cricket flour.

Statement of the problem in a general form.

The quality of ZBN in the storage process is ensured by the quantitative ratio of free and binding moisture, as well as the distribution of binding water between the biopolymers of the semi-finished product. In the process of storage, proteins and starch, which make up the basis of biopolymeric compounds in ZBN, undergo certain physico-chemical, biochemical and colloidal changes, as they lose a certain amount of moisture, as a result of which there is a loss of taste and aromatic indicators, and also the elasticity of the soft ZBN decreases.

One of the indicators of the quality of whipped flour semi-finished products is freshness, the preservation of which depends on the speed of the aging process. On the one hand, staleness is caused by the loss of water during storage, and on the other hand, it is the result of complex physicochemical, colloidal, and biochemical processes associated with changes in the properties of the main biopolymers of flour (starch and protein), which form the structure of the product [4].

It is known [6] that physical, chemical, and structural-mechanical changes occur in the product during storage, which change the structure of the pulp of the product due to retrogradation of starch and crystallization of sugar. Starch grains of flour swell during the kneading of the dough, in the process of baking, the starch is pasteurized, absorbing water. During the storage of products, starch grains begin to retrograde, restoring hydrogen bonds between chains of oligosaccharide residues. Starch becomes denser, loses previously bound water, pulp begins to crumble and the product becomes stale. The longer the moisture is retained in the product, the longer it remains soft.

Thus, the products undergo significant changes during storage, which leads to deterioration of quality, spoilage and staleness. Therefore, when adding new, innovative ingredients to ZBN, especially those with a high protein content, an important task is the effect of a certain concentration on the quality of the finished product.

Analysis of recent research and publications.

In view of previous studies on determining the optimal amount of flour from crickets in the recipe of a semi-finished biscuit, it is proposed to introduce an innovative product into the biscuit to improve its quality and increase its nutritional and biological value [1].

As far as we know, only a few authors have investigated the effect of replacing wheat flour with cricket flour on dough rheology and functional-technological properties of products [5, 6, 7]. It is believed that the properties of wheat flour are of great importance for determining technological indicators and are useful tools for predicting process efficiency and product quality [8]. The rheological properties of the dough can be evaluated using a wide range of approaches. The study of rheologi-
cal properties allows you to establish the duration of kneading, determine the amount of water that should be added to the flour in order to obtain the dough of the desired consistency. Others simulate rounding and shaping in the baking process and make it possible to determine the tensile strength of the dough, its strength, that is, the indicators necessary to predict the quality of a certain group of products [9].

Having analyzed the literary sources, we note that a small number of authors investigated the thermogravimetric study of moisture forms in biscuit semi-finished products. For example, the author T.O. Lisovska and co-authors [12] in their works determined the influence of corn flour in the process on the quality of semi-finished biscuit using the thermogravimetric method. From the analysis of the data specified in this work, it was determined that the loss of moisture in the control sample was 16.0%, while the amount of moisture in the test samples decreased by 10.0%.

The method of thermogravimetry was used to determine the traditional and new model cupcakes, which included innovative natural ingredients (powder of linden flowers, powder of flower pollen, pumpkin oil). According to the results of research, it was noted that due to the content of hydrophilic compounds and moisture-retain ing substances in the composition of natural ingredients, the content of firmly binding moisture increased by 15.9-17.4% and this caused a slowdown in its loss in cakes [4].

**Forming the goals of the article**

The purpose of the work was to study the processes, thermogravimetric research of the forms of moisture bonds in the whipped flour semi-finished product with the addition of cricket flour.

The object of the research was biscuit products with the addition of flour from crickets.

Thermogravimetric studies of the forms of moisture binding in ZBN during intermittent heating were carried out using a thermal analyzer "DerivatographQ-1500" (Hungary). This device is able to accurately measure all quantitative changes in the sample, which are associated with a decrease or increase in the mass of the product due to the redistribution of moisture during thermal exposure [10].

In the experimental samples, changes in temperature (T), mass changes (TG), rate of mass change (DTG), and heat of combustion (DTA) were simultaneously recorded as a function of time using a four-channel recording device. Derivatograms were used to determine the mass loss of the sample at the corresponding temperature m.

Thermogravimetric measurements were performed in a ceramic crucible under a quartz cap on a Q1500D derivatograph in dynamic mode with a sample weight of 2 g. A1203 fired to 1500°C was used as a standard. The sample was heated to 500°C at a heating rate of 2.5°C/min. Determination of the form of binding of water at all stages of introducing the component into the formulation was carried out on the basis of the analysis of temperature (T-curve), change in mass (TG) and its derivatives (DTG-curve) and enthalpy (DTA-curve). We studied moisture bonds after baking the semi-finished product.

**Presentation of the main research material**

Biscuit products were made according to the analogue of the round biscuit recipe [3], which included the following components: high-grade wheat flour, granulated sugar, egg yolks, egg whites, citric acid. Cricket flour was added by replacing wheat flour with cricket flour. Accordingly: model sample #1 contains 5.0% cricket flour, sample #2 contains 10.0% cricket flour, sample #3 contains 15.0% cricket flour.

After the manufacture of biscuit semi-finished products with the addition of flour from crickets, the experimental data obtained at the same time were studied by the methods of differential thermal and thermogravimetric analysis.

Measurements by the specified methods were carried out simultaneously on each of the studied samples, i.e., the temperature and mass of the studied sample were simultaneously recorded over time, as well as the difference in temperature and mass between the reference sample and the studied one. For clarity, the experimental data obtained by the methods of differential thermal (a) and thermogravimetric (b) analysis are shown on separate graphs.

![Fig. 1. Results obtained by the methods of differential thermal (a) and thermogravimetric (b) analysis for the control biscuit sample: kinetics of temperature (1) and mass (3) of the sample, kinetics of the difference in temperature (2) and mass (4) between the standard and the sample](http://grain-feed.ontu.edu.ua)
Fig. 2. Results obtained by differential thermal (a) and thermogravimetric (b) analysis methods for a biscuit product with a 5% concentration of cricket flour in wheat flour: temperature (1) and mass (3) kinetics of the sample, temperature difference kinetics (2) and masses (4) between the standard and the sample.

Fig. 3. Results obtained by differential thermal (a) and thermogravimetric (b) analysis methods for a biscuit product with a 10% concentration of cricket flour in wheat flour: temperature (1) and mass (3) kinetics of the sample, temperature difference kinetics (2) and masses (4) between the standard and the sample.

Fig. 4. Results obtained by differential thermal (a) and thermogravimetric (b) analysis methods for a biscuit product with a 15% concentration of cricket flour in wheat flour: temperature (1) and mass (3) kinetics of the sample, temperature difference kinetics (2) and masses (4) between the standard and the sample.
The kinetics of temperature and mass, as well as the kinetics of the difference in temperature and mass between the reference and the tested samples have the same character (Figs. 1–4).

The entire process of heating with a constant flow of heat to the test sample and the standard can be divided into areas separated in Fig. 1–4 by points marked with the letters A, B, C, and D. The positions of the selected points on the dependences reflecting the results obtained by the methods of differential thermal (a) and thermogravimetric (b) analysis, synchronized according to the determined values of moments of heating duration.

The section from the beginning of heating with a constant flow of heat supplied to the reference and test samples to point A corresponds to the heating of the dry substances of the test sample and the system water it contains (line 1 in fig. 1a, 2a, 3a, 4a). At the same time, there is practically no loss of mass, which is proved by the horizontal section on the kinetics of the mass of the sample (line 3 in Fig. 1b, 2b, 3b, 4b) from the beginning of the measurements to point A. By system water here is meant the water of the system, which is connected with its dry substances in various forms of connection: physically-chemical and chemically bound water [2].

Starting from point A, significant evaporation of the system water of the tested sample begins, which is accompanied by an increase in the temperature difference (line 2 in Fig. 1a, 2a, 3a, 4a) between the sample and the standard. This is evidenced, firstly, by the presence of an inflection point in the kinetics of the sample mass (namely point B on line 3), and secondly, by the presence of a minimum in the kinetics of the mass difference between the tested sample and the standard (line 4 in Fig. 1b, 2b, 3b, 4b). Thirdly, intense evaporation of system water is accompanied by heat absorption, which is evidenced by an increase in the temperature difference between the tested sample and the standard (line 2), with a slight increase in temperature (around point B on line 1).

In the section from point B to point C, the intensity of evaporation of the system water of the studied sample decreases. The kinetics of the temperature difference between the sample and the standard approaches zero (line 2). The angle of inclination of mass kinetics (line 3) to the abscissa axis decreases, while the kinetics of the mass difference between the studied sample approaches zero.

Starting from point C to point D, the sample is heated. The loss of mass in this area does not exceed 3...4%.

When point D is reached, the position of which corresponds to the temperature of the tested samples +200...220°C, the destruction of the components (including polysaccharides) begins.

The differences between the results shown in Fig. 1–4, obtained for different samples, lie in the position of selected points A, B, C, and D relative to temperature. It should be noted that for such products as biscuit products, more information is provided by temperatures lower than the destruction temperature of the components of this product, i.e. temperatures lower than +200°C. It is in the temperature range from +40...50°C to +140...150°C that the main information about the system water of such systems is found.

Based on this, it should be noted that the beginning of significant evaporation (point A) in the control sample and in samples in which a part of wheat flour was replaced by flour from crickets corresponds to a temperature of +40°C (point A on line 1 of Fig. 1a, 2a, 3a, 4a). As for the maximum intensity of evaporation (point B), for the control sample of the biscuit product, the position of this point corresponds to +93°C (point B on line 1 of Fig. 1a). For a biscuit product with a concentration of cricket flour of 5.0% in wheat flour, the position of point B corresponds to a temperature of +98°C (point B on line 1 of Fig. 1a), and for a biscuit product with a concentration of cricket flour of 10.0% and 15.0% – 91°C (points B on line 1 from Fig. 3a, 4a).

The temperature at which the end point of intensive evaporation of system water (point C) is reached for different samples also differs in value. Thus, for the control biscuit product, significant evaporation of system water ends at a sample temperature of +130°C (point C on line 1 of Fig. 1a). For a biscuit product with a concentration of cricket flour of 5.0% in wheat flour, the position of point C corresponds to a temperature of +148°C (point C on line 1 of Fig. 2a). For a biscuit product with a concentration of cricket flour of 10.0%, significant evaporation of system water ends at a temperature of +112°C (point C on line 1 of Fig. 3a, 4a), and for a product with a concentration of cricket flour of 15.0% – +102°C (point C on line 1 of Fig. 4a).

It should be assumed that for the reference sample, relative to which the temperature difference and the mass difference for the tested samples were found during the measurement, there are no phase transitions of the 1st kind, which is the initial condition of the applied research methods. Based on this, it is obvious that the area under the kinetics of the temperature difference and the kinetics of the mass difference between the standard and the sample under study in the range between points A and C is proportional to the amount of system water for which the I-type transition takes place in the temperature range corresponding to these points.

The area under the specified sections of the kinetics of temperature difference and mass difference between the reference sample and the studied samples was calculated according to the data shown in Fig. 5. The value of the mass difference between the standard and the test sample is normalized to the initial total mass of the test sample.

Calculation of the area under the kinetics of the temperature difference (S_{\Delta T}) and the area under the kinetics of the mass difference (S_{\Delta m}) between the standard and the tested samples, in the range between points A and C, was carried out, respectively, according to the expressions:

\[ S_{\Delta T} = \sum_{t=n_1}^{n_2} \left( t_{t+1} - t_t \right) \left( \Delta T_{t+1} + \Delta T_t \right) / 2 \]  

\[ S_{\Delta m} = \sum_{t=n_1}^{n_2} \left( t_{t+1} - t_t \right) \left( \Delta m_{t+1} + \Delta m_t \right) / 2 \]  

where \( n_1 \) and \( n_2 \) are the time coordinates of points A and C.

The calculation results are given for each of the studied samples in Table 1.
Fig. 5. The kinetics of the temperature difference and the kinetics of the mass difference between the standard and the tested samples of biscuit products: 1 – control; 2 – a sample with a concentration of flour from crickets of 5.0%; 3 – a sample with a concentration of flour from crickets of 10.0%; 4 – a sample with a concentration of cricket flour of 15.0%.

Table 1 - Area under the kinetics of the temperature difference ($S_{\Delta t}$) and area under the kinetics of the mass difference ($S_{\Delta m}$) between the standard and the tested samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\Delta t} \times 10^{-3}$ °C×с</th>
<th>$S_{\Delta m} \times 10^{4}$ (кг/кг)×с</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2.709</td>
<td>1.276</td>
</tr>
<tr>
<td>With a concentration of cricket flour 5%</td>
<td>2.619</td>
<td>1.246</td>
</tr>
<tr>
<td>With a concentration of cricket flour 10%</td>
<td>2.762</td>
<td>1.256</td>
</tr>
<tr>
<td>With a concentration of cricket flour 15%</td>
<td>2.811</td>
<td>1.320</td>
</tr>
</tbody>
</table>

From the given calculation results, it can be seen that the areas under the kinetics of the temperature difference ($S_{\Delta t}$) and the areas under the kinetics of the mass difference ($S_{\Delta m}$) between the standard and the tested samples differ by no more than 5..8%. Obviously, such a deviation can be neglected, since these calculated areas ($S_{\Delta t}$ and $S_{\Delta m}$) are proportional to the amount of water retained by the tested samples, so the samples have the same moisture content. That is, the amount of systemic moisture retained by the studied samples is the same.

Given the fact that the amount of water in the studied samples is the same, the differences within the ranges of increase and decrease in the intensity of evaporation of system water are explained by redistribution according to the forms of its connection with dry substances of these systems.

Thus, replacing 5.0% of wheat flour in the recipe of the control biscuit product with flour from crickets helps to shift the maximum intensity of evaporation from +93°C to +98°C. At the same time, the end of significant evaporation of system water for such a sample at a temperature of +148°C, while for the reference product this point occurs at a temperature of +130°C.

With a further increase in the amount of introduced flour from crickets in the amount of 10.0 and 15.0%, the point corresponding to the maximum intensity of the system water shifts to a lower temperature and is equal to +91°C. At the same time, the end of significant evaporation of system water for samples with a concentration of cricket flour of 10.0 and 15.0% also occurs at lower temperatures compared to the control sample, the values of which are equal to +102°C and +112°C, respectively.

Conclusion

Obviously, it was established that the replacement of wheat flour with flour from crickets in the amount of 5.0% helps to change the interaction of the components of the resulting biscuit product compared to the control. This entails a change in the distribution of forms of connection of system water with dry substances of such a system and, as a result, an expansion of the range of temperatures at which evaporation of water from this sample occurs. However, obviously, with the further increase in the amount of cricket flour, which is a protein-rich raw material, the amount of part of the system water connected with the proteins of this raw material increases. As a result, the range of temperatures at which water evaporates from biscuit products with cricket flour in the amount of 10 and 15% is reduced.

It should be noted that a wider range of forms of connection of system water with dry substances of such food products [11] is considered a more acceptable functional and technological property of products containing wheat flour, since the presence of different forms of water connection significantly determines organoleptic indicators of finished products, terms and conditions of their storage.

Thus, the studies carried out by the methods of differential thermal and thermogravimetric analysis indicate that, from the point of view of expanding the spectrum of forms of connection of system water with dry substances of the studied samples, it should be considered more acceptable to replace flour with wheat flour from crickets in the amount of 5.0 %.
TERMOGRAVIМETRICHNE DOSЛІДЖЕННЯ ФОРМ ЗВ’ЯЗКІВ ВОЛОГІ У ЗБИВНОМУ БОРОШНЯНому НАПІЯВФАБРИКАТІ З ДОДАВАНЯМ БОРОШНА ІЗ ЦВІРКУНІВ

Анотація
Методи термічного аналізу, насамперед термоґравіметричний аналіз (TGA), відіграють важливу роль у дослідженні фазових переходів і десорбуючих відсічіх активних компонентів, допоміжних речовин при нагріванні або охолодженні. Наїв-важливіші сфери застосування TGA у харчовій промисловості включають аналіз закономірностей зміни маси досліджуваної системи під час її нагрівання або охолодження через наявність фазових переходів і родючих хімічних реакцій. У даній роботі було проведено дослідження зміни маси бісквітних виробів під час нагрівання. Встановлено вплив заміни борошна пшеничного борошном і з цвіркунів у кількості 5,0%. Розглянуто, розширення діапазону температур, за якими відбувається випаровування води із цього зразка. Однак, при подальшому збільшенні у рецептурі кількості борошна із цвіркунів, яке має підвищений вміст білка, спостерігалась збільшення фазових переходів і деградації активних інгредієнтів відносно випаровування води із сухими речовинами системи і, як наслідок, розширення діапазону температур, за якими відбувається випаровування води із цього зразка. Однак, при подальшому збільшенні у рецептурі кількості борошна із цвіркунів, яке має підвищений вміст білка, спостерігалась збільшення фазових переходів і деградації активних інгредієнтів відносно випаровування води із сухими речовинами системи і, як наслідок, розширення діапазону температур, за якими відбувається випаровування води із цвіркунів у кількості 5,0%.

Ключові слова. деривотиграми, збивний борошняний напівфабрикат, термоґравіметричний аналіз, бісквітни́й виріб, борошно із цвіркунів.

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