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커피추출액의 냉동건조

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Freeze-drying of Coffee Extracts

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요 약

커피추출액을 시료로 하여 일정한 모델을 설정한 후, 건조속도로부터 유효확산 계수를 구하고, 냉동속도와 시료의 농도 그리고 압력이 건조속도에 미치는 영향을 조사하였다. Slush freezing을 한 시료는 건조할때 20~60 cm^2/sec의 유효확산계수를 나타냈고, 완만냉동을한 경우는 20~10 cm^2/sec, 그리고 급속냉동을 한 경우는 5~16 cm^2/sec을 나타냈다. Slush freezing과 완만냉동을 할때는 주로 bulk diffusion 에 의해 건조되고 급속냉동을 할때는 주로 Knudsen diffusion에 의해 건조되는 것으로 관찰되었다.

Abstract

An experimental investigation of freeze-drying of coffee extract is presented. Effects of freezing rate, concentration and pressure on the drying rate are determined and the results compared with a theoretical model, which expresses the drying rate in terms of the effective diffusivity of the material. The effective diffusivity of the coffee extract was found to be in the range of 20-60 cm^2/sec for slush freezing, 20-40 cm^2/sec for slow freezing, and 5-16 cm^2/sec for fast freezing. The mechanism of water vapor transport appeared to be mainly the bulk diffusion in the slow or slush freezing, and the Knudsen diffusion in the fast freezing.

1. Introduction

Freeze-drying process removes water in various foods by sublimation. This contrasts with the more conventional drying by heat, e. g. spray drying, sun drying and vacuum drying, in which liquid water is vaporized.[1-6] A freeze-dried food in general is superior in quality to a heat-dried one. This is probably because a frozen surface can maintain its shape while sublimation occurs on it. The freeze-drying method is advantageous in that the processing temperature is low, the liquid water practically absent, and the rate of dehydration fairly rapid. The low temperature, in particular, lessens the loss of volatile flavor and fragrance.

Despite the potential superiority mentioned in the above, the freeze-drying is still an expensive and slow process.[6-8] Good engineering design for faster drying rates is prevented by lack of fundamental understanding of relevant heat and mass transfer properties and their correlation with the rate of freezing or drying.[1,4,9] In this work, we investigate the freeze-drying of coffee extract. Experiments are designed to test a model, which relates the transport properties and the rate of freezing to the rate of drying.

2. Theory

Since the transfer of heat and mass determines the rate of drying, these two constitute the major consideration. Heat can be supplied to a material by radiation,[9] conduction,[7] convection[10] or even dielectric heating.[11] When a low pressure (usually 0.1 to 1.0 mmHg), instead of an inert gas, is employed in freeze-drying, one can safely ignore the heat transfer by convection mechanism. Similarly the mass transfer mechanism includes diffusion, hydronamic or slip flows.[3,5,8,12]

When the heat is transferred only by conduction across the frozen layers, we formulate a model based on the following assumptions:

1. Ice front retreats uniformly.[7,8]
2. One-dimensional heat and mass transfer.
3. Homogeneous and isotropic solution.
4. No heat transfer on the surface of the drying material.
5. Constant-temperature heat source.
6. Pseudo-steady heat and mass transfer.
7. Drying rates measured in the presence of water vapor.

The model based on these assumptions is depicted in *Fig.* 1.

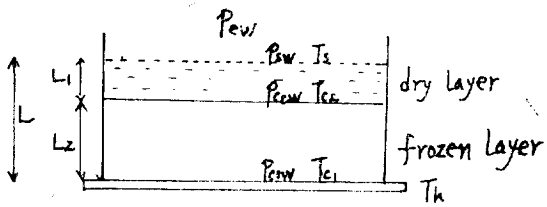


Fig. 1. Model.

The heat flux necessary to sublimate the ice can be expressed as

$$q=h(T_h-T_{c1})=\frac{K_f}{l_2}(T_{c1}-T_{c2})=\frac{T_h-T_{c2}}{\frac{1}{h}+\frac{l_2}{K_f}}=\frac{T_h-T_{c2}}{\frac{1}{h}+\frac{Lx}{K_f}} \qquad (1)$$

Similarly the mass flux can be expressed by the following equations:

$$N_w=\frac{D_e}{RT}\frac{(P_{c2w}-P_{sw})}{l_1}=\frac{K_c^*}{RT}(P_{sw}-P_{ew})=\frac{P_{c2w}-P_{ew}}{\left(\frac{l_1}{D_e}+\frac{1}{K_c^*}\right)RT}=\frac{P_{c2w}-P_{ew}}{\left[\frac{(1-x)L}{D_e}+\frac{1}{K_c^*}\right]RT} \qquad (2)$$

The drying rate $(-dx/d\theta)$ can be related to the heat and mass transfer rate equations as

$$N_w=\frac{P_{c2w}-P_{ew}}{\left[\frac{(1-x)L}{D_e}+\frac{1}{K_c^*}\right]RT}=\frac{L\rho}{18}(1-w)\left(-\frac{dx}{d\theta}\right) \qquad (3)$$

If the sensible heat is negligible in comparison to the latent heat and the temperature of the sublimation front does not change rapidly,

$$q=N_w\,\Delta H_s$$

thus

$$q=\frac{T_h-T_{c2}}{\frac{1}{h}+\frac{Lx}{K_f}}=\frac{L\rho(1-w)}{18}\left(-\frac{dx}{d\theta}\right)\Delta H_s \qquad (4)$$

Equations (3) and (4) may be rearranged to a form suitable for testing drying rate data consistent to this model and also suitable for deriving the transport coefficient from the drying rate data.

$$1-x=\frac{18D_e}{L^2RT\rho(1-w)}\left[\frac{P_{c2w}-P_{ew}}{\left(-\frac{dx}{d\theta}\right)}\right]-\frac{D_e}{K_c^*L} \tag{5}$$

$$x=\frac{18K_f}{L^2\Delta H_s\rho(1-w)}\left[\frac{T_h-T_{c2}}{\left(-\frac{dx}{d\theta}\right)}\right]-\frac{K_f}{hL} \tag{6}$$

If this mathmatical model is valid, the plot of $(1-x)$ *vs.* $(P_{c2w}-P_{ew})/\left(-\frac{dx}{d\theta}\right)$ should be linear with a slope $(18\ D_e/L^2RT\rho\ (1-w))$ and an intercept $(-D_e/K_c^*L)$. Also the plot of x *vs.* $(T_h-T_{c2})/\left(-\frac{dx}{d\theta}\right)$ should be linear with a slope $(18K_f/L^2\Delta H_s\rho\ (1-w))$ and an intercept $(-K_f/h\cdot L)$. From these, D_e, K_c^*, and K_f can be determined.

If (T_h-T_{c2}) and $(P_{c2w}-P_{ew})$ are constant, Eqs. (5) and (6) may be integrated to give;

$$\theta=\frac{L^2RT\rho(1-w)}{18D_e(P_{c2w}-P_{ew})}\left[\left(1+\frac{D_e}{K_c^*L}\right)(1-x)-\frac{1}{2}(1-x)^2\right] \tag{7}$$

$$\theta=\frac{L^2\Delta H_s\rho\ (1-w)}{18K_f\ (T_h-T_{c2})}\left[\frac{K_f}{hL}(1-x)+\frac{1}{2}(1-x)^2\right] \tag{8}$$

Since in practice the amount of bound water is negligible compared to that of free water, the drying time can be determined by putting $x=0$ into Eqs. (7) and (8): i. e.,

$$\theta_p=\frac{L^2RT\rho\ (1-w)}{18\ D_e(P_{c2w}-P_{ew})}\left(\frac{1}{2}+\frac{D_e}{K_c^*L}\right) \tag{9}$$

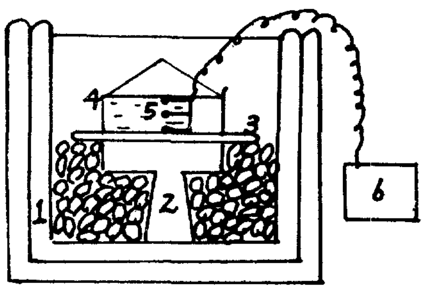
$$\theta_p=\frac{L^2\Delta H_s\rho\ (1-w)}{18K_f(T_h-T_{c2})}\left(\frac{1}{2}+\frac{K_f}{hL}\right) \tag{10}$$

3. Experimental

The concentration of coffee extracts used in the freeze-drying experiment was in the range of 20-30%. The vacuum in the drying chamber ensures that the suspended sample is uniformly heated only by conduction. The chamber itself consists of a vertical glass tube, L. 120 cm and I. D. 8 cm, with a 2 cm thick glass wool insulation. We could evacuate the chamber down to about 0. 2 Torr in 10 minutes with a Duo-Seal oil diffusion vacuum pump, used in conjunction with an acetone-dry ice cold trap. The pressure was kept constant ($<$ 1 Torr) by use of a manostat,[13-15] and measured with a MacLeod gauge and a Geisler tube.

The heat source was a hot plate, whose temperature, variable in the range of 20-30°C, was kept constant by a Gardesman by Weston controller.[16] Weight changes in the sample were periodically measured with a Cathetometer (Guk Dong Scientific Works) within ±0. 05mm. To keep the heat and mass transfer one-dimensional, the vertical side of the sample case was wrapped with a Teflon tape.

The freezing rates were measured by observing the temperature changes at the center of the frozen samples periodically with thermistors which had an accuracy of ±0. 005°C.



1. Dry ice
2. Aluminum rod
3. Copper plate
4. Sample dish
5. Thermistor
6. Precision thermometer

Fig. 2. Freezing apparatus.

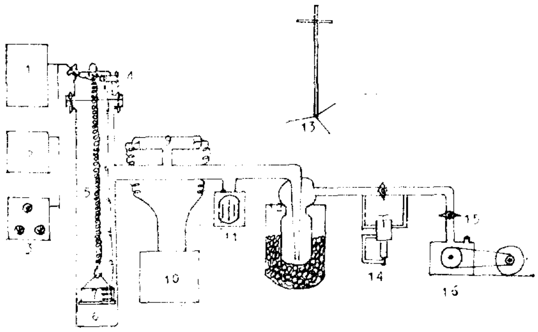
The freezing methods employed were;[17]

Slow freezing: Conduction freezing at −20°C and then solidifying it completely at −60°C (freezing rate: 0. 3°C/min to 0. 5°C/min)

Slush freezing: conduction freezing at −20°C with intermittent manual agitation and then solidifying it completely at −60°C

Fast Freezing: conduction freezing at −60°C with dry ice-ethanol (freezing rate: 8°C/min).

After freezing at different rates, the frozen samples were freeze-dried at various process conditions; the pressure (0.1 to 1 Torr) and temperature of the heating source (20°C to 30°C). As drying proceeded, the surface temperature, the center temperature, and the bottom temperature of the samples were recorded periodically with thermistors. The changes of weight were also read periodically by using a spring balance. About 50 drying curves were obtained under various conditions.



1. Controller
2. Slidac
3. Precision thermometer
4. Screw bolt
5. Drying chamber
6. Heating plate
7. Sample
8. Thermistor
9. Geisler tube
10. Neon transformer
11. MacLeod gauge
12. Cold trap
13. Cathetometer
14. Menostat
15. Leak Valve
16. Oil diffusion vacuum pump

Fig. 3. Freeze-drying apparatus.

4. Results and dicussions

(1) General

A typical drying cycle was illustrated in *Fig.* 4. T_{c1} was assumed equal to T_{c2} based on the experimental observations. The typical plots of Eqs. (5) and (6) are shown in *Fig.* 5 and *Fig.* 6 from *Table.* 1. If this model is applicable, a linear relationship should be

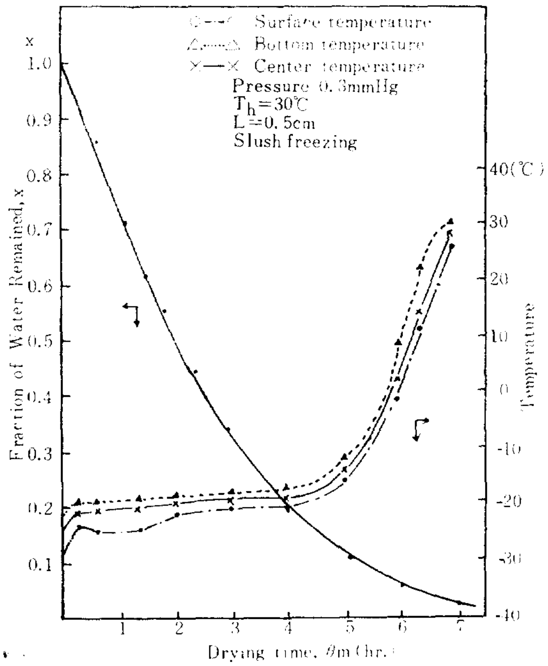


Fig. 4. Typical freeze-drying curve.

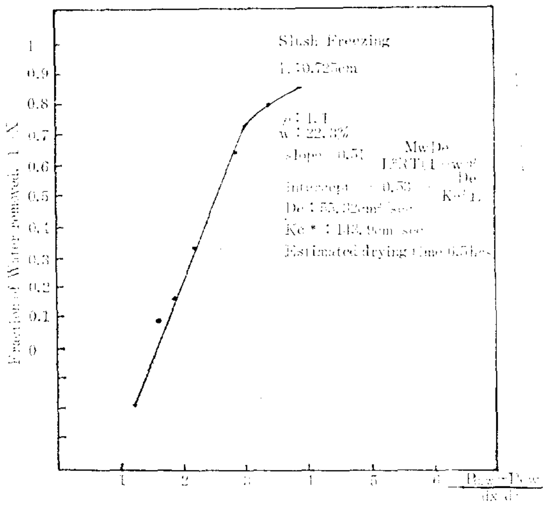


Fig. 5. Relation between fraction of water removed and mass transfer coefficient.

Table 1. Typical calculation.

	Drying time	Water cont. remained	Water cont. remained	Driving force for Mass Transfer	Drying rate	Driving force for Heat Transfer	$\frac{Pc_2w-Pew}{-\frac{dx}{d\theta}}$
Freezing	θ	x	$1-x$	Pc_2w-Pew	$-\frac{dx}{d\theta}$	T_h-Tc_2	
Fast F	0.5	0.91	0.09	0.70-0.3	0.150	30-(−21)	2.67
	1	0.83	0.17	0.75-0.3	0.154	30-(−20)	2.92
	2	0.70	0.30	1.25-0.3	0.150	30-(−15)	6.333
	3	0.58	0.42	1.25-0.3	0.114	30-(−15)	8.333
	4	0.47	0.53	1.25-0.3	0.100	30-(−15)	9.50
	5	0.37	0.63	1.25-0.3	0.09	30-(−15)	10.6
	6	0.28	0.72	3.0-0.3	0.082	30-(− 5)	32.9
	7	0.21	0.79	4.6-0.3	0.072	30	59.7
	8	0.15	0.85	5.0-0.3	0.061	30-5	77.1
	9	0.09	0.91	9.2-0.3	0.050	30-10	178
	10	0.05	0.95	12.8-0.3	0.038	30-15	329
	θ	x	$1-x$	Pc_2-Pew	$-\frac{dx}{d\theta}$	T_h-Tc_2	$\frac{Pc_2w-Pew}{-\frac{dx}{d\theta}}$
Slush F	0.5	0.92	0.08	0.56-0.3	0.16	30-(−23.5)	1.625
	1	0.84	0.16	0.60-0.3	0.16	30-(−22.5)	1.88
	2	0.67	0.33	0.64-0.3	0.155	30-(−22)	2.19
	3	0.52	0.48	0.64-0.3	0.15	30-(−22)	2.27
	4	0.36	0.64	0.64-0.3	0.12	30-(−22)	2.83
	5	0.21	0.79	0.64-0.3	0.10	30-(−22)	3.33
	6	0.12	0.88	3.0-0.3	0.08	30-(−5)	35.1
	7	0.06	0.94	3.5-0.3	0.05	30-(−3)	69.6
	8	0.02	0.98	4.93-0.3	0.03	30-1	165.4
	9	0.01	0.99	7.51-0.3	0.02	30-7	451
	10	0.005	0.995	15.5 -0.3	0.01	30-18	2083

obtained.

As shown in the figures, the experimental data gave rise to a good linearity in the range of $(1-x)$ from zero to 0.7.

It may be noticed that the data from slush freezing case are fairly consistent with the present model.

During drying, a dry crust formed gradually at the surface of the sample. The dry crust actually slowed down the process by impeding the flow of vapor from the inner ice front. The dry crust had little effect on slush freezing owing to the agitation; the effective diffusivity of the dry layer with slush freezing was higher than those obtained with other freezing method. (cf. *Fig.* 7)

As mentioned above, the model does not fit to the data from slow freezing and fast freezing as well as in the case of slush freezing. This may be attributed to the following reasons:

1) In slow freezing and fast freezing, the dry crust formed at the surface during drying was the mass transfer barrier which impeded drying.
2) In fast freezing, the randomly distributed ice crystal gave rise to the different partial pressure of water vapor at the ice front owing to the heterogeneous property of the frozen material. Accordingly, there arose the non-uniform retreat of the ice front.

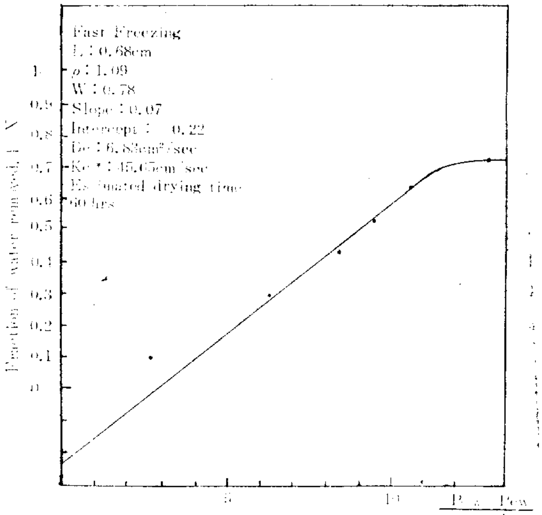


Fig. 6. Relation between fraction of water removed and mass transfer coefficient.

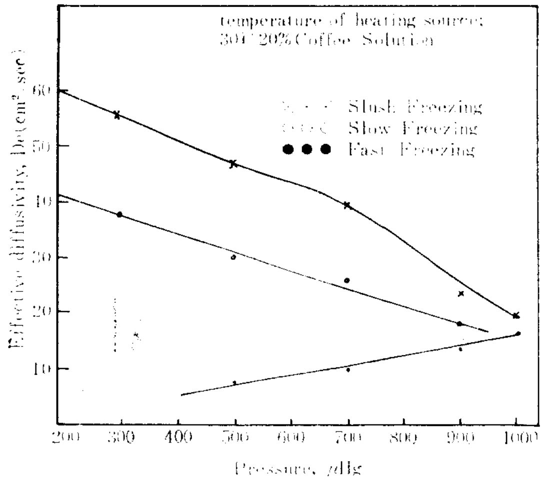


Fig. 7. Relation between the effective diffusivity and the pressure.

(2) Effect of the freezing rate

For 20%coffee extract, the solution began to freeze at $-2°C$. Freezing rates ranged from 0.3°C/min to 8°C/min. Observation through a reflection microscope revealed that fast freezing gave the formation of randomly distributed small ice crystals of size 10 micron whereas slow freezing gave the formation of large ice crystals.

The freezing conditions influenced the drying rates and the effective diffusivities were determined to be in the ranges of 20 to 60 cm^2/sec for slush freezing, 20 to 40 cm^2/sec for slow freezing, and 5 to 16 cm^2/sec for fast freezing, respectively.

(3) Effect of the sample thickness

After the frozen samples were dried, the plots of measured drying time *vs.* sample thickness revealed the following trend. (cf. *Fig.* 8)

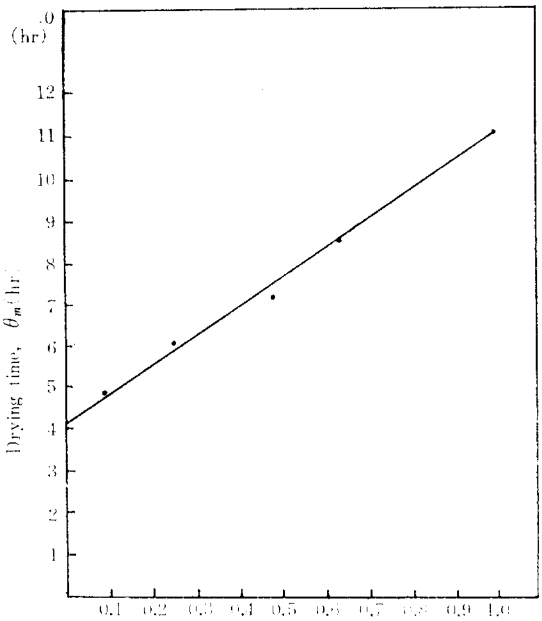


Fig. 8. Drying time *vs.* Sample Thickness; Slush Freezing; 20% Concentration.

From *Fig.* 8. measured drying time θ_m could be expressed by a quadratic equation of the sample thickness; i. e.,

$$\theta_m = \theta_e + CL^2$$

θ_e was considered as the sum of the equilibrium time at the beginning and the desorption time at the end of the drying cycle. This relation coincided well with the Eqs. (9) and (10).

(4) Effect of the temperature of heating source.

As heat was supplied through the frozen layer, there was little resistance to the heat transfer. But an increase in the temperature of the heating source raised the temperature of the frozen zone with a risk of partial melting. When it was increased beyond 35°C, the partial melting of the frozen layer took place. Foaming up or puffing of the sample surface was an evidence of the partial melting.

As the concentration of the coffee extracts increased, special care was needed in increasing the temperature of heating source because of the lower eutectic temperature of the solution.

(5) Effect of the sample concentration

The higher the initial solid content is, the denser the solid structure becomes and the smaller the freeze-drying rate is This implies a lower effective diffusivity of the dry layer. But it gave such a low eutectic temperature that it had to be dried at a low processing temperature to avoid the partial melting.[18]

In the solution of 20% soliod content, the values of effective diffusivity at the various chamber pressure varied in the range of 20 to 55 cm^2/sec (*Fig.* 9). In the 30% solution, however, they were almost uniform in the range of 20 to 23 cm^2/sec.

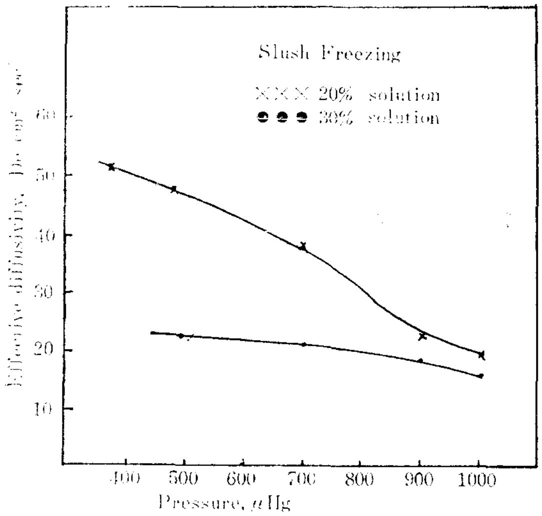


Fig. 9. **Effect of concentration on the effective diffusivity.**

(6) Effect of the operating pressure

At pressures higher than 4,519 μHg, liquid water can still exist. The pressure range from 0 to 4,519 μHg is the most favorable for freeze-drying.

As shown in *Fig.* 7, the effective diffusivities decreased with the pressure in case of slush freezing and of slow freezing. On the other hand, fast freezing gave the results less sensitive to the pressure. It was considered that for both the slush freezing and the slow freezing the water vapor in the dry layer would be mainly transferred by ordinary bulk diffusion but the fast freezing mainly by Knudsen diffusion. In the range of the experimental conditions, the mean free path of the water vapor in the dry layer is 10 to 18 μ.

(7) Comparison between the estimated drying time and the measured drying time

By using Eq. (10), the estimated drying time could be calculated from the effective diffusivity and the external mass transfer coefficient. As shown in *Table* 2, the measured drying time with slush freezing gave the agreeable results with the estimated drying time. But other freezing methods gave the irregular results and showed that the model was relatively inapplicable to the slow freezing and the fast freezing. For slush freezing, the measured drying time could be predicted to be about 1.3 times the estimated drying time; about 1.5 times for slow freezing; and about 1.7 times for fast freezing.

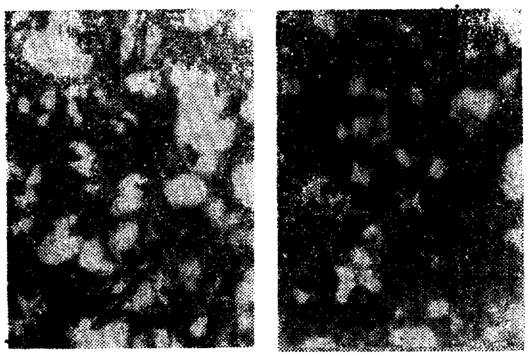
Table 2. Comparison between estimated and measured drying time.

P mmHg	T_h°C	L cm	Estimated drying time θ_m	Measured drying time θ_m	$\frac{\theta_m}{\theta_p}$	Freezing
0.5	25	0.70	6.05	7.5	1.24	Slush Freezing
0.3	30	0.70	6.77	7.5	1.11	〃
0.3	30	1.15	11.7	13.5	1.15	〃
0.3	27	0.64	4.65	7.0	1.50	Slow Freezing
0.3	30	0.45	5.30	7.0	1.32	〃
0.4	30	0.85	6.95	11.5	1.65	Fast Freezing
0.2	20	0.65	5.72	8.0	1.39	〃
0.3	30	0.68	5.97	7.5	1.26	〃
0.3	30	0.85	7.61	11.0	1.39	〃
0.4	30	0.80	7.50	11.0	1.33	〃
0.3	27	0.70	4.87	8.0	1.64	〃

(8) Microphotography of the Freeze-dried sample

After the drying precess was over, the freeze-dried samples were sliced with a razor blade to investigate the internal structure, so to speak, the pore structure and then were microphotographed (cf. *Fig.* 10).

(I) (II)



I; 30% Coffee extract slowly frozen

II; 30% Coffee extract fast frozen

Fig. 10. Microphotographs of the internal structure of freeze-dried coffee (Magnification 300).

The freeze-dried coffee was so hygroscopic that it had to be rapidly sliced and photographed. As shown in *Fig.* 15, slow freezing resulted the larger mean pore size than that resulted from fast freezing. It was considered that the significant increase in the volume of the ice during sublimation (10^6 times at $p=0.1$Torr) results in an explosive phenomenon involving a molecular shock wave. Therefore, the pore structure after drying was different from the ice crystal formed during freezing.

5. Conclusions

(1) Expressions for the estimated drying time was derived for the case of conduction heating

$$\theta_p = \frac{L^2RT\rho(1-w)}{18\ De\ (P_{c2w}-P_{ew})}\left(\frac{1}{2}+\frac{De}{K_c^*L}\right)$$

$$\theta_p = \frac{L^2\Delta H_s\rho(1-w)}{18K_f(T_h-T_{c2})}\left(\frac{1}{2}+\frac{K_f}{hL}\right)$$

(2) Slush freezing gave the result which agreed well with the model in coffee extract.

(3) The measured drying time can be expressed by a quadratic equation of the sample thickness in case of slush freezing.

(4) Under the experimental conditions, effective diffusivities were measured to be in the range of 20 to 60 cm^2/sec for slush freezing, 20 to 40 cm^2/sec for slow freezing, and 5 to 16 cm^2/sec for fast freezing, respectively.

(5) For both the slush freezing and the slow freezing, the water vapor appears to be mainly transferred by bulk diffusion but for the fast freezing mainly by Knudsen diffusion.

Nomenclature

D_e	effective diffusivity of water vapor in the dry layer, cm^2/hr.
h	heat transfer coefficient between the heating plate and the bottom of the frozen layer, cal/cm^2 hr °C.
ΔH_s	latent heat of sublimation, 12168 cal/g mole at-20°C.
K_c^*	external mass transfer coefficient, cm/hr.
K_f	thermal conductivity of the frozen layer, cal/cm hr °C.
L	sample thickness ($=l_1+l_2$), cm.
l_1	thickness of the dry layer, cm.
l_2	thickness of the frozen layer, cm.
N_w	mass flux of water vapor, g $mole/cm^2$ hr.
P_{c1w}	partial pressure of the water vapor in equilibrium with T_{c1}, mmHg.
P_{c2w}	partical pressure of water vapor in equilibrium with T_{c2}, mmHg.
P_{ew}	partical pressure of water vapor in vacuum chamber, mmHg.
P_{sw}	partial pressure of water vapor at the surface, mmHg.
q	heat flux, cal/cm^2 hr.
R	gas constant, mmHg cm^3/g mole °K.
T_{c1}	temperature of the bottom of the frozen material, °C.
T_{c2}	temperature of the ice front, °C.
T_h	temperature of the heating source, °C
T_s	temperature of the surface of the dried material, °C.
w	weight fraction of solute in solution.
x	fraction of initial water remained.
ρ	density of the frozen materical, g/cm^3.

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