APPLICATION OF FREEZE DRYING TO FOOD PRODUCTS WITH SPECIAL REFERENCE TO TRANSPORT PHENOMENA IN COFFEE PROCESSING

Yasuyuki Sagara

Department of Agricultural Engineering,
Faculty of Agriculture,
The University of Tokyo,
Bunkyo-ku, Tokyo, Japan

ABSTRACT

A mathematical model was developed to determine the thermal conductivity and permeability for the dried layer of the sample during drying process. Aqueous solutions of 29—45% soluble coffee solid were freeze-dried at constant sample surface temperatures ranging from -7 to 70°C under the chamber pressure ranges used in commercial operations using radiant heating upon the sample surface. The transport properties of the dried layer were determined by applying the drying data to the model. Thermal conductivity decreased in proportion to the porosity of the dried layer, and its temperature and pressure dependances were not appeared. The permeability increased with increasing the porosity, pressure and temperature of the dried layer. The results indicate that in commercial operations the solute concentration is one of the critical processing factors since this factor decisively governs the structure of a solute matrix formed during freezing of coffee solutions and the transport properties mainly depend upon the nature of this structure during drying.

INTRODUCTION

Basic Theory

Freeze drying is defined as the process of removing water from a food product by sublimation while the food remains frozen; therefore, it must take place at low temperature and at a low vapor pressure. Freeze drying can be explained by reviewing the temperature-pressure phase diagram for water. In Fig. 1 we can observe that phase diagram of water is divided into areas where we have ice, liquid water and vapor. Freeze drying must take place along the curve $Q_1 Q_2$ since $Q_1 Q_2$ represents the sublimation curve of ice. Both air drying and vacuum drying normally take place somewhere along the line $P_1 P_2$. Fig. 2 shows the regression of ice phase boundary or sublimation front during sublimation dehydration of food products. Food materials to be freeze dried should be frozen rapidly so that ice crystals are small with a minimum of cell rupturing and maximum of void. The void spaces remaining after sublimation of the ice are pores of capillary size with a diameter in the range of 100 microns. These pores present a tortuous path for the molecules of water vapor generating from the sublimation front and this contributes partly to the decreased drying rate. The thermal conductivity of the dried region presents a

major resistance to the flow of heat that must be moved to the subliming ice front. For example, the thermal conductivity of beef is about 0.06 (W/m-K)(1) and this value is equivalent to that of insulating materials.
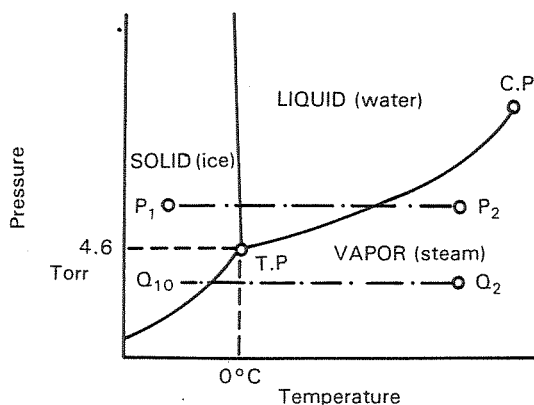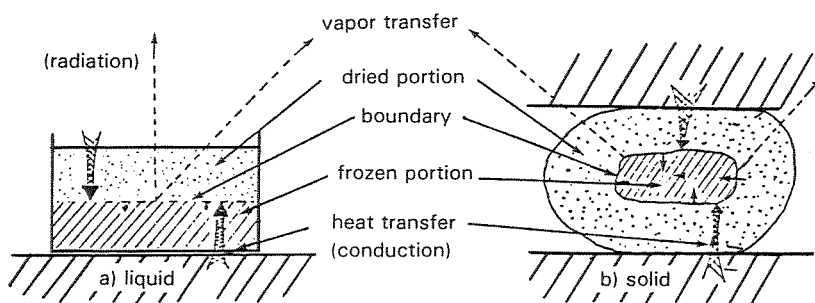

Fig. 1. Phase diagram of water.

Fig. 2. Regression of ice phase boundary during freeze drying.

Advantages

Advantages commonly associated with the freeze drying process were as follows:
1) Freezing stops virtually all bacterical and enzymatic action in most food products, and these remain inactive while the products are in the dry state.
2) More of the nutrients, taste, and flavor constituents remain than with any other known industrial drying process.
3) There is little or no change in volume during drying.
4) The end products are light in weight (moisture content; 3 − 5% w.b.).

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5) The molecular constituents remain in their original orientation during drying.

6) The low temperature and low pressure during the drying period tend to minimize the loss of volatile constituents.

Objective of Study

Freeze drying has had a great impact upon the production of dehydrated food because of the superior quality of the product obtained, and promises continued expansion of the number of applications. However, the process is only feasible if the cost of production can be lowered by optimum plant operations. This requires not only a good engineering design and control to minimize the drying time, but also detailed knowledge for the transport properties of the material to be dried and its characteristic behavior during freezing and freeze drying.

Since the rate of freeze drying is limited by heat and mass transfer rates across a dried material, the thermal conductivity and permeability of the dried layer and the effects of processing factors on these transport properties are fundamental informations to determine the drying rate. The economic consideration in the process of freeze drying coffee make it desirable to prepare a concentrated solution of 30−50% prior to freeze drying. Values of transport properties for this concentration range have not been measured systematically, and the data for freeze drying characteristics were not appeared in the literature.

The objective of this work was to determine the thermal conductivity and permeability of the dried layer in connection with controllable factors such as the solute concentration, temperature and pressure of the dried layer.

THEORETICAL MODEL

A model used to determine the thermal conductivity and permeability of the dried layer is described next and shown in Fig. 3. The sample is assumed to have the geometry of a semi-infinite slab and the dried layer is separated from the frozen layer by an infinitesimal sublimation interface retreating uniformly from the sample surface. The assumption of infinitesimal sublimation front was based on the fact that a sharp sublimation zone had been observed to separate the completely dried layer and the frozen layer in the previous experiments (2). In addition, it is assumed that drying proceeds under quasi-steady-state condition; namely, the movement of sublimation front and the changes in temperature as well as in pressure within the sample are negligible at any instant of drying time. The bottom of the sample is insulated while the surface is exposed to a 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
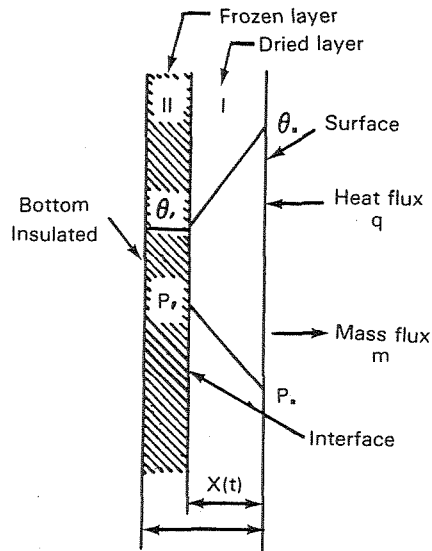
Fig. 3. Freeze-drying model for transport properties analysis.

of the dried layer, the temperature of the frozen layer can be supposed to be uniform and same as that of sublimation front at any instant of time.

Equations representing the rates of heat and mass transfer to and from the frozen layer may be written with these assumptions. The expression for the rate of heat transfer across the dried layer is taken from Massey and Sunderland (3);

$$\overset{\bullet}{q} = \frac{\lambda}{X(t)} (\theta_s - \theta_f) - \overset{\bullet}{m} \int_{O_f}^{O_s} C_p \, d\theta \qquad (1)$$

The specific heat of water-vapor c_p was assumed constant and equal to the value of pure water-vapor. The first term on the right side of this equation represents the heat conducted across the dried layer and the second term represents the energy absorbed by the water-vapor flowing through the dried layer. Similarly, the mass flux may be expressed as where K is the permeability between the sample surface and the sublimation front with the partial pressure of water-vapor p_f.

$$\overset{\bullet}{m} = \frac{KM_w}{RTX(t)} (p_f - p_s) \qquad (2)$$

An expression for the equilibrium vapor pressure (torr) of pure ice as a function of temperature is given by I.C.T. (4);

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$$\log p_f = -2445.5646/T_f + 8.2312 \log T_f$$
$$-0.01677006 T_f + 1.20514 \times 10^{-5} T_f$$
$$-6.757169 \tag{3}$$

As heat supplied across the dried layer may be considered to be dissipated as the latent heat of sublimation, the sublimation front acts as the heat sink which can be represented by;

$$\overset{\bullet}{q} = \overset{\bullet}{m} \Delta H \tag{4}$$

The mass transfer rate can be related to the drying rate as;

$$\overset{\bullet}{m} = \rho_w 1 \left(-\frac{dX}{dt} \right) \tag{5}$$

where ρ_w is the density of ice or frozen liquid and X is the fraction of internal water still remained in the sample. Sagara and Hosokawa (2) have presented the configuration of water within the sample during sublimation dehydration process. According to this configuration, the fraction of X be expressed as

$$X = (m_d + m_f + m_w)/m_o \tag{6}$$

where m_d is the residual water as the sample is fully dried, m_f is the water contained in the frozen layer, m_w is the water vapor flowing through the dried layer, m_i is the dehydrated water and m_o is the initial water. By neglecting the mass of water-vapor as well as residual water which does not take part in deciding the position of interface the value of X is approximated by

$$X = m_f/(m_o/(m_o - m_d) \tag{7}$$

If it is assumed that complete drying except the residual water occurs during the retreat of the frozen layer, the thickness of the dried layer may be expressed in term of the fraction of water remaining, X;

$$x(t) = (1 - X) 1 \tag{8}$$

Substitution of equation (5) into equation (4) gives

$$\overset{\bullet}{q} = \rho_w 1 \Delta H (-dX/dt) \tag{9}$$

Following a substitution of equation (8) into equations (1) and (2), equations (1) and (9) may be combined to give the fraction of dehydrated water;

$$(1 - X) = \frac{\partial (0_s - 0_t)}{\rho_w 1^2 \left(\Delta H + \int_{0_t}^{0_s} c_p \, d0 \right) \left(-\frac{dX}{dt} \right)} \tag{10}$$

Similarly, from equations (2) and (5);

$$(1 - X) = \frac{KM (p_f - p_s)}{\rho_w 1^2 RT_f \left(-\frac{dX}{dt} \right)} \tag{11}$$

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Equations (10) and (11) were used to test drying rate data for conformity to the model and to deduce the transport properties from drying rate data. By rewriting equations (10) and (11), the following equations for the thermal conductivity and permeability are determined, respectively;

$$\lambda = \alpha \rho_w 1^2 \left(\Delta H + \int_{0_f}^{\Theta_s} c_p \, d0 \right) \qquad (12)$$

$$K = \beta \rho_w 1^2 RT_f / M_w \qquad (13)$$

where,

$$\alpha = \frac{(1 - X)}{(0_s - 0_f)/(-dX/dt)} \qquad (14)$$

$$\beta = \frac{(1 - X)}{(p_s - p_f)/(-dX/dt)} \qquad (15)$$

In this study, the average transport properties in quasi-steady state periods were determined with the average values of α and β in these periods.

EXPERIMENTAL

Experimental Freeze Dryer

The vacuum chamber and adjacent parts of the apparatus are illustrated in Fig. 4. The vacuum chamber was a cylindrical, thermally insulated iron enclosure of 92.2 mm in inside diameter by 470 mm long, with a Plexiglas door of 30 mm thick. A rotary vacuum pump was connected through a external condenser and a main valve to the lower part of the vacuum chamber. The chamber pressures were measured by using both Pirani- and diaphragm-type analyzers. A diffusion pump was used to evacuate a diaphragm-type pressure sensor head and to adjust its zero-point. Both internal and external condensing systems were used to collect and freeze the water vapor sublimed from the sample and to prevent moisture from reaching the vacuum pump. A refrigerator for these condensers is a 1.5 kW (R-22 Refrigerant) air-cooled condensing unit with sufficient capacity to reduce the coil surface temperature to -45°C. Radiant heat was supplied by electrically heated plate located about 40 mm above the sample surface. Then the sample surface temperature was controlled with the PID controller by regulating the electrical power to the radiant heater.

The weight loss of the sample was followed by supporting a sample holder on a balance located in the center of the vacuum chamber and recorded as a displacement of a platen equipped with a balance against the drying time. This was accomplished by mounting an electrical differential transformer with the balance. Thus weight readings to within about 0.01 g could be made.

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-⊗- Expansion valve
-⋈- Gate valve
-⋈- Solenoid valve
-☐- Dryer
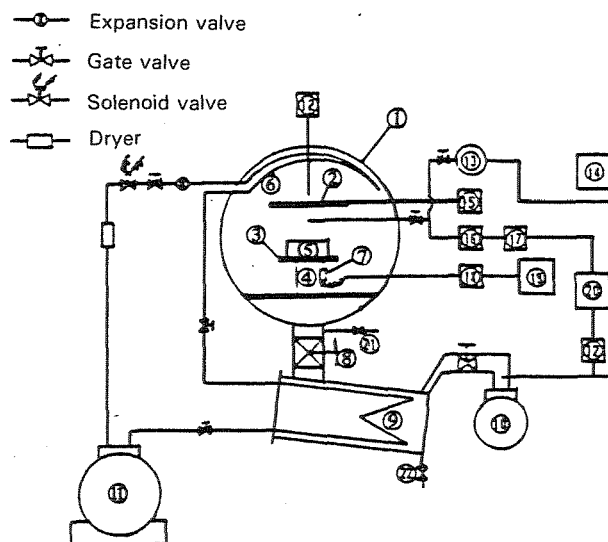
1. Vacuum chamber 2. Heater 3. Platen
4. Balance 5. Sample 6. Internal condenser
7. Displacement transducer 8. Main valve
9. External condencer 10. Vacuum pump
11. Refrigerator 12. Pirani-type vacuum
gage 13. Diffusion pump 14. Thermo-
recorder 15. Temperature controller
16. Diaphragm-type pressure sensor head
17. Pressure indicator 18. Displacement
meter 19. Weight-recorder 20. Pressure
recorder 21. Leak valve 22. Drain

Fig. 4. Schematic diagram of experimental freeze-dryer.

Sample Holder

The sample holder and measuring locations of temperature in the sample were shown in Fig. 5. The sample holder was a Plexiglas dish of 70.5 mm in inside diameter and 28 mm in height. To promote one-dimensional freezing and freeze-drying, a fiber-glass insulation was placed around the side of the sample holder. After the sample was frozen the sample holder was placed on a 50 mm by 150 mm square piece of Polyuretane foam fixed on the platen.

Six thermocouple probes were permanently placed in the center of the sample holder and equally spaced from the exposed surface of the sample. These thermocouples were made from 0.2 mm copper-constantan wire and calibrated with the standard mercury-in-glass thermometer.
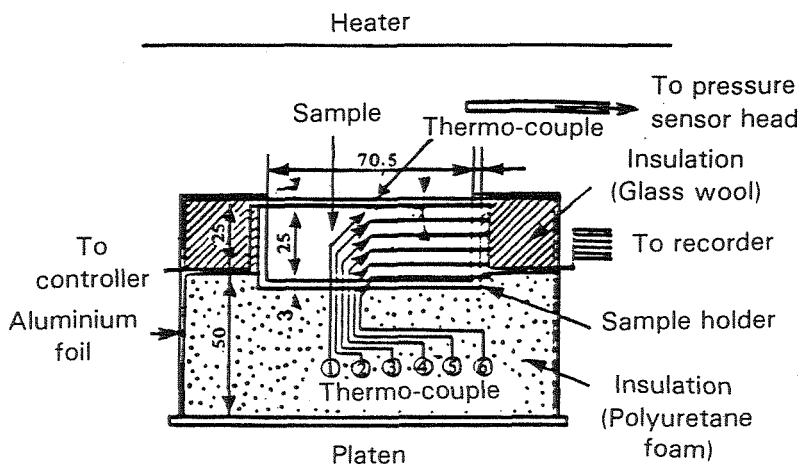
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Fig. 5. Sample holder and measuring points of temperatures.

Procedure

Instant coffee powder was thoroughly mixed with distilled water at temperature ranging 50–100°C and allowed to cool to room temperature. Then it was poured into the sample holder and frozen with freezing-mixture (Dry ice-Ethanol) from the bottom of the sample holder. Freezing continued until uniform temperature of the sample was obtained, resulting in a relatively fast freezing rate with crystallization period under 30 min. and a final sample temperature below -65°C within 60 min. This method of freezing produced a simple, capillary-type solute matrix with its grain orientation parallel to direction of heat and mass transfer. The frozen sample was then transfered into the vacuum chamber, and freeze drying began within about 6 min. Freeze drying continued until constant weight of the sample was obtained, resulting in a final water content below 4% w.b. Then the water content of the dried sample was determined by Karl Fisher titration method.

RESULTS AND DISCUSSION

Drying Characteristics

Table 1 presents the drying conditions for the coffee samples used in this study. The sample temperatures and vapor pressures indicate the average values obtained during quasi-steady-state periods and these values were used to calculate the transport properties. Heater temperature represents the maximum or minimum value appeared during drying process. The physical properties for the initial and dried samples were presented in Table 2. Porosity,

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volume, and density were assessed from cumulative composition using 0.625 specific volume for pure coffee solubles (5), since meaningful value of the volume was appeared to be difficult to measure.

Table 1. Drying conditions for the Coffee Samples.

Sample No.	Concen-tration (% w.b.)	Sample temperature (°C)		Vapor pressure (Pa)		Heater temperature (°C)		Drying time (hr)
	C	θ_s	$-\theta_f$	p_s	p_f	Ohmax	Ohmin	t
1*	28.5	59.0	21.3	11.0	91.7	260.0	88.2	43.3
2*	33.7	29.1	21.2	6.9	92.6	138.7	35.5	44.7
3*	38.6	0.0	22.2	10.4	83.8	88.1	0.0	67.4
4*	40.2	-6.5	21.7	8.1	88.4	67.8	-6.8	69.1
5	40.3	19.1	21.9	9.2	86.5	66.2	19.3	38.0
6	40.4	24.3	21.3	9.3	91.7	74.5	24.8	36.8
7	40.4	28.9	22.2	12.4	84.0	77.4	31.6	29.2
8	40.6	35.2	21.3	9.1	91.7	77.4	35.5	27.7
9	40.5	39.5	21.3	8.7	91.7	83.6	39.8	32.0
10	40.2	49.7	18.9	9.9	115.5	90.0	48.3	45.3
11	40.3	54.5	20.3	9.1	101.0	119.7	54.8	22.3
12	40.0	60.5	18.2	10.1	123.5	128.7	58.5	25.1
13	40.1	70.7	18.6	10.0	118.9	130.7	68.0	22.4
14	45.0	19.6	20.3	9.5	101.0	76.9	21.3	32.0

Condenser temperature 0_c = -43.1~ -45.4 (°C).
* Without scraping.

Table 2. Physical properties of initial and dried samples.

Sample No.	Volume (cm³)	Poro-sity (—)	Mass (g)				Water content (% w.b.)		Density (g/cm³)		
	V_0	Ψ	m_0	m_d	m_s	m_w	w_0	w_d	ρ_0	ρ_d	ρ_w
1	105.0	0.80	118.55	34.72	33.81	84.74	71.5	2.61	1.129	0.331	0.807
2	103.6	0.76	120.19	41.92	40.55	79.64	66.3	3.28	1.160	0.405	0.769
3	102.5	0.71	123.00	50.12	47.52	75.48	61.4	5.36	1.200	0.490	0.736
4	103.1	0.69	125.57	54.05	50.48	75.09	59.8	6.61	1.218	0.524	0.729
5	92.8	0.70	111.56	46.79	44.91	66.65	59.7	4.01	1.202	0.504	0.718
6	92.9	0.70	111.30	46.50	44.92	66.38	59.6	3.39	1.198	0.501	0.715
7	92.5	0.70	111.01	46.56	44.87	66.14	59.6	3.62	1.200	0.503	0.715
8	92.3	0.70	110.54	46.30	44.90	65.64	59.4	3.03	1.198	0.502	0.711
9	93.4	0.70	111.36	46.21	45.14	66.22	59.5	2.31	1.193	0.495	0.709
10	93.9	0.70	111.82	46.01	44.94	66.88	59.8	3.03	1.191	0.490	0.712
11	93.8	0.70	111.96	46.39	45.12	66.84	59.7	2.73	1.194	0.495	0.713
12	94.0	0.70	111.85	45.77	44.73	67.12	60.0	2.27	1.189	0.487	0.714
14	94.1	0.70	111.71	45.57	44.74	66.97	59.9	1.83	1.187	0.484	0.712
14	92.8	0.65	114.41	53.81	51.51	62.90	55.0	4.27	1.233	0.580	0.678

The samples numbered from 1 to 4 were dried without scraping after freezing. As shown in these samples, the solute concentration exerts a great influence on the sample surface temperature. For example, the surface temperature of about 40% solution was not be allowed to heat to above -6.5°C in order to avoid the puffing in the sample. Scraping a expanded portion at the sample surface was found to be successful for removing the surface film effect and thus the surface temperatures, which had been limmitted as low as -6.5°C for 40% solution, were allowed to heat up to 70°C or higher, resulting in a reduced drying time by one-third as shown in sample No. 13. The data for the samples of 40% solutions indicate that the scraped volume is about 10 per cent of initial.

A typical freeze drying characteristics and corresponding drying conditions are shown in Fig. 6. The sample surface temperature increased until it approached the control temperature and then remained constant. The temperature at any given location in the sample appeared to reach a minimum
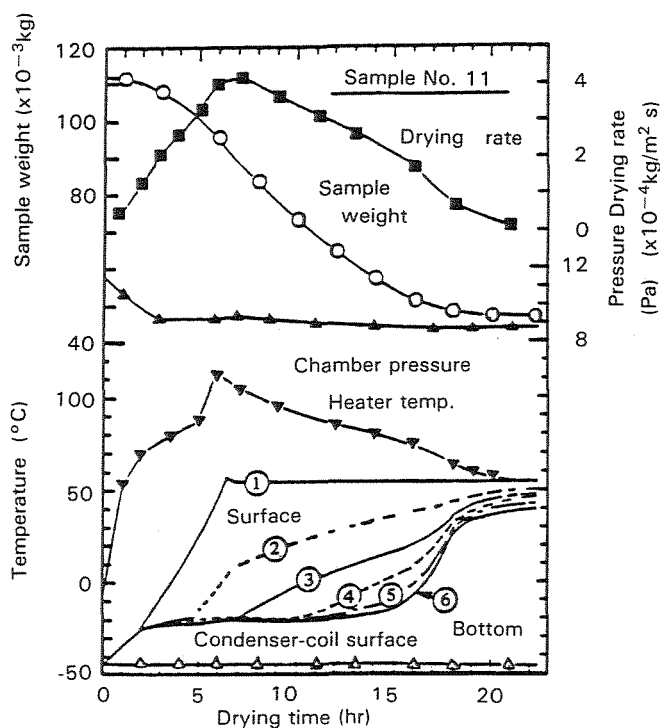

Fig. 6. Experimental data obtained during freeze-drying of 25 mm layer of a 40.3% aqueous solution of soluble coffee at surface temperature 54.5°C.

value just before it began to rise and then rose toward the surface temperature indicating the passage of retreating sublimation front. The temperature of sublimation front was found to decrease as the chamber pressure gradually decreased. Same behavior was observed for all samples used and this indicates the fact that the drying process was heat transfer controlled; namely, the drying rate is much more sensitive to the thermal conductivity of the dried layer than to the permeability.

The weight loss curves of about 40% solutions at various surface temperatures are shown in Fig. 7. Drying time decreased with increasing the sample surface temperature as expected. The sample without scraping (See sample No. 4) required an extremely longer drying time compared with other samples for reason that the sample surface temperature had to be kept lower as described above.
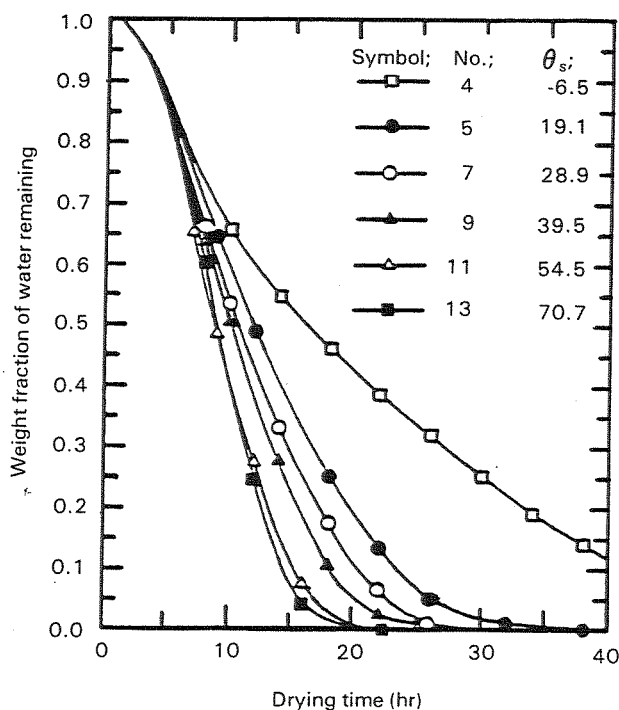

Fig. 7. Experimental drying curves of 40% solutions at various surface temperatures.

Transport Properties

The thermal conductivity and permeability of the dried layer are given in Table 4. Because the sample surface temperature did not instantly jump to a constant value at the start of drying as shown in Fig. 6, only drying data obtained during a quasi-steady-state period, which was appeared after the sample surface temperature reached the constant temperature, was applied to the model. During this period the ratio of heat flow density to mass was essentially constant indicating a constant temperature of the sublimation front. The temperatures and pressures listed in Table 4 indicate the average values for the dried layer obtained during the quasisteady-state periods.

Table 4. Thermal conductivities and permeabilities for coffee solutions.

Sample No.	Concentration (% w.b.) C	Porosity (−) Ψ	Temperature* (°C) $\overline{\theta}$	Pressure* (Pa) $\overline{p}$	Thermal conductivity (W/m-K) λ	Permeability ($\times 10^{-2}$ m^2/s) K
1	28.5	0.80	18.9	51.4	0.153	0.593
2	33.7	0.76	4.0	49.8	0.170	0.398
3	38.6	0.71	-11.1	47.1	0.241	0.293
4	40.2	0.69	-14.1	48.3	0.277	0.213
5	40.3	0.70	-1.4	47.9	0.197	0.419
6	40.4	0.70	1.5	50.5	0.209	0.460
7	40.4	0.70	3.4	48.2	0.196	0.555
8	40.6	0.70	7.0	50.4	0.208	0.562
9	40.5	0.70	9.1	50.2	0.203	0.585
10	40.2	0.70	15.4	62.7	0.210	0.540
11	40.3	0.70	17.1	55.1	0.203	0.649
12	40.0	0.70	21.2	66.8	0.202	0.554
13	40.1	0.70	26.1	64.5	0.195	0.625
14	45.0	0.65	-0.2	55.3	0.224	0.391

* Average value for the dried layer.

The thermal conductivity for the sample without scraping was found to increase with increasing the solute concentration, and its value for about 40% solution was about 20 per cent greater than those of scraped samples. It was observed that in the samples dried without scraping a markedly low permeability was assessed as shown in sample No. 4 and the effects of concentrated surface film on permeability was decreased with decreasing solute concentration as indicated in sample No. 1−4. Effects of temperature and pressure of the dried layer on thermal conductivity were not appeared definitely under experimental condition and the average of 40% solutions was assessed to be 0.203 W/m-K. The results obtained in the present and previous studies show

clearly that thermal conductivity is markedly affected by solute concentration or the porosity of the dried layer as shown in Fig. 8. A linear relationship between thermal conductivity and porosity was obtained and the equation for a regression line fitted to all of the data is also presented.
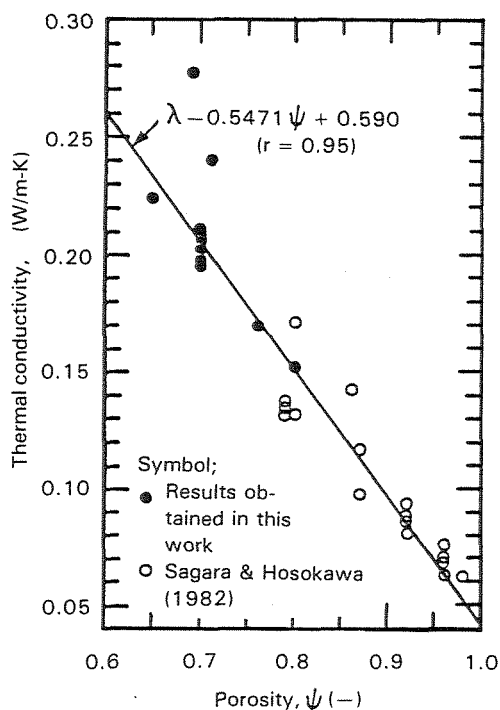

Fig. 8. Thermal conductivity versus porosity.

For all samples of about 40% solutions whose surface layers scraped prior to drying, the permeability was found to increase with the pressure and temperature of the dried layer as shown in Table 4. This behavior is in good agreement with Mellor and Lovett's theoretical investigations (6) based on the collision theory, and also with their experimental results obtained for several kinds of solutions.

The relationship between permeability and porosity at various sample surface temperature is shown in Fig. 9. The data obtained in the previous work (2) are also plotted on the figure. Permeability was found to depend mainly on the solute concentration or the porosity of the dried layer and then other factors such as temperature or pressure of the dried layer.
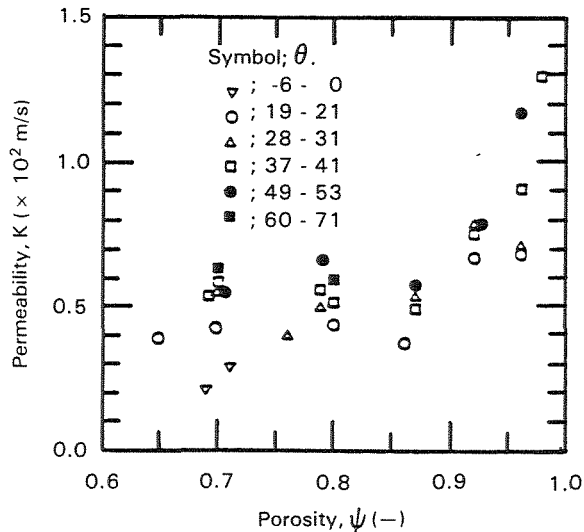
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Fig. 9. Permeability versus porosity for various surface temperatures.

These results indicate 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. In commercial plant operations the solute concentration is one of the critical processing factors since this factor decisively governs the structure of solute matrix formed during freezing of coffee solution and this structure is remained as that of the dried layer during sublimation dehydration process.

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