The modeling of grain groats cooking as the process of moisture diffusion and swelling of starch granules

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Abstract. The modeling of grain groats cooking taking into account the processes of diffusive saturation with moisture and chemical kinetics of starch granules swelling up to their maximum size is executed. On the basis of experiment on cooking and photographing the parts of a material under a microscope it is established that near the limit of the section "firm phase-liquid" the size of granules reaches the highest possible magnitude, then they burst after that they come off and pass into a liquid phase. The kinetics of swelling was modelled on the equation of chemical reaction of the second order, and diffusive saturation with moisture – on the equation of non-stationary diffusion. The time of starch granules swelling was determined by a way of numerical integration, and the time of diffusive grain groats saturation by the equation of the non-stationary diffusion the numerical solution of which was executed by a method of nets according to the implicit scheme. It was established that in an initial period of time the process is limited by the speed of chemical reaction.

Introduction

In existing technologies of alcohol production all methods of transferring the starch-containing raw materials into soluble condition are based on grinding grain, mixing it with water and subsequent water-thermal treatment at high temperatures [1].   The technology of low-temperature regime of cooking the grain with the use of hydrodynamic and enzyme treatment [2] is more progressive. According to it the crushed raw materials (passage 80...90% through a sieve with apertures Ø 1 mm) is mixed with water to which is added a small amount of thinning enzymes, mainly α - amylase, and is heated up to 60...100 C for dissolution and partial enzymatic hydrolysis of starch.

Modeling this process the semi-empirical methods, based on a generalization of the experimental data are used [3]. Proceeding in the process of cooking of the saturation with moisture, the groat particles can be completed on the basis of numerical solution of non-stationary diffusion using the net method [4]. Along with diffusion it is necessary to consider the swelling of starched granules. This question is considered in a number of works [5-12], and the equations describing it are received. The real process of groat cooking includes both of these stages, which proceed simultaneously.

The swelling process is described as the kinetics of chemical reactions with the use of the equations of the reactions of the 1st, 2nd, 3rd orders, and also as diffusive mechanism. The detailed survey is presented in this article [13]. Summarizing [5] based on the equation of the reaction of 2-nd order is used in the work.

Main part

In the process of groats cooking the moisture diffusion inside the particles of the material and swelling of starched granules occurs. The photos we made under a microscope, which shows the range of the separation phase of cooking particles with liquid testify it.

Figure 1A shows the edge of the initial particle, filled up with liquid, which clearly shows the starched granules. In the figure 1B there is the edge of the particle in the process of groats boiling, swollen starch granules and the separation of a starch layer with the burst granules. Therefore, when modeling it is necessary to consider simultaneously the diffusion problem of particle saturation with water and the kinetics of chemical reaction of swelling in condition of the moving boundary of phase division (Stefan problem), as figure 1 shows the starch granules swell, burst, break off and move into a liquid phase.

For modeling the particles after rolls 1 mm thick are taken. It is accepted, they are flat. The moisture transportation is described with the one-dimensional equation of non-stationary diffusion. (1)

$$\frac{\partial C}{\partial \tau} = D(t)\frac{\partial^2 C}{\partial x^2}, \qquad (1)$$
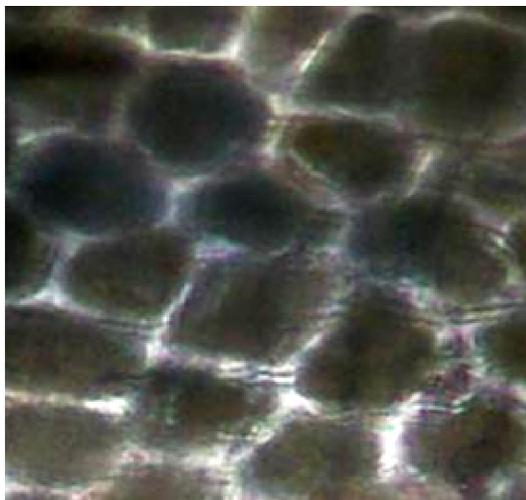
a) the initiall   starch granules
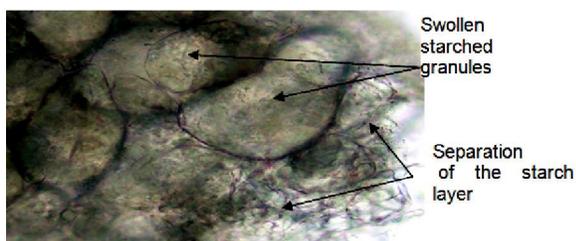
b) swollen starch granules and the separation of the starch layer

Figure 1. The appearance of the starch granules in grains at increase in   900 times

Where C - is the humidity of material, which changes in time and space, m3 water/m3 wet material; - time, c; x - coordinate in the direction of part thickness, m; is the diffusion coefficient of water in the material, m2/s

The dependence of the diffusion coefficient on temperature is presented by a   well-known expression

$$D(t) = D_{0d} e^{-E_{ad}/RT},\qquad (2)$$

Where D_{0d} is the pre-exponential factor (factor of diffusion); E_{ad} -is the energy of activation for the diffusion of adsorbed water, j/mol; T is the absolute temperature, K; R is the gas constant, R=8,314 j/(mol•K); the index d - diffusion.

The description of the process of starch granules as a chemical reaction presented in works [5, 9, 10]. The results summarized using the value X [5].

$$X = \frac{D_t - D_0}{D_m - D_0},\qquad (3)$$

Where D_0 is the diameter of the original (dry) starch granules, mm; D_m - maximal diameter of swollen starch granules, mm; D_t - current diameter of starch granules (at swelling), mm. The authors [5] accepted the description of kinetics of the swelling process with the reaction of the second order

$$\frac{dX}{d\tau} = V(\tau)(1 - X)^2 \qquad (4)$$

Where $V(\tau)$ is a velocity constant which depends on temperature and is calculated by the Arrhenius equation

$$V(\tau) = V_0 \exp\left(-\frac{E_a}{RT(\tau)}\right),\qquad (5)$$

Where V_0 is the pre-exponential multiplier, c^{-1}, E_a - activation energy, j/mol; R =8,314 - universal gas constant, j/(mol•K); T- is the temperature, K.

It should be noted that the kinetics of swelling granules was investigated using thermomechanical impact in the laboratory setup [5]. Laboratory setup allowed observing the change of viscosity of starch dispersion depending on the temperature profile, the speed of heating and cooling, as well as the shear velocity in the ranges found in industrial processes. By sampling starch dispersions at different stages of thermomechanical processing the data on changes in the distribution of starch granules sizes were obtained. It was established, that the best results, describing the experimental data, yields the equation (6).

$$\frac{X}{1-X} = \frac{D_t - D_0}{D_m - D_t} = V_0 \int \exp\left(-\frac{E_a}{RT(\tau)}\right)d\tau.\qquad (6)$$

To determine the value of activation energy of the reaction a large volume of literature and own experimental data were studied and the value of kJ/mol. was found. The results of identification are shown in figure 1, where the dots are the average values $(D_t - D_0)/(D_m - D_t)$, and the vertical lines, carried out through points, the dispersion of experimental data is shown. With acceptable accuracy for practical calculations in the range, in which the experiment was made, the dependence of the value $(D_t - D_0)/(D_m - D_t)$ from $\int \exp\left(-\frac{E_a}{RT(\tau)}\right)d\tau$ is presented in the form of a straight line (figure 2) [5].
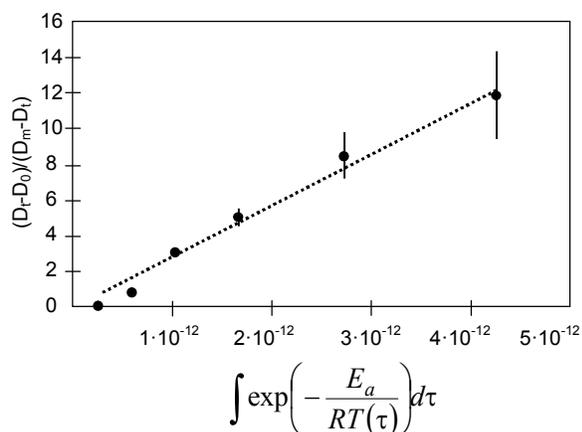
Figure 2 – Dependence $(D_t - D_0)/(D_m - D_t)$

as function from $\int \exp\left(-\dfrac{E_a}{RT(\tau)}\right)d\tau$

According to figure 2 the pre-exponential multiplier V_0 is a constant, equal to $2{,}84 \cdot 10^{12}$ c^{-1}.

Before using the results given above for modeling groats cooking , it is advisable to assess, in what field the process takes place: in kinetic, diffusive or mixed. Unfortunately, the equation (6) doesn't allow calculating the time of full swelling of a starch granule as at full swelling $D_t = D_m$ and the expression at the left – hand member of equation (6) becomes equal ∞. If you take into account the accuracy of measurement of the maximum diameter at which the granule will inflate and will come off a particle, it is possible to find the time of chemical reaction. In this regard the results of experiment which are used at size determination [5] were analysed previously. Authors made heating of water suspension of granules in water from 20 ºC to 120 ºC with a speed of 1 ºC / with, i.e. during 100 sec. During that time the maximum diameter was reached. We'll define the rating value of the diameter D_t at the time of experience equal to 100 sec., and at a variable temperature. For this purpose we will find from the equation (6) the value D_t.

$$D_t = \frac{D_0 + D_m\left[V_0\int \exp\left(-\dfrac{E_a}{RT(\tau)}\right)d\tau\right]}{1 + V_0\int \exp\left(-\dfrac{E_a}{RT(\tau)}\right)d\tau} \quad (7)$$

Numerical integration of expression $\int \exp\left(-\dfrac{E_a}{RT(\tau)}\right)d\tau$ at the basic data is given in [5]: $D_0 = 15{,}5$ mkm, $D_m = 40{,}0$ mkm. makes $D_t = 39{,}886$ mkm. The relative deviation expressed in percents, is equal to 0,28%.

We use this result in relation to the data provided on figure 1 from which it is found that $D_0 = 18$ micron and $D_m = 31{,}42$ micron. Reasoning from that on the equation (7), the necessary time for chemical reaction of swelling at a relative deviation of 0,28% i.e. at $D_t = 31{,}332$ micron is determined. It was equal to 7,3 min. at 70 ºC.

So as this mode of operation is close to the mode of grain groat cooking of barley [3], in the first approximation, the comparison between cooking and chemical swelling of starch granules in mixed diffusive – kinetic field was completed. The duration of the process of groat cooking was 225 min, i.e. the chemical reaction proceeds 30 times faster than the real process. However it is necessary to consider that the speed of the process of diffusion is variable and at an initial stage of time the gradients of water concentration at a surface of a material go to infinity, and the speed of diffusion is higher than the speed of chemical reaction. Therefore, for the final characteristics of the process of graot cooking it is necessary to carry out its modeling taking into account the stages of diffused and chemical (swelling of the starch granules).

According to the equations (1), (2) and (6) the diffusion and swelling proceed independently from each other.

The time of the chemical stage is determined by the equation (7) when the size of starch granules is $D_t = 31{,}332$ microns.

We'll consider the method of diffusive stage calculation.

The solution of the equation of non-stationary diffusion (1) was carried out numerically using the net method. To eliminate the divergence of calculations the implicit scheme is applied.

Through i marked the layers for coordinate (axis of abscissas), through j – for time (axis of ordinate). The values of humidity of groats element are in the net nodes. The values of humidity on the lower temporal layer are known, on the top layer – should be defined.

The system of the linear equations with three – diagonal matrix derived at every temporal layer was solved with the method of consecutive exception of

variables. The equation (1) in finite differences has the form

$$\frac{C_{i,j+1} - C_{i,j}}{\Delta \tau} = D(t) \frac{(C_{i-1,j+1} - C_{i,j+1}) - (C_{i,j+1} - C_{i+1,j+1})}{(\Delta x)^2}. \quad (8)$$

After transformations we'll receive

$$-\text{Fo} \cdot C_{i-1,j+1} + (1 + 2\text{Fo}) C_{i,j+1} - \text{Fo} \cdot C_{i+1,j+1} = C_{i,j}, \quad (9)$$

where

$$\text{Fo} = \frac{D(t)\Delta \tau}{(\Delta x)^2}. \quad (10)$$

Initial conditions: $\tau = 0 \quad C_{i,1} = C_0$.

Boundary conditions:
   on the border of the contact with water

$$x = 0 \qquad C_{0,j} = C^*,$$

   in the particle center

$$x = \frac{\delta}{2} \qquad C_{n-1,j} = C_{n,j}.$$

where C_0 – initial grain humidity (C_0 = 0,194 vol. part. or 0,147 mass. part.); C^* – steady – state moisture concentration in solids on the frontier of phase division (found at identification and compiles 0,888 vol. part. or 0,85 mass. part.); when $x = \dfrac{\delta}{2}$ derivative

$$\frac{\partial C}{\partial x} = 0 \text{, т.е. } C_{n-1,j} = C_{n,j}.$$

   It is presented below the algorithm of the decision of the linear system equations with the three – diagonal matrix which are received using the implicit scheme by splitting the spatial coordinate into *n* segments and numbers of steps in integration on time k (figure 3).

   For the initial temporal layer ($j = 1$) and second layer ($j = 2$) for *n* steps of integration along the coordinate (9) the equation takes the form

$$-\text{Fo} \cdot C_{0,2} + (1 + 2\text{Fo}) C_{1,2} - \text{Fo} \cdot C_{2,2} = C_{1,1} \quad (11)$$

$$-\text{Fo} \cdot C_{1,2} + (1 + 2\text{Fo}) C_{2,2} - \text{Fo} C_{3,2} = C_{2,1} \quad (12)$$

$$-\text{Fo} C_{2,2} + (1 + 2\text{Fo}) C_{3,2} - \text{Fo} C_{4,2} = C_{3,1} \quad (13)$$

$$-\text{Fo} \cdot C_{n-2,2} + (1 + 2\text{Fo}) C_{n-1,2} - \text{Fo} C_{n,2} = C_{n-1,1} \quad (14)$$

$$C_{n-1,1} = C_{n,1} \quad (15)$$

Denote

$$A_i = -\text{Fo} ; \quad B_i = (1 + 2\text{Fo}); \quad D_i = -\text{Fo} ;$$

$$\varepsilon_1 = C_{1,1} ; \quad \varepsilon_2 = C_{2,1} ; \quad \varepsilon_3 = C_{3,1} ; \quad \ldots$$

$$\varepsilon_{n-1} = C_{n-1,1} \quad ; \qquad \varepsilon_n = C_{n,1} \quad ;$$

$$\varepsilon_1' = \varepsilon_1 - A_1 C^*; \ B_1' = B_1.$$

Consider, that $C_{0,j} = C^*$, and get

$$B_1' C_{1,2} + D_1 C_{2,2} = \varepsilon_1' \quad (16)$$

$$A_2 C_{1,2} + B_2 C_{2,2} + D_2 C_{3,2} = \varepsilon_2 \quad (17)$$

$$A_3 C_{2,2} + B_3 C_{3,2} + D_3 C_{4,2} = \varepsilon_3 \quad (18)$$

$$A_{n-1} C_{n-2,2} + B_{n-1} C_{n-1,2} + D_{n-1} C_{n,2} = \varepsilon_n \quad (19)$$

$$C_{n-1,1} = \varepsilon_n \quad (20)$$

The system of the equations (16)-(20) is solved by the process of elimination of variables. After transformations the following system of the equations is received

$$B_1' C_{1,2} + D_1 C_{2,2} = \varepsilon_1' ; \quad (21)$$

$$B_2' C_{2,2} + D_2 C_{3,2} = \varepsilon_2' ; \quad (22)$$

$$B_3' C_{3,2} + D_3 C_{4,2} = \varepsilon_3' ; \quad (23)$$

....

$$B_{n-1}' C_{n-1,2} + D_{n-1} C_{n,2} = \varepsilon_{n-1}'. \quad (24)$$

So as $C_{n-1,2} = C_{n,2}$, then from the equation (24) the concentration $C_{n-1,2}$ is defined, from the equation (23) – the concentration $C_{3,2}$, from the equation (22) – the concentration $C_{2,2}$, from the equation (21) – the concentration $C_{1,2}$. Thus, from the system of the equations (21)-(24) the concentrations on the 2nd temporary layer are found.

$$C_{n-1,2} = \frac{\varepsilon_{n-1}'}{B_{n-1}' + D_{n-1}}; \quad (25)$$

$$C_{3,2} = \frac{\varepsilon_3' - D_3 C_{4,2}}{B_3'}; \quad (26)$$

$$C_{2,2} = \frac{\varepsilon_2' - D_2 C_{3,2}}{B_2'}; \quad (27)$$

$$C_{1,2} = \frac{\varepsilon'_1 - D_1 C_{2,2}}{B'_1} . \qquad (28)$$

In a similar way the transition from the second layer to the third, etc. was carried out, up to the determination of concentration in all net nodes. Extending the obtained result by $i = 1...n - 2$ and $j = 2...k$, we have

$$C_{i,j} = \frac{\varepsilon'_i - D_i C_{i+1,j}}{B'_i} , \qquad (29)$$

By $i = n$ and $i = n - 1$ we have

$$C_{n-1,j} = \frac{\varepsilon'_{n-1}}{B'_{n-1} + D_{n-1}} ;$$

The coefficients are defined by the following equations

$$B'_i = B_i - D_{i-1} \frac{A_i}{B'_{i-1}} , \qquad (30)$$

where $i = 2...n$; $B'_1 = B_1$

$$\varepsilon'_i = \varepsilon_i - \frac{A_i}{B'_{i-1}} \varepsilon'_{i-1} , \qquad (31)$$

where $i = 2...n - 1$.

According to the above – stated method the moisture concentration in the net nodes in all coordinate and temporary layers is determined. Until in the bound with the liquid phase layer the humidity won't be reached, near which the starch granules burst and break away from the grain particle.

The separation of starch layer was modeled in two variants: purely diffusive and swelling the starch granules on chemical kinetics. In purely diffusive variant knowing the concentration of moisture $C_{i,j}$ in net nodes, from the equation of material balance of a dry substances defined the diameter of a bulking-up granule of starch, having presented at the first approximation a granule in the form of a sphere.

$$D_{i,j} = D_0 \sqrt[3]{\frac{1 - C_0}{1 - C_{i,j}}} . \qquad (32)$$

In the version of swelling the starch granules on chemical kinetics by equation (7) the required time for chemical reaction of swelling was determined.

To judge what stage is limitative it's possible to define the time of progress of both stages. By integration of the equation (7) the time of the chemical reaction of swelling is determined and by the technique of diffusive saturation – the time of the layer saturation, adjoining with a liquid phase.

If on the equation of diffusion the demanded humidity is reached, and on the equation of chemical

kinetics the swelling isn't reached, the separation of a layer won't occur. For a separation it is necessary that on the diffusive mechanism the moisture was delivered by transport and that for the same time or smaller by chemical reaction passed the swelling of starched granules up to the size corresponding to their separation, i.e. to $D_t = 31,332$ micron. If on diffusion the demanded amount of moisture for swelling of granules isn't delivered, the separation of a layer won't occur. Therefore, the decision was conducted in the following sequence. The time of starched granules swelling by a chemical reaction on equation (7) was calculated. And the time of diffusion according the above mentioned method of non-stationary diffusion until reaching the moisture concentration, returning for the maximum diameter of a starch granule 31,42 micron, that corresponds to moisture concentration 80 % wt.. The separation of a layer was carried out by the maximum of these two times.
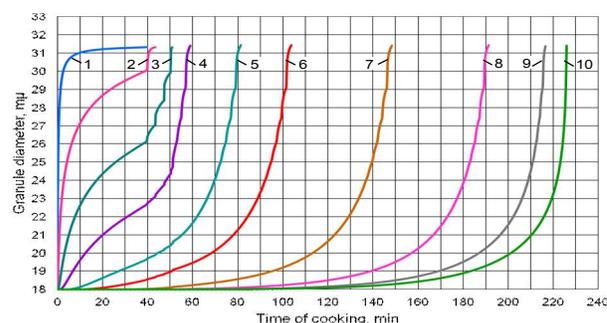
Layer number: $1 – 1^{st}$; $2 – 2^{nd}$; $3 – 5^{th}$; $4 – 10^{th}$; $5 – 20^{th}$; $6 – 30^{th}$; $7 – 50^{th}$; $8 – 70^{th}$; $9 – 85^{th}$; $10 – 100^{th}$

Figure 3. Evolution of the granules diameter changes in time taking into account the kinetics of chemical reaction of swelling

When calculating the first layer the swelling time on the equation of chemical kinetics of a starch granule (7) it turned out more time of diffusive saturation, therefore the separation of a layer was carried out on swelling time. When $D_{i,j}$ reached the value 31,332 microns, the layer breaks away, and the border of phase division moved to the next layer. Further calculations were carried out similarly. Since the seventh layer, the time of diffusive saturation exceeded the swelling time on chemical reaction. The further separation of starch granules was carried out on the diffusive mechanism.

Modeling results for the described algorithm are given in figure 4. As it can be seen from figure 4, the layer comes off only when granules swelled on kinetics of chemical reactions. After layer separation there appear large gradients of concentrations and the

diffusive process is accelerated. After a separation of the 6th layer the time of the diffusive mechanism becomes more than the time of kinetics of chemical reaction. The total time of cooking is 225, 7 min.

For comparison the results of modeling on purely diffusive variant are given in figure 5. The time of cooking was 224, 2 min. Thus, the swelling kinetics for the cooking process from the point of final result can be not considered.

Conclusions

The model of grain groats cooking taking into account the processes of diffusive moisture saturation and chemical kinetics of starch granules swelling, which is coordinated with the experimental data, is developed.

The stage of swelling is described by integration of the equation of chemical kinetics of swelling of the 2nd order. The diffusive stage is described by the equation of non-stationary diffusion which is solved numerically by a method of nets according to the implicit scheme. The comparison of this model with a method of calculating the process of cooking on purely diffusive mechanism is executed. The kinetics of starch granules swelling for the process of cooking can be ignored.

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