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Thermodynamic factor and vacuum crystallization

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Abstract:
Sucrose crystallization depends on various thermal phenomena, which makes them an important scientific issue for the sugar industry. However, the rationale and theory of sucrose crystallization still remain understudied. Among the least described problems is the effect of time and temperature on the condensation rate of sucrose molecules on crystallization nuclei in a supersaturated sugar solution. This article introduces a physical and mathematical heat transfer model for this process, as well as its numerical analysis.

The research featured a supersaturated sugar solution during sucrose crystallization and focused on the condensation of sucrose molecules on crystallization nuclei. The study involved the method of physical and mathematical modeling of molecular mass transfer, which was subjected to a numerical analysis.

While crystallizing in a vacuum boiling pan, a metastable solution went through an exothermal reaction. In a supersaturated solution, this reaction triggered a transient crystallization of solid phase molecules and a thermal release from the crystallization nuclei into the liquid phase. This exogenous heat reached 39.24 kJ/kg and affected the mass transfer kinetics. As a result, the temperature rose sharply from 80 to 86°C.

The research revealed the effect of temperature and time on the condensation of solids dissolved during crystalline sugar production. The model involved the endogenous heat factor. The numerical experiment proved that the model reflected the actual process of sucrose crystallization. The obtained correlations can solve a number of problems that the modern sugar industry faces.

Keywords: Vacuum boiling pan, sucrose, phase, metastable solution, heat, dissolution, condensation, crystallization

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INTRODUCTION

Vacuum boiling pans are an essential component of sugar and starch production. A vacuum pan is a crystallizer filled with a liquid solution of sucrose, salts, or other substances.

A metastable liquid solution behaves like a homogeneous liquid. If it is oversaturated, a thin suspension or a solid phase introduced into the crystallization nuclei can trigger a rapid and powerful thermal reaction. This reaction turns the homogeneous solution into a heterogeneous liquid system called massecuite.

The thermal release during crystal formation is caused by two factors. On the one hand, the force of attraction accelerates the flow of sucrose molecules to the crystallization nuclei. On the other hand, when the molecule clusters stop on the surface of the crystallization nucleus, the accumulated kinetic energy is spent on embedding the molecules into the crystal lattice, as well as on internal energy. As a result, molecules get accumulated on the crystallization nucleus, and this process is known as crystallization of sucrose in a vacuum pan.

In the sugar industry, energy production relies on all physical forms of thermal energy of water, be it liquid or vaporized. Thermal equipment turns water into steam, which acts as the main heat generator to obtain sugar or sugar products. After that, the steam serves as a heater and evaporates moisture from another heterogeneous liquid system, e.g., beet juice. The steam can also go into a new physical state: it settles on the cooled solid walls of the equipment, turns into a liquid, and releases the heat.

This phenomenon illustrates the law of energy conservation. Water molecules move in this gaseous medium and settle down on the equipment walls. As vapor transforms into liquid, it releases thermal energy, which is a powerful and efficient reaction. As a result, the temperature inside the environment rises, which makes steam the main source of thermal energy in sugar production.

The same law of energy conservation is responsible for crystallization, which occurs in a supersaturated sugar solution when the distance between the crystallization nuclei becomes small enough to trigger the forces of attraction between sucrose molecules. Hence, crystallization happens when sucrose molecules concentrate on the surface of the crystallization nuclei.

A lot of studies concentrate on the scientific and technical issues of metastable and supersaturated solutions because these phenomena are crucial for sugar production technology [1–19].

For instance, Saifutdinov *et al.* focused on the effect of various organic solvents on the molar changes in the Gibbs energy, enthalpy, and entropy during adsorption [1]. They established the role of intermolecular interactions in the solution and at the phase boundary.

In another article, Saifutdinov *et al.* reported the adsorption thermodynamics for some 1,3,4-oxadiazoles and 1,2,4,5-tetrazines from water-acetonitrile and water-methanol solutions on the surface of porous graphitized carbon at 313–333 K [2]. The absolute values of the change in the Gibbs energy and enthalpy increased during the adsorption from water-organic solutions as the surface area of adsorbate molecules became larger, the absolute values of the change in entropy decreased, and the Van der Waals volume of molecules increased.

Makhmudov *et al.* calculated the thermodynamic parameters for the phenol and sulfonol sorption from wastewater on activated carbon and anion exchanger [3].

Sagitova *et al.* described the sorption of cobalt ions by native and modified organic pharmacophores of pectins [4]. They determined the effect of acidity, temperature, and solution/sorbent module on the distribution of cobalt ions in the heterophase system of polysaccharide sorbent and aqueous solution. This research also revealed the effect of various biosorbents on the thermodynamics of cobalt ions.

Sharma *et al.* used the method of isothermal microcalorimetry to determine the dilution enthalpy of fluorosiloxane rubber and polychloroprene solutions in various organic liquids [5]. The dissolution processes of polychloroprene were accompanied by exothermic processes, while those of fluorosiloxane rubber – by endothermic ones.

Sayfutdinov and Buryak applied liquid chromatography to study the adsorption of isomeric dipyridyls and their derivatives from aqueous acetonitrile, aqueous methanol, and aqueous isopropanol solutions on a graphite-like carbon [6].

Fedoseeva and Fedoseev proved that size changes the state and physicochemical properties of dispersed systems in small (nano-, pico-, femtoliter) volumes [7]. The scientists used digital optical microscopy to interpret the concepts of chemical thermodynamics. Their experiments established the effect of such geometric parameters as radius and contact angle on the kinetics of phase and chemical transformations. The research featured polydisperse accumulations of droplets in organic and water-organic mixes that interacted with volatile gaseous reagents.

Other publications reported on the kinetics, mechanism, and heat of crystallization processes [8–15]. Some of them [8–10] focused on phase thermal effects in the sugar industry based on the laws of thermodynamics and the Gibbs theory.

Jamali *et al.* studied such independent kinetic factors as thermodynamics and sucrose crystal transfer that occur in an aqueous sugar solution during crystallization [16]. They used high-precision tools and scaling to prove that the experimental results confirmed the precalculated fluid densities, thermodynamic factors, shear viscosity, self-diffusion coefficients, and the Fick diffusion coefficients.

Li *et al.* described a modern view on crystal nucleation [17]. Traditional physical organic chemistry always combined kinetics and thermodynamics to study crystallization. The authors studied sucrose and p-aminobenzoic acid to show how solution chemistry, crystallography, and kinetics complement each other to provide a complete picture of all nucleation processes.

Kumagai proved the effect of the water sorption isotherm on the interaction of water and solids in food products [18]. In thermodynamics, the Gibbs free energy (ΔGs) describes the interaction of a solid substance and water. Therefore, the plasticizing effect of water on food products can be evaluated by applying the Gibbs free energy.

Ebrahimi *et al.* studied a mix of 1-butanol + water with or without sugars and their effect on clouding [19]. This experiment established that 1-butanol + water solution fortified with sucrose or alcohol reduced clouding.

These publications give a thorough account of phase transition of liquid to vapor and back, but they provide a poor quantitative assessment of the heat released or absorbed in each case.

The present paper introduces the thermal problem of heat propagation in the intercrystal solution volume adjacent to crystallization nuclei (instantaneous heat source).

STUDY OBJECTS AND METHODS

The research featured a supersaturated sugar solution in a vacuum boiling pan under the conditions of industrial sugar production.

The methods included physical and mathematical modeling of heat and mass transfer in heterogeneous liquid systems.

Modeling. Heat transfer in a vacuum pan is a difficult task for physical and mathematical modeling,

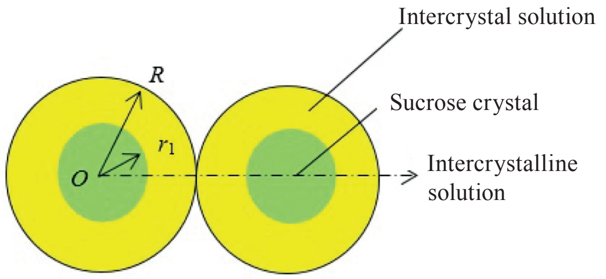

Figure 1 Heat and mass transfer for sucrose crystallization in a vacuum boiling pan

while its numerical calculation provides a scheme that reflects the actual process [13].

The modeling relied on the assumption that crystallization nuclei are uniformly distributed in the vacuum pan. Therefore, the calculations relied on the spherical symmetry of the liquid + solid mix relative to center *O* in the region of $0 < r < R$, where *r* is the radius of the model sphere and *R* is the average radial distance between the spheres (Fig. 1).

The boundary value problem was based on the theory of thermal conductivity for an isolated model particle of sucrose near the crystallization nucleus. A certain volume of intercrystalline solution was represented as a spherical region with radius *R* and center point *O* at saturation temperature T_s. The volume included a model sucrose particle represented as a sphere with radius $r = r_1$ and center *O*. The initial instantaneous heat source distributed over spherical surface $r = r_1$ (Fig. 1) with force Q_l (J). Heat exchange occurred in accordance with the boundary condition of the third kind between sphere surface $r = R$ and its environment. The task was to find the temperature field in the region of $0 < r < R$ and the average temperature of the medium over time.

The heat transfer equation looks as follows:

$$\frac{\partial\,[rT(r,\tau)]}{\partial\tau} = a\,\frac{\partial^2[rT(r,\tau)]}{\partial r^2} \qquad (1)$$
$$(\tau > 0, 0 < r < R)$$

where $T(r,\tau)$ is the temperature, K; τ is the time, s; and *a* is the thermal diffusion coefficient, m²/s.

The initial data include:

$$T(r,0) = \begin{cases}(T_0 + \delta T)\text{ at } r \le r_1 \\ T_0 at\ r > r_1\end{cases} \qquad (2)$$

where

$$\delta T = Q_{sp}/c_0 \qquad (3)$$

temperature difference between sphere surface $r = r_1$ and the environment, K; Q_{sp} is the specific heat of crystallization, J/kg; and c_0 is the heat capacity of the solution, J/(kg· K).

Boundary conditions:

$$\frac{\partial T(0,\tau)}{\partial r} = 0, T(0,\tau) \ne \infty, \text{at } \tau > 0 \qquad (4)$$

$$\frac{\partial T(R,\tau)}{\partial r} + H[T(R,\tau) - T_1] = 0 \qquad (5)$$

where T_0 and T_1 are the initial temperature (*K*) of the environment (massecuite) and the temperature on sphere surface $r = R$, m, respectively; $H = \alpha/\lambda$, α is the thermal diffusion coefficient, Vt/(m²·K); and λ is the thermal conduction coefficient, Vt/(m·K).

If we introduce the following substitution

$$t(r,\tau) = T(r,\tau) - T_1 \qquad (6)$$

the boundary problem (1)–(5) looks as follows:

$$\frac{\partial[rt(r,\tau)]}{\partial\tau} = a\frac{\partial^2[rt(r,\tau)]}{\partial r^2}\ (\tau > 0, 0 < r < R) \qquad (7)$$

$$t(r,0) = n\begin{cases}(\Delta t + \delta T)\text{at } r \le r_1 \\ \Delta t \text{ at } r > r_1\end{cases} \qquad (8)$$

$$\frac{\partial t(0,\tau)}{\partial r} = 0, t(0,\tau) \ne \infty, \text{at } \tau > 0 \qquad (9)$$

$$\frac{\partial t(R,\tau)}{\partial r} + Ht(R,\tau) = 0 \qquad (10)$$

where $t(r,\tau)$ is the reduced temperature, $\Delta t = T_0 - T_1$, and δT is defined according to (3).

Boundary problems (7)–(10) are based on the following correlation [20]:

$$(r,\tau) = \frac{b}{4\pi R}\cdot\sum_{n=1}^{\infty}\frac{1}{rr_1}\cdot\frac{\mu_n}{\mu_n - \sin\mu_n\cos\mu_n}\cdot$$
$$\cdot\sin\frac{\mu_n r_1/R}{r_1}\cdot\sin\frac{\mu_n r/R}{r}\cdot\exp(-\mu_n^2\,Fo) \qquad (11)$$

$b = V\cdot t(r,0), V = 4\pi r_1^3/3$, sucrose crystal volume, m³; $t(r,0)$ as in (8), K; and μ_1 and μ_2, are the roots of the characteristic equation:

$$tg\mu = -\mu/(Bi - 1) \qquad (12)$$

where $Bi = \alpha h/\lambda$ – Biot number (thermal), $Fo = \alpha\tau/R^2$ – Fourier number [20].

According to (11),

$$(r,\tau) = \frac{b}{4\pi R}\cdot\sum_{n=1}^{\infty}\frac{1}{rr_1}\cdot\frac{[(Bi-1)^2 + \mu_n^2]^{1/2}A_n}{Bi}\cdot \qquad (13)$$
$$\cdot\sin(\mu_n r_1/R)\ \cdot\sin(\mu_n r/R)\ \cdot\exp\ (-\mu_n^2 Fo)$$

where A_n is the table coefficients [20].

Formula (6) provides the following solution for (7)–(10):

$$T(r,\tau) = T_1 + t(r,\tau) \qquad (14)$$

where $t(r,\tau)$ is the calculated according to (13).

Mean temperature $0 < r < R$ is calculated as follows:

$$T_m(\tau) = \frac{3}{R^3}\int_0^R T(r,\tau)r^2 dr \qquad (15)$$

where function $T(r,\tau)$ under the integral depends on correlation (14).

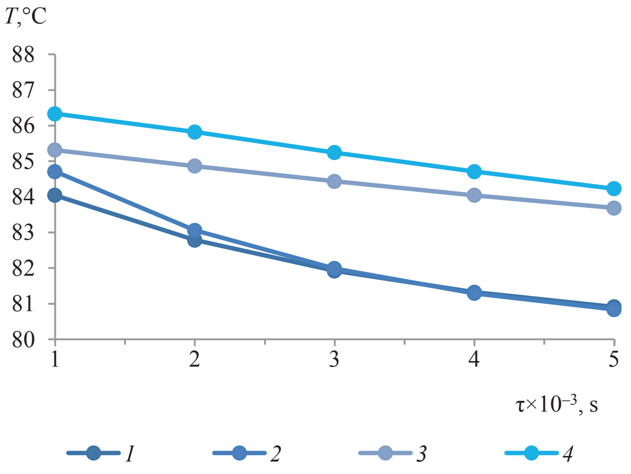

Figure 2 Correlation of temperature T on surface r_1 of the model sucrose particle with volume concentration c of the solid phase in the solution and crystallization time τ ($r_1 = 1\times10^{-5}$ m: *1* – $c = 40\%$, *2* – $c = 50\%$; $r_1 = 2\times10^{-5}$ m: *3* – $c = 40\%$, *4* – $c = 50\%$)

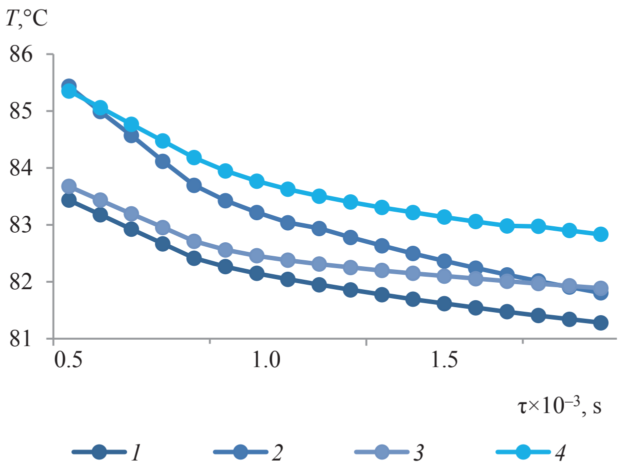

Figure 3 Correlation of mean massecuite temperature T with volume concentration $\boldsymbol{c}$ of the solid phase in the solution and crystallization time τ ($r_1 = 1\times10^{-5}$ m: *1* – $c = 40\%$, *2* – $c = 50\%$; $r_1 = 2\times10^{-5}$ m: *3* – $c = 40\%$, *4* – $c = 50\%$)

The temperature and the mean temperature in the vacuum pan depend on the processing time and are calculated based on correlations (14) and (15). As follows from the assumption about the uniform distribution of the crystallization nuclei, the calculated thermal characteristics for the selected elementary volume with radius R are also valid for the entire volume of the vacuum pan.

RESULTS AND DISCUSSION

The initial data included: crystal radius $r_1 = 1\times10^{-5}$ and 2×10^{-5} m; volume concentration $c = 40$ and 50% ($c = 0.4, 0.5$); density of intercrystalline solution (massecuite) $\rho = 1450$ kg/m^3; thermal conduction and diffusion coefficient (for water at 80°C), respectively, $\lambda = 0.56$ Vt/(m·°C), $c_0 = 1250$ J/(kg·K), heat transfer coefficient $\alpha = 240$ Vt/(m^2·°C) [10, 21].

The resulting thermal diffusion coefficient is $a = \lambda/(c_0{\cdot}\rho) = 3.09\times10^{-7}$ m^2/s. The equivalent radius of elementary volume was calculated as follows:

$$R = r_1{\cdot}c^{-1/3} \tag{16}$$

Biot number $Bi = \alpha{\cdot}r_1/(\lambda{\cdot}c^{1/3})$.

The specific heat of sucrose crystallization was as in [13]: $Q_{sp} = 13.42$ kJ/mol (39.24 kJ/kg).

The numerical simulation was based on MATHCAD software.

Sum (13) was calculated based on (12)–(16) with the same four additive components, while the parameters of A_n and μ_n in (13) were based on the tables published in [20].

Temperatures T_0 and T_1 were 80°C all the time, which means that ΔT (9) = 0.

Figures 2 and 3 show the calculation results at the accepted values of the thermal process: volume concentration c of the solid phase in the solution, time τ, and temperature T on surface r_1 for model sucrose particle and mean massecuite temperature T.

Figures 2 and 3 show that the heat transfer into the sugar solution during crystallization of the model sucrose particle proceeded very quickly and took some thousandths of a second. That was why the thermal regime in the intercrystalline solution stabilized so quickly.

Figures 2 and 3 also demonstrate the same gradual exponential decrease in temperature, which is typical for heat transfer problems. If particles differed in radius by a factor of two, smaller particles with a larger specific surface area and a greater heat transfer cooled faster than particles with a larger radius. For curves 1 and 2, the temperature rise rate of the particles with radius $r_1 = 1\times10^{-5}$ m exceeded curves 3 and 4 for particles with a radius twice as large. The accumulation and release of heat for crystals with radius $r_1 = 2\times10^{-5}$ m was eight times bigger than those for crystals with a radius two times smaller. Figure 3 clearly demonstrates that curves 3 and 4 are much higher than curves 1 and 2.

CONCLUSION

The equation of non-stationary Fourier diffusion with initial and boundary conditions of the third kind was applied to calculate the endogenous heat released into the solution during the condensation of sucrose molecules on a spherical particle of a sucrose crystal in a supersaturated sugar solution.

The numerical study involved conditions close to the actual sucrose crystallization process in a vacuum boiling pan. It revealed an increase in temperature as a result of the phase transition from 80 to 86°C in 2×10^{-3} s, which means the process was almost instantaneous. The calculations were confirmed in practice. The results can facilitate calculating the effect of temperature on massecuite viscosity, wash water temperature, and other characteristics of massecuite vacuum processing in the sugar and starch industries.

CONTRIBUTION

E.V. Semenov and A.A. Slavyanskiy supervised the project. D.P. Mitroshina and N.N. Lebedeva performed the experiments.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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