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THE INFLUENCE OF THE FREEZING STAGE ON TRANSPORT PROPERTIES AND DRYING PROCESS

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Abstract: In this paper the freeze-drying is analyzed under the viewpoint of the relationship between process conditions, transport properties and drying rate. The understanding of the fundamental phenomena involved in this complex process allows efficient process optimization.

1. INTRODUCTION

In the food industry, it is used to dry a wide range of products, including dairy products, meats, coffee and vegetables and is enjoying a recent burst of popularity due to the success of break-fast cereals containing freeze-dried fruits, high quality freeze dried ingredients for inclusion in dried ready meals, milk, dried soups, bakery products, snacks, fruits, etc.

Some other advantages of freeze-drying are protection against chemical decomposition, minimum loss of activity due to low processing temperatures, and reduction of the moisture content to very low levels.

The fundamental stages of the lyophilisation are: *freezing, primary and secondary drying.* The freezing step influences the process to a large extent: morphology and ice crystal distribution, shape and pore connectivity, which will limit or enhance internal mass transfer during the subsequent drying.

2. THE INFLUENCE OF THE FREEZING STAGE ON TRANSPORT PROPERTIES AND DRYING PROCESS

The freezing stage represents the first separation step in the freeze-drying process, and the performance of the overall freeze-drying process depends significantly on this stage. The relationships among the freezing condition, structure and transport properties (thermal conductivity and permeability) of the dried layer are fundamental information to design the optimum drying cycle and control the quality of final products.

The quality of the final freeze-dried product is greatly influenced by the freezing process. For instance, the freezing process controls the color and the flavour of freeze-dried coffee extract or retention of volatile compounds. Proteins cells, subjected to freeze-drying, can be damaged during the freezing process already.

One important goal of the freezing step is to produce a uniform product batch, which is difficult because of the stochastic nature of nucleation. The degree of super-cooling, defined as the difference between the equilibrium freezing point and the temperature at which ice crystals first form, is both a statistical or random event as well as one that depends on the solution properties and process conditions. The degree of super-cooling is important because it determines the number of nuclei at any time, and thus determines the number of ice crystals formed. More ice crystals from the same amount of water means smaller crystals, which means smaller pore size and thus longer primary drying time. Nucleation rates increases rapidly with the degree of super-cooling, yielding ice crystal sizes that are inversely proportional to the degree of super-cooling. Thus, as super-cooling is increased, the resulting increases in nucleation rate cause the ice crystal particle size distribution to shift to smaller sizes.

A large portion of most freezing processes used in freeze-drying may be regard as directional solidification, i.e. the growth direction of the solidification interface is opposite to the main heat flow direction. The solidification pattern is governed by two parameters: velocity of solidification interface general case and mean temperature gradient at the interface ice-liquid interface in the direction of ice finger growth.[10] A complete description of the geometric form of dendrites or cells in freezing aqueous solutions is difficult to achieve because of complexity of the theoretical models.

3. EFFECTS OF STRUCTURAL PARAMETERS ON TRANSPORT PROPERTIES AND DRYING RATE

The transport properties, such as *the thermal conductivity and the permeability*, have a great influence on the processing factors, and finally on the drying rate. Various methods, both transient and steady state, have been proposed to determine the transport properties of freeze dried food, the latter gives better accuracy.

To analyze the effects of the structural parameters on transport properties and drying rate, one physical and mathematical model is necessary.

To this end, let consider a material to be dried on a tray (Fig. 1). The thickness of the sides and bottom of the tray is small and thermal conductivity of the material of tray is high, such that the resistance of the tray to the heat transfer could be considered negligible. As a result, the temperature of the tray can be considered equal with the temperature of the heating plate.

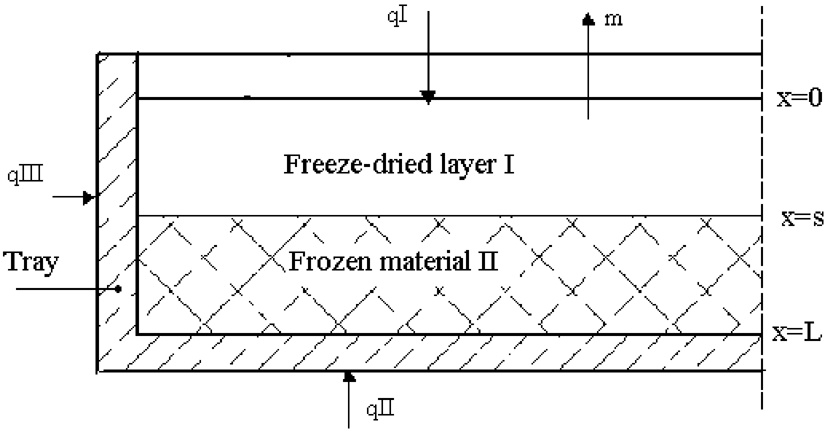

Fig. 1- Drying of the material in a tray

Heat q_I could be supplied to the material by conduction, convection and /or radiation.

The heat q_{II} is supplied by a heated plate and is conducted through the bottom of the tray to the material. The heat q_{III} represents the amount of heat transferred between the environment in the drying chamber and the vertical sides of the tray. The contribution of the q_{III} is negligible when compared to the contribution of q_I and q_{II}.

The study of the freeze-drying can be done in the following cases (Fig.):

1. $q_I \neq 0$ and $q_{II} = 0$,
2. $q_I = 0$ and $q_{II} \neq 0$ and

$q_I \neq 0$ and $q_{II} \neq 0$.

The transport properties of the dried layer were determined by applying the drying data to a model based on heat and mass transport in a sample, and then the effects of processing parameters on transport properties and drying rate in connection with the freezing operations.

The sample is assumed to have the geometry of a semi-infinite slab dried layer is separated from the frozen layer by an infinitesimal sublimation interface retreating uniformly from the sample surface. The bottom of the sample is insulated while the surface is exposed to an evacuated space at the temperature θ_s and pressure p_s. Since the thermal conductivity of the frozen layer is 20 - 50 times greater than that of the dried layer, the temperature of the frozen layer can be supposed to be uniform and same as that of sublimation front.

An approximate method was developed for predicting the structural parameters of the dried layer by assuming this layer to be a bundle of capillary tubes with the pore space having an equivalent pore radius, porosity and tortuosity factor.

The expression of the rate of heat transfer across the dried layer according to Massey and Sunderland,[45] is:

$$\dot{q} = \frac{\lambda}{m(t)}(\theta_s - \theta_f) - \dot{m}\int_{\theta_f}^{\theta_s} c_p d\theta \tag{1}$$

The mass flux may be expressed as

$$\dot{m} = \frac{KM_w}{RT} grad.p \tag{2}$$

Equations representing the thermal conductivity *k* and permeability *K* are presented by Sagara[44] and expressed as:

$$k = \alpha\rho_w l^2 (\Delta H + \int_{\theta_f}^{\theta_s} c_{pw} d\theta) \tag{3}$$

$$K = \beta\rho_w l^2 RT_f / M_w \tag{4}$$

where:

$$\alpha = \frac{1-m}{(\theta_s - \theta_f)(-dm/dt)} \tag{5}$$

$$\beta = \frac{1-m}{(p_s - p_f)(-dm/dt)} \tag{6}$$

The thermal conductivity was found to increase with increasing the solute concentration and is markedly affected by the porosity of the dried layer and the permeability was found to increase with pressure and temperature of the dried layer. This behavior is in good agreement with Mellor and Lovett's theoretical investigations[46] based on the collision theory, and also with their experimental results obtained for several kinds of solutions. The expressions for the permeability coefficient given by Mellor and Lovett are:

$$K = \frac{\varepsilon}{\tau} D_K \Omega \tag{7}$$

where:

$$\Omega = \frac{3\pi}{64}\frac{r}{\lambda} + \frac{\pi}{4}\frac{2r/\lambda}{(1+2r/\lambda))} + \frac{1}{1+2r/\lambda} \tag{8}$$

Ω indicates the contributions due to Poiseule`s flow, slip flow and Knudsen`s flow.
The mean free path of water vapor molecule λ is given by:

$$\lambda = \frac{\kappa \cdot T}{\sqrt{2} \cdot \pi\sigma_w^2 p} \tag{9}$$

and Knudsen diffusivity is defined in terms of the pore radius *r* and the average molecular velocity as follows

$$D_K = \frac{2}{3} vr \tag{10}$$

where:

$$v = \left(\frac{8RT}{\pi M_w} \right)^{1/2} \tag{11}$$

One can conclude that the transport properties mainly depend upon the structural nature of the dried layer and secondary on the operating factors such as pressure or temperature.

4 CONCLUSIONS

The freeze-drying is analyzed under the viewpoint of the relationship between process conditions, transport properties and drying rate.

Since a change in heat transfer has an effect on mass transfer and a change in pressure has an effect on heat transfer, the relationship between the two processes is quite complicated. Thus, differentiating between the two processes in order to determine which one is the limiting factor can be difficult.

The freezing process has a strong influence on the entire freeze-drying procedure.

The transport properties – conductivity and permeability - mainly depend upon the structural nature of the dried layer (porosity) and secondary on the operating factors such as pressure or temperature.

Modification of operative conditions for enhancing the transfer fluxes is used.

Process improvements can be obtained if an accurate interpretation of the phenomena involved is available.

Notation

c_p - specific heat at constant pressure, J/(kg K); D_K – Knudsen diffusion coefficient, m^2/s; k - thermal conductivity, W/(m K); K – permeability, m^2/s; l – thickness of slab, m; ΔH – latent heat of sublimation, J/kg; m – fraction of initial water still present in sample, (-); M_w – molecular weight of water vapor, kg/kmol; p – pressure, Pa; r - equivalent pore radius, m; R – universal gas constant, J/(mol K); t – time, s; T - Temperature, K; v – molecular velocity, m/s; X(t) – position of the sublimation front, (-); α - defined by equation (5); β - defined by equation (6); ε – porosity, (-); θ - temperature, °C; κ – Boltzman`s constant, J/kg; λ - mean free path of the gas molecules, m; ρ - density, kg/m^3; σ – molecular diameter of water vapor, m; τ – tortuosity factor, (-); Ω - defined by equation (8); *Subscripts:* f – sublimation front or interface;i – ice; s – exposed surface; w - water vapor

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