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A Mathematical Model for Freeze-Drying

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Abstract Based on the experiments on freeze-drying carrot and potato slabs, the effects of some parameters, such as heating temperature and pressure on the freeze-drying process are examined. A simple model of freeze-drying is established to predict drying time and the mass variations of materials during the drying. The experimental results agree well with those calculated by the model.
Keywords freeze-drying, model, heat and mass transfer

1 INTRODUCTION

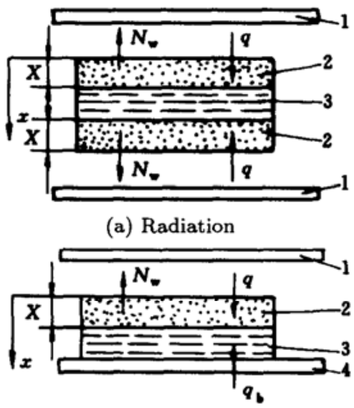
Freeze-drying is a dehydration process in which water is removed by sublimation from the frozen state. The major advantages of freeze-drying are less loss of flavor and aroma, keep the structural rigidity of product and maintenance of the initial shape and dimensions of the material being dried, and easy and rapid rehydration of freeze-dried products. It is useful for dehydration of biological materials, pharmaceuticals, biochemical products, foodstuffs, *etc.* However, freeze-drying is generally a slow and costly process because of the slow rate of drying under vacuum. Much attention has been paid to increase the rate and reduce the time of freeze-drying.

Many variables may affect freeze-drying process, so that experimental approach examining various operation policies is tedious, expensive, and time-consuming. Therefore, development of mathematical models for freeze-drying is desirable. King[1] postulated a uniformly retreating ice front (URIF) model for predicting the drying time for removal of the first 75%—90% of the moisture. Sheng and Peck[2] proposed a model that takes both free and bound water removal into account and gives good agreement with experimental data over the entire drying period. However, it can only be used for the processes with constant surface and interfacial temperature and controlled by heat transfer. Liapis and Litchfield[3] proposed a sublimation model which shows better agreement in predicting the time of free water removal than that by King[1], but it is suitable only for removing of free water too. Litchfield and Liapis[4] developed a sorption-sublimation model describing the whole drying process, in which desorption and sublimation are taken place simultaneously. However, because of the difficulty in obtaining the absorption equilibrium data, the model is not convenient to use in most cases.

The purpose of this paper is to develop a simplified model for freeze-drying and to investigate the effects of temperature and pressure. Experiments are carried out using carrot and potato in that their transport properties can be easily obtained with large sample.

2 MODEL

In almost all freeze-drying processes, the materials to be dried are made into chips or thallus. In the period of sublimation drying the moving interface comparts the material into dried and frozen zones. The heat to sublime ice must be transferred to the frozen zone across the dried material with increasing thickness, while the water vapor generated must be transferred out across this layer, as shown in Fig. 1.



(a) Radiation

(b) Mixing heating

Figure 1 Model of freeze-drying
1—radiation plate; 2—dried zone;
3—frozen zone plate; 4—steel plate

When the temperature in the drying layer is raised, the bound water is desorbed. As the interface disappears, the sublimation drying process ends and the desorption drying process starts until the drying layer reaches a set temperature. The following assumptions are made in developing of the mathematical model:

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(1) The heat and mass flows are both one-dimensional;

(2) Sublimation occurs at an interface, and the thickness of the interface is infinitesimal;

(3) At the sublimation interface, the concentration of water vapor is in equilibrium with the ice;

(4) The frozen zone is homogeneous, and contains an insignificant proportion of dissolved gases;

(5) In the drying layer, the solid matrix and the enclosed gases are in thermal equilibrium;

(6) All gases in the drying layer are ideal gases because of the low pressure;

(7) The heat of sublimation is identical to the heat of desorption at a constant value;

(8) The flux of water passing through the drying layer is constant.

According to the conservation of mass and energy, the following differential equations can be derived. In the drying layer

$$\frac{D_{\rm e}}{RT}\frac{\partial^2 p_{\rm w}}{\partial x^2} = \frac{\varepsilon}{RT}\frac{\partial p_{\rm w}}{\partial t} - C_{\rm H}\frac{\partial T}{\partial t} \qquad (1)$$

$$N_{\rm w} = -\frac{D_{\rm e}}{RT}\frac{\partial p_{\rm w}}{\partial x} \qquad (2)$$

$$k\frac{\partial^2 T}{\partial x^2} - N_{\rm w}c_{p,\rm w}\frac{\partial T}{\partial x} = (c_{\rm s}c_{p,\rm s} + \Delta H_{\rm s}C_{\rm H})\frac{\partial T}{\partial t} \qquad (3)$$

$$C_{\rm H} = -\frac{\partial c_{\rm sw}}{\partial T} \qquad (4)$$

In the frozen zone

$$-\frac{\partial q_{\rm b}}{\partial x} = \frac{\partial(\rho_{\rm b}h_{\rm b})}{\partial t} \qquad (5)$$

Since there is little change in the temperature in the frozen zone, the physical properties of the frozen zone can be considered independent of time. Therefore, Eq. (5) is redacted to

$$\partial q_{\rm b}/\partial x = 0 \qquad (6)$$

In the interface

$$-k\frac{\partial T}{\partial x} + k_{\rm b}\frac{\partial T_{\rm b}}{\partial x} + N_{\rm w}\Delta H_{\rm s} = V\rho_{\rm s}(c_{p,\rm s}T - c_{p,\rm b}T_{\rm b}) \qquad (7)$$

$$V = \frac{\partial X}{\partial t} = \frac{N_{\rm w}}{\rho - \rho_{\rm b}} \qquad (8)$$

Boundary conditions are

$$q = \varepsilon\sigma\left[\left(\frac{T_{\rm h}}{100}\right)^4 - \left(\frac{T_{\rm s}}{100}\right)^4\right] \quad x = 0 \qquad (9)$$

$$q_{\rm b} = const. \quad x = X \qquad (10)$$

Initial conditions

$$T = T_{\rm b} = T_{\rm X} = T^0(x) \quad t \leqslant 0 \qquad (11)$$

$$p_{\rm w} = p_{\rm w,o} \quad x = 0, \quad t > 0 \qquad (12)$$

$$p_{\rm w} = p_{\rm w}^0 \quad 0 < x \leqslant X_{\rm T}, \quad t \leqslant 0 \qquad (13)$$

Eqs. (1)—(6) together with the boundary and initial conditions, Eqs. (7)—(13), are non-linear, so that an analytical solution is not obtainable. In order to use the method of Crank-Nicholson to obtain a numerical solution, the moving boundary of the system must be immobilized using the two dimensionless variables

$$\xi = \frac{x}{X} \qquad 0 \leqslant x \leqslant X \qquad (14)$$

$$\phi = \frac{x - X}{X_{\rm T} - X} \qquad X < x < X_{\rm T} \qquad (15)$$

With transformation by the two dimensionless variables, Eqs. (1)—(3) become

$$\left(\frac{\partial p_{\rm w}}{\partial t}\right)_\xi = \frac{C_{\rm H}}{X}\left(\frac{\partial T}{\partial \xi}\right)_t + \frac{\xi}{X}\frac{{\rm d}X}{{\rm d}t}\left[\left(\frac{\partial p_{\rm w}}{\partial \xi}\right)_t - \left(\frac{\partial T}{\partial \xi}\right)_t\right] - \frac{RT}{\varepsilon X}\left(\frac{\partial N_{\rm w}}{\partial \xi}\right)_t \qquad (16)$$

$$N_{\rm w} = -\frac{D_{\rm e}}{RTX}\left(\frac{\partial p_{\rm w}}{\partial \xi}\right)_t \qquad (17)$$

$$\left(\frac{\partial T}{\partial t}\right)_\xi = \frac{\alpha_{\rm e}}{X^2}\left(\frac{\partial^2 T}{\partial \xi^2}\right)_t - \frac{N_{\rm w}c_{p,\rm w}}{c_{\rm s}c_{p,\rm s} + \Delta H_{\rm s}C_{\rm H}}\left(\frac{\partial T}{\partial \xi}\right)_t + \frac{\xi}{X}\frac{{\rm d}X}{{\rm d}t}\left(\frac{\partial T}{\partial \xi}\right)_t \qquad (18)$$

The method of Crank-Nicholson is used in this work because it is superior to other methods in stability and execution time. The accuracy of the solution with 6 point's formula was found to be satisfactory. In order to shorten the execution time, two techniques are used: (1) All the variables at time n were defined by one new array; (2) The entire unknown arrays are substituted by the newest known arrays. The results show that the calculating process is predigested with the execution time about one third of that by the unreformed method.

It should be noted that some coefficients in the equations become infinite at X=0, so that a solution cannot be obtained. The initial time step size is constrained to be about 1/20 second, and the initial value of the interfacial position is about 5×10^{-4} m for stability of the numerical solution.

3 EXPERIMENTAL

Low-pressure freeze-drying experiments are conducted in an apparatus shown in Fig. 2. The apparatus, a pilot apparatus designed for this work, allows the system pressure to be controlled of from 5 Pa to 2000 Pa, measured by a Pirani vacuum meter. The temperature of the heating plates can be adjusted from 30℃

to 80℃, as determined by thermocouples of copper-constantan. The weight loss during drying was determined by an electron-balance.

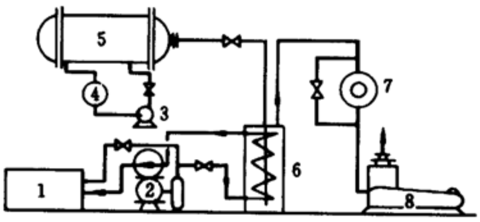


Figure 2 Schematic diagram of freeze drier
1—freezing chamber; 2—freezer; 3—oil pump; 4—tank of oil; 5—drying chamber; 6—condenser; 7—lobe pump; 8—vacuum pump

Preparation of samples

The measurements are made on the carrot and potato slabs that are cut into 10-centimeter thickness. The copper-constantan thermocouple is threaded lengthways into the center of each slab. The samplers are frozen in a low-temperature freezer maintained below −40℃. When the temperature at the center reaches its crystal point, the samplers are transported into the vacuum drying chamber quickly. After the pressure in the chamber is controlled under 500 Pa, the temperature of the heating plates is increased till approaching a prescribed temperature. The physical properties for the carrot and potato slabs are shown in Table 1.

4 RESULTS

The central temperature profiles of the two materials are shown in Fig. 3. The weight-loss curves for drying in the presence of water vapor only are given in Fig. 4. Table 1 lists all parameters used in the simulations, with the calculated results appearing in Figs. 3 and 4. It may be noted that a good agreement exists between the simulation and experimental results. The agreement extends over the entire drying period. The drying time for carrot is longer than that for potato because of its higher contents of the bound water.

4.1 Effect of chamber pressure

When the pressures are lower than 350 Pa, the drying times become longer as shown in Fig. 5. This is because the effective thermal conductivity increases and the effective mass transfer coefficient decreases as the pressure increases. When the pressures are lower than 350 Pa and the heating temperatures (T_h) are lower than 320 K, the temperatures of the interface increase in sublimation process but do not exceed the melting point of the dried materials. Therefore, the driving force for mass transfer increases as the pressures increase, so that the rates of mass transfer increase in the sublimation process and the drying time becomes shorter. If the temperature of the interface is lower than the melting point of the dried materials, the process is controlled by heat transfer. When the pressures are higher than 600 Pa, the interfacial temperature reaches quickly to the melting point. Under this condition, the driving force for mass transfer is unchanged, but the resistance to mass transfer increases as the thickness of the dried layer increases. Therefore, the rate of mass transfer decreases in the sublimation process and the drying time becomes longer. The process is controlled by mass transfer in this case in which the interfacial temperature approaches the melting point of the dried materials. It should be pointed out that there is an optimal pressure for radiation heating at which the drying time is the shortest, as indicated in Fig. 6. At a higher pressure, the drying time is longer for mixing heating as shown in Fig. 7 because the quantity of sublimation heat is supplied mainly by conduction from the frozen zone. The rate of heat conduction is enhanced by the higher pressures from the dried layer, but the water vapor cannot be escaped from the dried layer. Therefore it is desirable to keep the pressure at the lowest value possible for this system.

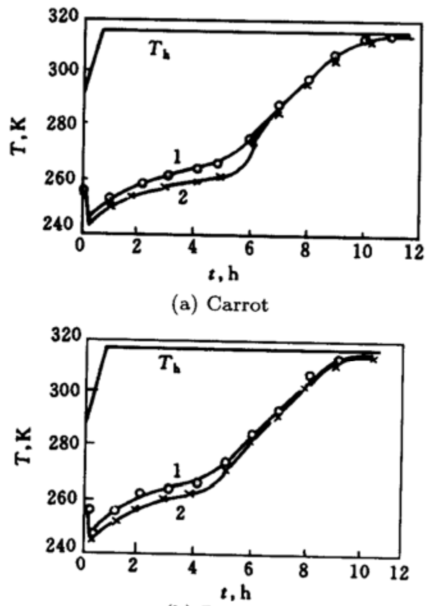


Figure 3 Curves of freeze-drying
1—centre temperature; 2—surface temperature; ○ × experimental; —simulating

Table 1 Model parameters and experimental conditions[7]

Material	T_h K	X_T m	T_c K	ρ_b kg·m^{-3}	ρ kg·m^{-3}	C_H kmol·m^{-3}·K^{-1}	K W·m^{-1}·K^{-1}	ΔH_v kJ·kg^{-1}	p Pa	p_{in} Pa	ε	D_e m^2·s^{-1}
Carrot	313	0.01	225	1013	320	0.2822	0.052	2791.2	100	0	0.80	4.92×10^{-5}
Potato	313	0.01	225	1106	245	0.2688	0.055	2791.2	100	0	0.79	5.97×10^{-5}

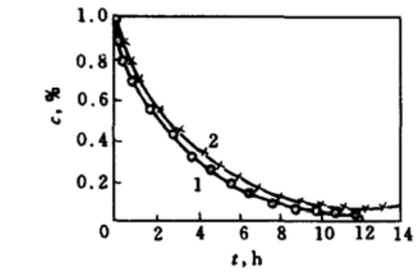


Figure 4 Water fraction *vs.* time plots
1—centre temperature; 2—surface temperature
○ × experimental; ——simulating

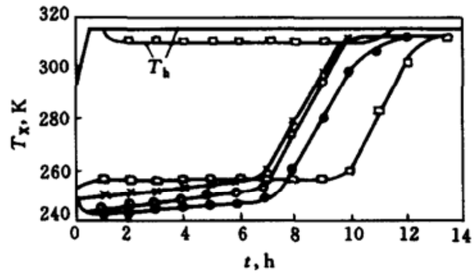


Figure 5 Freeze-drying of carrot in radiation
p, Pa: □ 600; × 350; ○ 100; ● 10

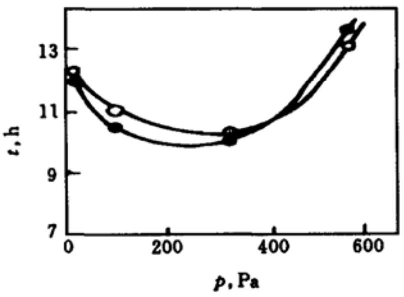


Figure 6 Effect of pressure on drying time in radiation
○ potato; ● carrot

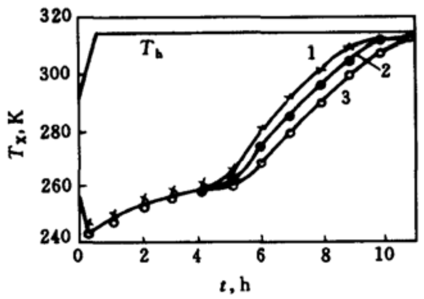
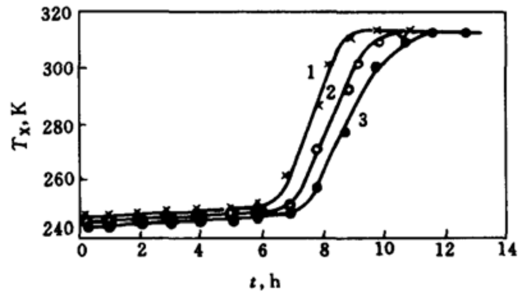


Figure 7 Freeze-drying of carrot in mixing heating
p, Pa: 1—10; 2—100; 3—200

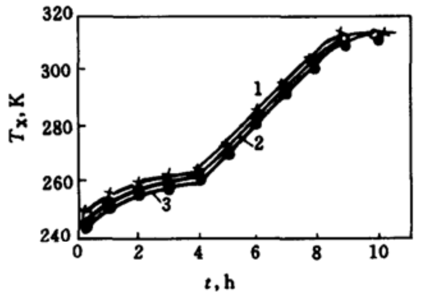
4.2 Effect of temperature of heating plates

The lower the temperature of the heating plates, the lower the temperature of the interface as shown in Fig. 8(a). Under this condition, the rate of mass transfer becomes smaller and the drying time becomes longer. The drying process is controlled by heat transfer, and therefore, it is feasible to increase the temperature of the heating plates as well as the flux of radiation heat.

The sublimation heat is supplied mainly from the frozen side, as shown in Fig. 8(b). Although the temperature is not high, it has reached the melting point of the dried materials toward the end of sublimation drying. Therefore the drying time can not be shortened by increasing temperature of the heating plates.



(a) Radiation heating



(b) Mixing heating

Figure 8 Freeze-drying of potato at different heating temperature
T_h, K: 1—325; 2—318; 3—313

5 CONCLUSIONS

A simple mathematical model for freeze-drying has been developed. The model permits the sublimation and adsorption to take place simultaneously. The experimental results agree well with those calculated by the model, so it is possible to predict the overall drying time accurately by the mathematical model.

For radiation heating, it is feasible to adopt a higher temperature of the heating plates at an optimal pressure. For mixing heating, it is desirable to maintain a low temperature of the heating plates with the pressure in the chamber kept at the lowest value.

NOMENCLATURE

C_H	parameter of bound water, kmol·m^{-3}·s^{-1}
c	mass fraction of water, %
c_p	heat capacity, kJ·kg^{-1}·K^{-1}
c_s	volumetric mass fraction of dried material, kg·m^{-3}
D_e	overall mean diffusivity, m^2·s^{-1}
ΔH_s	enthalpy of sublimation of freeze water, kJ·kg^{-1}
ΔH_v	enthalpy of vaporization of combined water, kJ·kg^{-1}
h_b	enthalpy of liquid of ice, kJ·kg^{-1}
k	thermal conductivity of drying layer, W·m^{-1}·K^{-1}

k_b thermal conductivity of frozen layer, $W\cdot m^{-1}\cdot K^{-1}$
N_w water vapor flux, $kg\cdot m^{-2}\cdot s^{-1}$
p total pressure in drying layer, Pa
p_w partial pressure of water vapor, Pa
q radiant energy flux, $W\cdot m^{-2}$
q_b mixing energy flux, $W\cdot m^{-2}$
R universal gas constant, $J\cdot mol^{-1}\cdot K^{-1}$
T temperature in drying layer, K
T_b temperature in frozen layer, K
T_c temperature of condenser, K
T_h temperature of plate, K
t drying time, s
V velocity of moving interface, $m\cdot s^{-1}$
X position of frozen interface, m
X_T thickness of dried material, m
x distance, m
α_e thermal diffusivity in drying layer, $m^2\cdot s^{-1}$
ε voidage fraction
ξ defined in Eq. (14)
ρ density of drying layer, $kg\cdot m^{-3}$
ρ_b density of frozen layer, $kg\cdot m^{-3}$
σ Stefan-Boltamann constant, $W\cdot m^{-2}\cdot K^{-4}$
ϕ defined in Eq. (15)

Superscripts

0 saturation value

Subscripts

b frozen layer
e effective
g gas
h heat
o initial
s surface
w water vapor
X interface

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