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NANOSCALE EFFECTS IN FOOD-PRODUCTION TECHNOLOGIES

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A working cell with a nanoscale membrane and channels for liquid food systems has been considered. Thermodynamic substantiation of the nanoprocesses is given. Analysis of the electrokinetic effects upon extraction and barothermal activation of the raw material has been performed. The conditions for barodiffusion initiation and development in the processes of heat and mass transfer have been established. The energy of the nanoprocesses in pasteurization, drying, concentration, and extraction has been considered.

Introduction. It is forecast that in the 21st century advances in nanotechnologies will lead to radically new production processes, and the turnover of the global market of nanoproducts in 2010 will amount to 145–900 billion U.S. dollars [1]. The use of nanotechnologies in the food industry will permit developing radically new products having no analogs in present-day cookery.

The basic processes of food production are accompanied by an impartation of energy to a product [2]. If the product is a liquid, then the modeling is based on the phenomenological approach and reduces to the analysis of a continuous system. The modeling scheme is based on the use of the laws of conservation of matter, energy, and momentum. The phenomenological laws incorporate the known linear relations between irreversible processes: the Fourier and Fick laws. The results of the modeling are material and energy balances and space-time distributions of P, E, T, ρ, and C.

Such an approach proved to be reasonable in analyzing many chemical-technological processes with a slow change in the parameters. However, liquid food systems (suspensions, aerosols, etc.) are specific. The presence of the cellular-fibrous structure is ignored in the above approach. Since the content of cells is the main aim of the technology, the model should reflect the transfer kinetics at the cell–medium interface, inside the pore and the capillary. The understanding of such laws is the basis for the intensification of the processes and the realization of radically new technologies of food production. In principle, these are food-production nanotechnologies, since the action is realized at the nanoscale level: on the membranes of cells, microorganisms, and pores. The realization of such nanotechnologies will permit obtaining radically new, low-energy-consuming foodstuffs [3]. A particularly interesting result would be expected with a sharp change in the parameters in the volume, at a pulsed energy input [4], and for a combined advancement of the processes. It seems that the approach to the modeling of combined processes in food systems should also provide for combined techniques in the system analysis.

Thermodynamical Prerequisites. Let us represent a food medium as a homogeneous continuous system in which the parameter distribution determines the boundary conditions for the working cell (cell, solid porous or fibrous phase). The working cell is formed as a heterogeneous system (see Fig. 1). The surface (shell) of phase 2 can be solid-phase fibers, elastic cell and microorganism membranes. As a rule, the phase-2 surface is permeable and has channels of hydraulic connection with the environment. For these cases, in the processes of combined action on the system, various known and unexpected effects are possible.

The reasons for the growth of ΔT in phase 2 may be the discrepancy between the heat inflow into this phase and the outflow of heat from it. As a result, part of the liquid phase may pass into vapor, which will lead to an increase in the pressure (by ΔP). The process may develop according to the following schemes: a mass flow M is initiated from phase 2 into phase 1; a break of the phase-2 shell occurs.

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It is possible that $P + \Delta P$ in phase 2 is also achieved due to a sharp decrease in the pressure in the continuous phase 1. At a stepwise decrease in the pressure, because of the incompressibility, the continuous phase 1 will instantaneously react and switch the process to the shell, the boundary surface (see Fig. 1). Technically, $P + \Delta P$ can be achieved by imparting phase 1 with a large volume. Then in phase 2, and sometimes in phase 1 as well, an increase in the volume should take place. The process can develop as follows: the liquid in phase 1 boils; splitting of phase 2 occurs; the phase-2 shell bursts.

The thermodynamic-phenomenological description of the process before the moment of catastrophic change in phase 2 (splitting, shell burst), with certain simplifications, is reduced to the expressions for the substance's mass flow M and the heat flow Q through a valve (membrane, pore):

$$M = a_{11} V \Delta P + a_{12} \frac{\Delta T}{T}, \quad Q = a_{21} V \Delta P + a_{22} \frac{\Delta T}{T}. \tag{1}$$

Thus, the problem is reduced to hydraulic processes. The quantities a_{ij} are phenomenological coefficients, and T can be considered as the mean temperature of the system. If we denote the flow section of the valve by f and its thickness by δ, then we can write the inequalities

$$a_{11} V \frac{\delta}{f} = A, \quad \frac{a_{12}}{T} \frac{\delta}{f} = B, \quad a_{21} V \frac{\delta}{f} = C^*, \quad \frac{a_{22}}{T} \frac{\delta}{f} = \lambda_0, \tag{2}$$

where A is the filtration factor; B is the thermoosmotic coefficient; C^* is the osmotic thermocoefficient; and λ_0 is the heat-conductivity coefficient.

From this point of view, one can describe the known processes and forecast new technologies: drying and extraction, material activation, increase in the juice yield in an electromagnetic field [3]; dispersion, homogenization, and low-temperature pasteurization in the processes of discrete-pulsed energy input [4].

The main problem is the determination of the phenomenological coefficients a_{ij}. Consider in more detail some of the processes in continuous-heterogeneous systems.

Electrokinetic Effects in Extraction. The extraction process is the key process in the production of sugar, oils, instant coffee, and brandy alcohols, and in pharmaceutical technologies. As a rule, this is a rather labor-intensive, low-efficiency process, which, nevertheless, determines both the quality and the economic indices of production (e.g., in brandy technologies the extraction process goes on for years). Therefore, it was proposed to intensify the extraction technology by using a combined electrophysical action on the process [5, 6].

The mechanism of combined mass transfer of extractive substances from the fibrous structure to solution is explained by the electrodiffusion model [6]. The diffusion in the solid phase is determined by Fick's law. Then the solvable substances move in the center of capillaries to the wood surface, where the concentration is determined by the diffusion resistance under constrained conditions. In parallel to the traditional flow j_1, due to the electromagnetic field a flow j_2 arises. Essentially, this is a barodiffusion determined by the pressure P_{cap} growing in the capillaries. Individual capillaries, where the conditions for vapor-phase generation have been attained, begin to discharge the liquid into the flow periodically. The frequency of discharges and the number of functional capillaries increase with increasing N. Analogy with the vaporization centers is proposed. The flow j_2 turbulizes the boundary layer, and the resistance to the mass transfer by barodiffusion can be a few orders of magnitude lower than in the traditional mass-yield schemes.

The hydrodynamic situation in the flow is determined by the turbulent flow of the extractant complicated by the eddy diffusion from the wood channels and the pulsed character of the field, determining the number and productivity of point mass-transfer centers. By the "dimensional analysis" method the structure of the generalized-variable equation has been determined. The influence of the electromagnetic field is taken into account by the vaporization number: $\text{Bu} = N(rwd^2\rho)^{-1}$. The physical meaning of the number Bu is as follows: the relationship between the radiant energy and the energy needed for the whole solution passing through the extractor to transform into vapor is established. The closer the number Bu to unity, the greater the amount of the vapor phase, the higher the pressure gradient, the more intensive the saturated-extractant release from the capillary depth, and the stronger the boundary-layer turbulization.

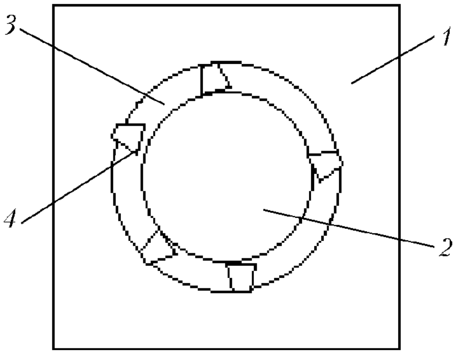

Fig. 1. Working cell with a nanoscale membrane and channels: 1) dispersed phase (P, C, T, E); 2) dispersed phase ($P+\Delta P$, $C+\Delta C$, $T+\Delta T$, $E+\Delta E$); 3) cell, pore or microorganism membrane; 4) channels, holes.

As a result of complex experimental studies including determination of the conditions for phase equilibria and extraction kinetics, we established the constants in the criteria equation [6]:

$$\text{at} \quad \mathrm{Re} < 2300 \qquad \mathrm{Sh} = 36.58\,\mathrm{Re}^{0.33}\,\mathrm{Sc}^{0.33}\,\mathrm{Bu}^{1.54}\,, \tag{3}$$

$$\text{at} \quad \mathrm{Re} > 2300 \qquad \mathrm{Sh} = 0.87\,\mathrm{Re}^{0.8}\,\mathrm{Sc}^{0.33}\,\mathrm{Bu}^{1.96}\,. \tag{4}$$

These relations became the key relations in the program for calculating extractors with an electromagnetic intensifier of the process.

Effects of Barothermal Activation of the Raw Material. The wastes of many food factories processing raw materials of vegetable origin are structured and it is necessary to activate them — destroy the structure of cells in order to extract and further reprocess valuable components. The basic processes of their reclamation technology are destruction, extraction, and drying.

We consider a system whose phases differ mainly in temperature and pressure. Substance transfer occurs through a valve (capillary, porous wall, membrane) (see Fig. 1) at a marked deviation of ΔP from the equilibrium state. In [3], we proposed the following mechanism of barothermal activation, which includes three stages. In the first stage, the change in the cell volume V_c with allowance for the temperature T_c, the pressure P_c, and the concentration in it of solvable components C_c is given as follows:

$$\tau_0 < \tau < \tau_{\mathrm{lim}}\,, \quad P_0 < P_{\mathrm{ext}} \le P_{\mathrm{lim}}\,, \quad T_0 < T_{\mathrm{ext}} \le T_{\mathrm{lim}}\,,$$

$$\frac{dV_\mathrm{c}}{d\tau} = \beta\varepsilon F\,\frac{\rho_{\mathrm{ext}}}{\rho_\mathrm{c}}\,[C_{\mathrm{ext}}(\tau) - C_\mathrm{c}(\tau)] + F_\mathrm{c}\varepsilon\,\frac{P_{\mathrm{ext}}(\tau) - P_\mathrm{c}(\tau)}{\delta} + \frac{1-\varepsilon}{r\rho}\int q_\mathrm{s} dF\,. \tag{5}$$

In relation (5), the first term takes into account the mass-transfer effect, the second term — the change in volume due to filtration, and the third term — the change in volume due to heat transfer. The heat flow transferred to the cell is expended in heating the "dry" part and the heating and partial evaporation of the liquid:

$$Q_\mathrm{c} = \int\limits_V \int\limits_0^\tau c_{pd}\left\{[1 - C_\mathrm{c}(\tau)]\, V_\mathrm{c}(\tau)\right\} \rho_\mathrm{d} dV d\tau + \int\limits_V \int\limits_0^\tau c_{p\mathrm{air}} C_\mathrm{c}(\tau)\, V_\mathrm{c}(\tau)\, dV d\tau + \int\limits_V \int\limits_0^\tau q_V dV d\tau\,. \tag{6}$$

Representing the cell membrane as a hollow sphere of radius R, we can write the temperature field in the cell in spherical coordinates. The diffusion processes change the concentration of extracted substances in the cell:

$$\frac{d\,(C_{\mathrm{c}}\,(\tau))}{d\tau} = \frac{\beta F_{\mathrm{c}}}{V_{\mathrm{c}}}\,[C_{\mathrm{ext}}\,(\tau) - C_{\mathrm{c}}\,(\tau)]\,. \tag{7}$$

The current value of the concentration in the cell, depending on the radius, is of the form

$$C_{\mathrm{c}}\,(\tau) = C_{\mathrm{c,max}} - [(C_{\mathrm{c,max}} - C_{\mathrm{c}})/\Delta R^3]\,R^3\,. \tag{8}$$

The second stage requires holding for the mass-transfer processes to be realized.

In the third stage, a sharp depressurization occurs, which leads to an intensive release of the content through the cell-membrane pores, a consequence of which is an intensification of the process of subsequent extraction. The degree of breakdown of the cell membranes in the whole of the reaction mass determines the degree of activation. Under definite conditions an increase in the pore diameter in the cell walls as well as a partial or complete break of the membrane is possible.

Subsequently, the problem can be represented in the form of the known model of the stressed state of a spherical membrane with through holes. With the aid of the proposed mathematical model the direction of investigations in the macroregion has been determined and the tasks of experimental studies have been established.

Cryoelectrical Effects. Analysis of the cryoelectrical methods of freezing-out [7, 8] takes into account the irreversible processes of heat, substance, and electric energy exchange between the ice block and the solution. Both phases are separated by a natural boundary — the ice-formation front. The phases are connected through narrow channels in the ice block. The temperature, pressure, concentration, and electric potential change stepwise in going through the interface and are functions of time. In freezing-out from solutions of electrolytes, the electric potential difference leads to a displacement of the existing mobile ions and the appearance of electric current.

The thermodynamic analysis of combined cryoelectrical processes shows ways of controlling the flows. Combinations of gradients of T, P, E, and C determining the required rates and directions of motion of the components and the efficiency of the processes have been established [7, 8].

Initiation of Barodiffusion. In a one-dimensional writing along the x-axis, the differential mass-transfer equation is of the form

$$\frac{dC}{d\tau} = D\,\frac{\partial^2 C}{\partial x^2} + \frac{\partial C}{\partial x}\,w_x\,. \tag{9}$$

The field of concentrations C is defined by the combined effect of the microkinetics (the first term) and the macrokinetics (the second term). Consider the problem of diffusion in the body capillary in the process of extraction. The displacement of extractive substances inside the capillary to the surface of the body is determined by the concentration gradient along the x-axis and the value of the diffusion coefficient D. The rise of the process temperature somewhat increases the value of the diffusion coefficient. However, the constraint under the capillary conditions does not give an appreciable intensification of the process. Moreover, the temperature level is a contradictory factor, since the requirements on quality of the product dictate the expediency of its decrease. However, in relation (9) there is one more term that takes into account the convective transfer in the capillary due to the displacement of the solution at velocity w_x. The question of initiating such a motion arises.

In such a formulation the problem is split into two: the first (purely hydraulic) one is the problem on estimation of the hydrodynamic resistance of the capillary; the second (thermodynamical) one is the problem on determination of the energy needed to overcome this resistance. Let us calculate from this point of view the required splitting work. We shall perform calculations for a capillary channel of a vegetable raw material. We take the capillary diameter d_{cap} to be 0.2 mm and its length l = 4 mm. The hydrodynamical resistance of such a channel ΔP is determined by the flow velocity of the liquid w, its density ρ, the sum of local resistances ξ, and the surface-tension forces σ:

$$\Delta P = \frac{\rho w^2}{2}\left[\frac{\lambda l}{d_{\mathrm{cap}}} + \Sigma\xi\right] + \rho g l + \frac{\sigma}{d_{\mathrm{cap}}}\,. \tag{10}$$

TABLE 1. Thermodynamic Parameters in Barodiffusion Development

Parameters	v', m^3/kg	v'', m^3/kg	v_{mix}, m^3/kg	i', kJ/kg	i'', kJ/kg	I_{mix}, kJ/kg	X_{mix}
$P_1 = 0.1$ MPa	0.00103	1.695	0.0027	335	2676	337.34	0.001
$P_2 = 0.12$ MPa	0.00104	1.113	—	419	2711	445.5	0.0015

The product of ΔP and the value of the displaced liquid volume V will yield the energy needed for the mechanical action on the liquid in the capillary, i.e., for the filtration process.

To initiate barodiffusion under the energy action, it is necessary to overcome the resistance of the channel due to the transition of a part of the liquid to the vapor phase. Therefore, it is necessary to determine the thermodynamic parameters of the vapor-water mixture in the channel at the initial pressure P_1 and the pressure that provides barodiffusion: $P_2 = P_1 + \Delta P$. The change in the state of the vapor-water mixture in the channel occurs at a constant volume. Therefore, the quantity of heat needed for reaching the pressure P_2 will be equal to

$$Q = M\,[(i_2 - P_2 v_{\text{mix}}) - (i_1 - P_1 v_{\text{mix}})]\,. \tag{11}$$

The specific volume of the mixture in the channel is determined depending on the values of the specific volumes of the liquid (v') and vapor (v'') phases and the vapor quality X. As a result of supplying energy, the liquid enthalpy in the channel will increase from i_1 to i_2. In this case,

$$i_1 = i_1' + r_1 X_1\,,$$
$$i_2 = i_2' + r_2 \frac{v_{\text{mix}} - v_2'}{v_2'' - v_2'}\,. \tag{12}$$

For the chosen values of d_{cap} and l the determining effect is produced by the kinetic pressure. At $w < 1$ its contribution amounts to 95%, and the value of ΔP is in the limit of 20 kPa. The values of the thermodynamic parameters at the calculated pressures are given in Table 1.

Thus, for mechanical removal of the liquid from the capillary channels of the assumed sizes (filtration process) an energy $E^* = 20$ J/kg is needed, and due to the phase transition — $Q = 85$ kJ/kg. The realization of these approaches requires adequate designs, naturally, different for extractors and driers.

Energy of Food-Production Technologies. Most food-production technologies feature a low energy efficiency [2, 7]. The approaches and principles that have become customary because they have been used for many decades, from the energotechnological point of view are sometimes simply absurd. Let us carry out an analysis of the technologies widely used in food production.

Pasteurization. The aim of the process is to inhibit the activity of microorganisms by increasing their temperature. The technological parameters of the process are lethal temperature T_{let}, current time τ, and initial amount of microorganisms N_{m0}, and at time τ, N_{m} is determined by means of the lethal time index D_{let} needed to decrease the number of microorganisms ten times from the initial level at T = const:

$$\log\left(\frac{N_{\text{m0}}}{N_{\text{m}}}\right) = \frac{\tau}{D_{\text{let}}}\,. \tag{13}$$

It is known that log N_{m} decreases linearly with time, and the dependence of log (D_{let}) on T_{let} is also linear.

In practice, the pasteurization problem is solved by heating the whole mass of the product to the level of lethal temperature. If we compare the energy that should be supplied directly to the microorganisms with the total expenditure of energy, then we obtain that the energy efficiency of the pasteurization process does not exceed 0.004%. If we take into account that pasteurization is followed, as a rule, by cooling with the use of refrigerators, the efficiency will decrease by an order of magnitude.

TABLE 2. Energy Effect of Nanotechnologies

Technological process	Mechanism	Effect
Low-temperature pasteurization	Selective action on the microorganism	Increase in energy efficiency by a factor of 10^3
Energy-effective drying	Volume energy supply, initiation of barodiffusion	Decrease in energy consumption by a factor of 40–50
Conductive-convective drying of grain	Local heat supply to the grain layer, deep recirculation of the heat-transfer material, heat recovery	Decrease in fuel consumption by 18–40%
Cryoconcentration of solutions	Passage of water into the solid phase, ice recycling	Decrease in energy consumption by a factor of 2–5
Thermal treatment of viscous products	Mechanical action on the boundary layer by a heat-exchange module	Intensification of the process by a factor of 2–20
Extraction with an electromagnetic intensifier	Volume energy supply, initiation of barodiffusion	Intensification of mass transfer by a factor of 5–1000

It seems that the search for nontraditional solutions of the problem of selective action on the microorganism is topical even if the capital costs of equipment increase.

Drying. This process is the final stage of many food-productions technologies. It is the drying that largely determines both the quality of the finished product and the power consumption of the whole technology [9] and in the most popular convective drying of vegetable raw materials is characterized by the opposite direction of temperature gradients and moisture contents in the product. The heat-transfer medium is also a diffusion medium. In this connection, there are a whole number of unsolved problems characteristic of the traditional convective drying, the main ones being the long duration of the process and the unjustifiably high specific energy expenditures exceeding, the values of the phase-transition heat for water by a factor of 2–4.

Concentration. Every year, in developed countries at food-industry enterprises up to 100 billion kg of water are evaporated from sugar syrup, juices, milk, extracts, etc., for which $3 \cdot 10^{11}$ MJ of energy is expended. Moreover, the thermal methods of water removal (evaporation) decrease the quality indices of the product: a boiling aftertaste appears, denaturation of protein occurs, the smell and color worsen.

The change in the traditional approaches and the orientation toward high technologies permit forecasting new principles of organization of the process based on its combined advancement. In food-production nanotechnologies, energy is supplied in practice to the element or component of the system that needs it. Estimates of the efficiency of some new principles are given in Table 2.

Practical Confirmation of the Hypotheses. Under the conditions of cognac production, an extractor with an electromagnetic intensifier has been tested. Under different operating conditions, the mass-transfer intensity increased tens and thousands of times. The test data have confirmed the proposed mechanism of a combined process of extraction and the prospects of the technology. Tasters noted positive structural changes in the product, primarily in aromatic components. The possibility of collecting a bouquet of alcohol at the nanoscale level appears.

Laboratory tests of cryoelectric freezers in concentrating milk serum have shown that the possibility of fractionation of serum proteins, i.e., obtaining from secondary raw materials ingredients with a high commercial cost, has been found.

CONCLUSIONS

The complex of investigations and production tests carried out confirms the mechanisms and hypotheses formulated above. Apparently, combined processes open up new possibilities in controlling structural changes in the product and permit decreasing the power consumption of production and organizing radically new food-production nanotechnologies.

NOTATION

a_{ij}, phenomenological coefficients; Bu, vaporization number; C, concentration; c_p, specific heat capacity; D, diffusion coefficient; d, diameter; E, electric potential; E^*, energy; F, surface area; f, valve cross section; g, gravitational constant; i, enthalpy; j, diffusion-current density; l, length; M, mass flow; N, radiation power; P, pressure; Q, heat flow; q, heat-flow density; R, membrane radius; r, latent heat of phase transition; Re, Reynolds number; Sc, Schmidt number; Sh, Sherwood number; T, temperature; V, volume; v, specific volume; x, coordinate; X, vapor quality; w, velocity; β, mass-transfer coefficient; δ, thickness; ε, porosity; ρ, density; σ, surface-tension forces; τ, time; ξ, coefficient of hydrodynamic resistance. Subscripts: s, source; c, cell (pore); 0, initial; lim, limiting; d, dry; mix, mixture; e, extractant; m, microorganism; let, lethal; max, maximum; $'$, liquid phase; $''$, vapor phase; p, pressure; a, air; cap, capillary.

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