MEASUREMENT OF TRANSPORT PROPERTIES FOR THE DRIED LAYER OF SEVERAL FOOD MATERIALS UNDERGOING FREEZE-DRYING

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ABSTRACT

The transport properties of several food materials have been presented as fundamental information to determine the drying rate of freeze-drying process. As an example, the measuring method of thermal conductivity and permeability has been demonstrated for the samples of sliced and mashed apples undergoing freeze-drying. Both samples were freeze-dried at constant surface temperatures ranging from −10 to 70 under the usual pressure range of commercial operations. A mathematical model, based on a quasi-steady state analysis, was formulated and then applied to the drying data to determine these transport properties for the dried layer of the sample undergoing freeze-drying. Values of thermal conductivity were found to be almost the same between sliced and mashed samples. However, the permeability data of the mashed apples were more than 4 times greater than that of sliced apples. Both temperature and pressure dependences on these transport properties were not recognized apparently, and the effects of freezing rate on transport properties were found to be critical for the mashed samples. The results indicated that the drying rate of sliced samples was limited by the transfer rate of water vapor flowing through the dried layer.

The transport properties for raw beef, minced beef, shrimp and coffee solutions were also presented indicating the effects of operating conditions as well as the structural parameters of the samples on these values.

Key words : freeze-drying, dried layer, thermal conductivity, permeability

INTRODUCTION

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. Since the rate of freeze-drying is limited by heat and mass transfer rates across a dried material which surrounds the frozen portion of the product, thermal conductivity and permeability of the dried layer and the effects of processing factors on these transport properties are fundamental information to determine the drying rate. Various method, both

transient and steady state, have been used to determine the transport properties of freeze-dried food. The transient method used in this study was based on a quasi-steady-state analysis of actual drying data, and was described by Lusk et al. (1), Massey and Sunderland (2), Hoge and Pilsworth (3), Stuart and Closset (4), Bralsford (5), Gaffney and Stephenson (6) and Sandall et al. (7). The transport properties of cellular food materials were measured using a steady-state method by Harper and Sahrigi (8) as well as Harper (9). Harper and Sahrigi (8) reported the values of thermal conductivities for freeze-dried apples and pears in the presence of various gases over a pressure range of 1 Pa to atmospheric. Harper (9) presented the effects of these gas pressure on permeabilities and thermal conducti- vities of freeze-dried apples and peaches. However, available literatures on the transport properties for the dried layer of cellular food materials were limited.

In this paper, thermal conductivity and permeability for the dried layer of both sliced and mashed apples were demonstrated to show the measuring method as an example. Furthermore, the transport properties for raw beef, minced beef, shrimp and coffee solutions were also presented indicating the effects of operating conditions as well as the structural parameters of the samples on these values.

THEORETICAL MODEL

Figure 1 shows a model (Sagara et al. (10)) to determine the transport properties for the dried layer of the

material undergoing freeze-drying. In the model the material is assumed to be a semi-infinite slab and the direction of heat and mass transfer is the one-dimension. The insulated bottom can be regarded as the center line of the material heated by radiation from both surfaces. Furthermore, the model has several assumptions; that is, 1) The sublimation front retreats uniformly from the surface of the material. 2) Drying proceeds under a quasi-steady state condition, and thus the changes in temperature and pressure in the material and the movement of the sublimation front are negligible during calculation. 3) The linear distribution in temperature and pressure exists across the dried layer, and the temperature of the frozen layer is uniform and equal to that of sublimation front. 4) The heat supplied through the dried layer is consumed completely as the latent heat at the sublimation front.

Based on these assumptions, the equations of the heat and mass flux were introduced, and thus the thermal conductivity and permeability are given as the following equations, respec- tively:

$$\lambda = \alpha \rho_w l^2 (\Delta H + \int_{\theta_f}^{\theta_s} Cpd\theta) / N \qquad [1]$$

$$K = \beta \rho_w l^2 RT_f / NM_w \qquad [2]$$

where,

$$\alpha = \frac{(1-m)}{(\theta_s - \theta_f)/(-dm/dt)} \qquad [3]$$

$$\beta = \frac{(1-m)}{(p_f - p_s)/(-dm/dt)} \qquad [4]$$

EXPERIMENT METHOD

Sample holder

Two types of the sample holder were prepared for solid and granular as well as liquid materials. The sample holder for solid materials or a sliced apple is shown in Figure 2. The sample, whose circumference was insulated with the fiber-glass, was located at the central position of the apparatus. Thus both sample surfaces were heated by
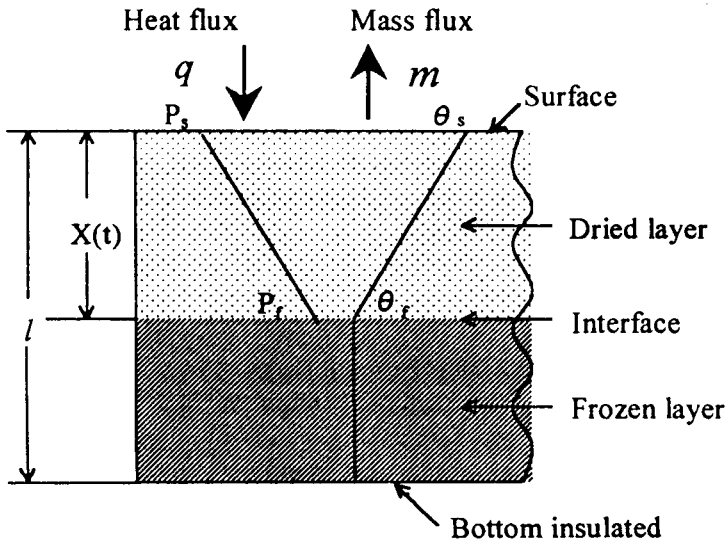

Figure 1 Freeze-drying model for transport properties analysis
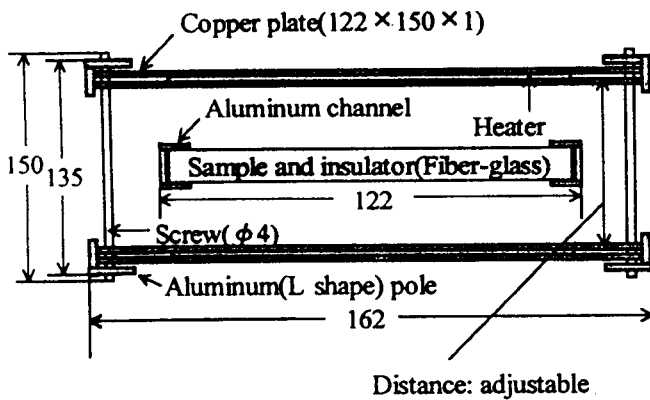

Figure 2 Schematic diagram of sample holder
for solid materials

radiant heaters assembled with a silicon heater and copper plates. The distance between heater and sample surface was adjustable with screws to increase the accuracy of the temperature control. Temperatures of the sample were monitored at both surfaces as well as center by using thermocouple probes made of 0.2 mm copper-constantan wires.

Figure 3 shows another sample holder prepared for the mashed sample and measuring locations of temperature within the sample. The sample holder was a Plexiglas dish of 70.5mm inside diameter and 15mm in height. To promote one-dimensional freezing and freeze-drying , a fiber-glass insulation was placed around the side of the sample holder, and its bottom was insulated with a Polyurethane foam plate. All over the exposed surfaces of the insulating materials were covered with reflecting aluminum foil to reduce radiant heat transfer to both side and

bottom of the holder. Change in temperature distribution within the sample was measured with four thermocouple probes, which were permanently placed at the center of the sample holder and equally spaced from the exposed surface of the sample. The thermocouple junction for monitoring and controlling the surface temperature was placed just under the exposed surface, and all leads were shielded from the direct radiant heat transfer by passing them through the insulation materials.

Materials and Procedure

Both sliced and mashed apples of 15mm thick were prepared as the samples. Sliced samples were cut out horizontally at the equator part, which has the largest diameter in the range from 80 to 90mm. The cores of them were removed with the cork borer whose inside diameter was 20mm, since transport properties of the core, in
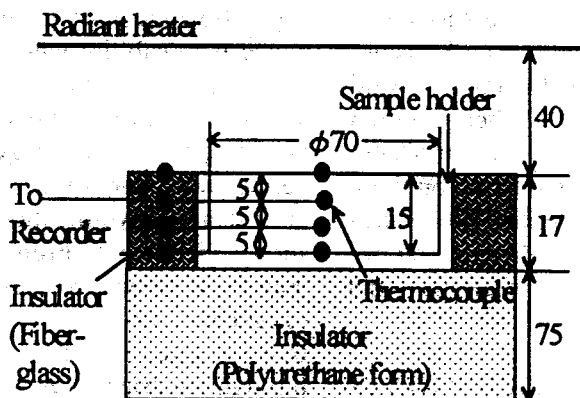

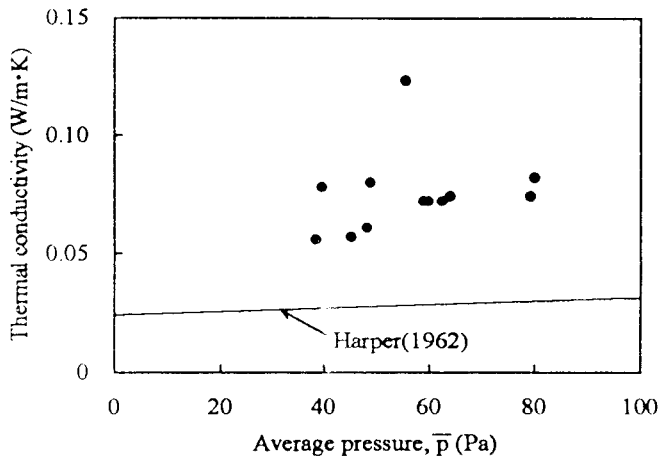Figure 3 Schematic diagram of sample holder for mashed samples

Figure 4 Pressure dependence on thermal conductivity for sliced samples

which drying proceeded faster than that of flesh, was found to be different from that of flesh during preliminary drying experiment. Mashed ones were set in the sample holder as shown in Figure 3.

The sample was frozen one dimensionally by using a cooling copper plate at the surface temperature of –27 to –44 °C, and then freeze-dried at constant surface temperatures ranging from –10 to 70 °C under the usual pressure range of commercial operations. Moisture contents of the dried samples were determined by Karl Fisher titration method, and the initial moisture contents were calculated based on these data. As for other samples, procedures are all the same, though temperatures are different during freezing and freeze-drying stage.

RESULTS AND DISCUSSION

Sliced apples

Table 1 shows values of the thermal conductivity and permeability for sliced samples. Both temperature and pressure dependence on these transport properties were not recognized apparently under our experimental conditions, although some theory, such as Chapman-Enskog formulas for transport properties, showed the influences of temperature and pressure (11).

Y. H. Ma et al. (12) pointed out that the freeze-drying rate of foods was hardly limited by the rate of water vapor flowing through the dried layer as the permeability value for the dried layer of the material shows more than 0.1 ($\times 10^{-2}$ $m^2 s^{-1}$) under the usual operating pressure range. Values of permeability for sliced samples· were less than above-mentioned ones, as shown in Table 1. From this result, it may be concluded that the drying rate of sliced apples was limited by the transfer rate of water vapor flowing through the dried layer.

Values of the thermal conductivity for the dried layer of sliced samples were plotted against the average pressure as shown in Figure 4. The tendency of the plots against pressures
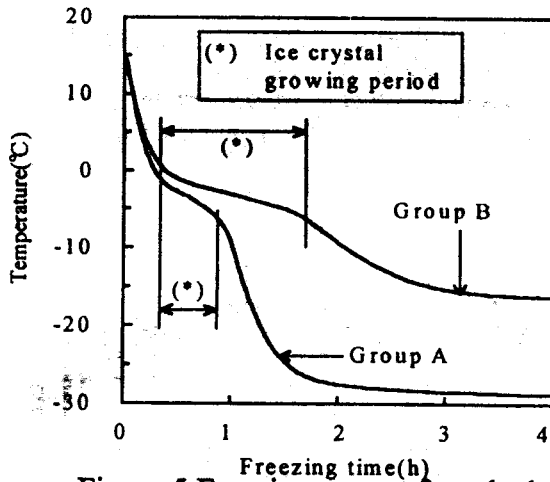
Figure 5 Freezing curve of mashed samples

was similar to that of freeze-dried apples obtained by Harper's (9) steady state method, showing the increasing trend with increasing pressure. However, its absolute values were relatively larger than the empirical curve presented by Harper (9), because in this study the "effective" values of thermal conductivity were measured under the existing conditions of temperature and pressure gradients across the dried layer of the sample undergoing freeze drying.

The kinetic theory of the thermal conductivity (λ) shows that λ is proportional to the square of absolute temperature and is independent of the pressure, because the mean free path of a molecule is inversely proportional to the pressure. However, as shown in Figure 4, the thermal conductivity has a tendency to increase with increasing pressure. This shows that the mean free path of water vapor is greater than a cell's diameter of sliced apples, and as for cellular food materials, the diameter of each cell has a crucial effect upon the thermal conductivity. For the future, measurement of a cell's diameter is

indispensable in order to analyze these data from a viewpoint of transport phenomena.

Mashed apples

Figure 5 shows the freezing curves for mashed samples. The change with time of the center temperature during freezing could be regarded as the index of the freezing rate, and based on these indexes, mashed samples were classified with group A and B. The freezing rate of group A was relatively larger and B was smaller. Temperature of group B was higher than that of A by over 10 °C after 4 hours since freezing process had started. In order to obtain the quantitative index, the period between two infliction points was defined as ice crystal growing period, as shown in Figure 5 (13).

Table 2 shows values of the thermal conductivity and permeability for mashed samples. Ice crystal growing periods of the group A and B were in the range from 19 to 28 min., from 60 to 80 min., respectively. Then marked difference has been observed in the values of transport properties among

these two groups. Values of thermal conductivity in group A were about 2 times larger than that of B. On the other hand, the permeability data in group B were about 4times larger than that of A. The results indicated that effects of freezing rate on transport properties were critical for the mashed samples.

Table 1 Thermal conductivity and permeability for sliced apple samples

| Sample No.	Sample Surface Temperature (°C) θ_s	Position of Sublimation Front from Sample Surface (mm)	Temperature* (°C) $\bar{\theta}$	Pressure* (Pa) $\bar{p}$	Thermal conductivity (W/m·K) λ	Permeability (×10⁻² m²/s) K
1	-10	1.5 ~ 4.5	-16.4	48.9	0.080	0.066
2	-10	3.9 ~ 4.7	-15.5	55.6	0.123	0.072
3	-10	4.6 ~ 5.3	-17.7	39.5	0.078	0.105
4	0	5.1 ~ 5.8	-11.5	48.2	0.061	0.058
5	0	5.0 ~ 6.2	-11.9	45.2	0.057	0.089
6	0	2.8 ~ 4.9	-12.8	38.4	0.056	0.120
7	5	5.4 ~ 5.8	-7.3	62.6	0.072	0.076
8	5	4.0 ~ 5.3	-7.6	59.9	0.072	0.087
9	5	4.6 ~ 6.0	-5.8	80.0	0.082	0.063
10	10	4.9 ~ 6.0	-5.0	59.0	0.072	0.098
11	10	3.8 ~ 5.3	-3.4	79.2	0.072	0.064
12	10	3.9 ~ 5.2	-4.6	64.1	0.074	0.088

*Average value for the dried layer
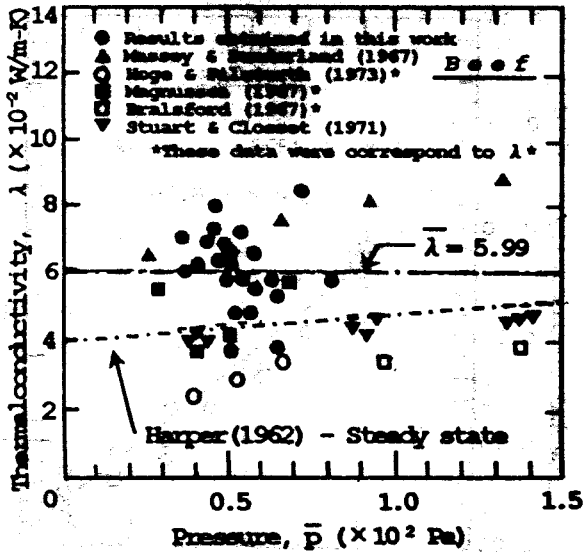
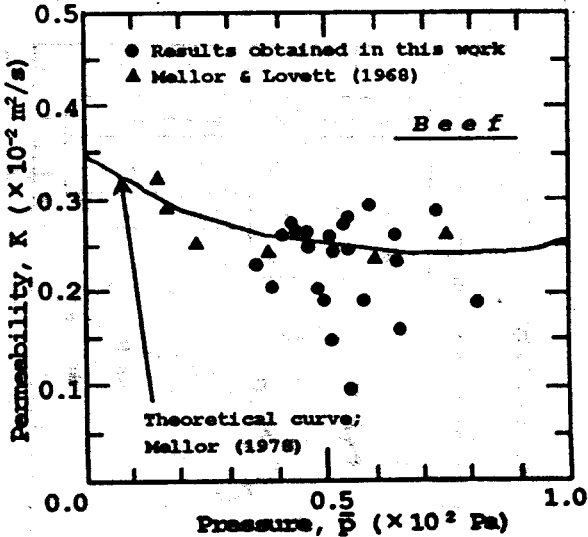Figure 6 Thermal conductivity for beef
samples (Sagara (16))

Figure 7 Permeability vs. pressures of the
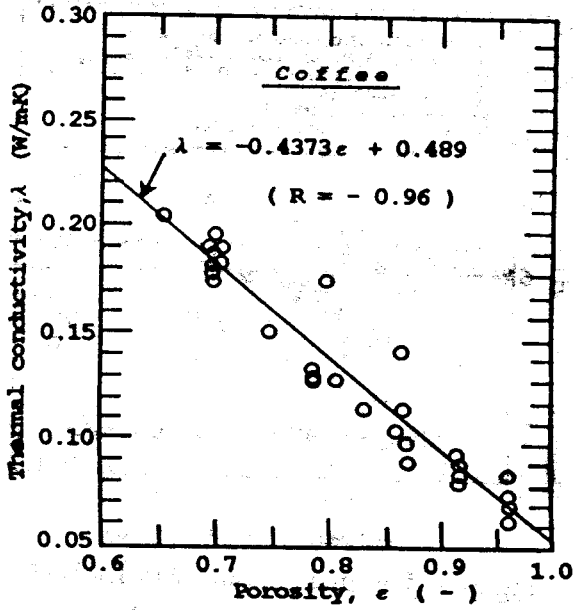dried layer for beef samples
(Sagara (16))

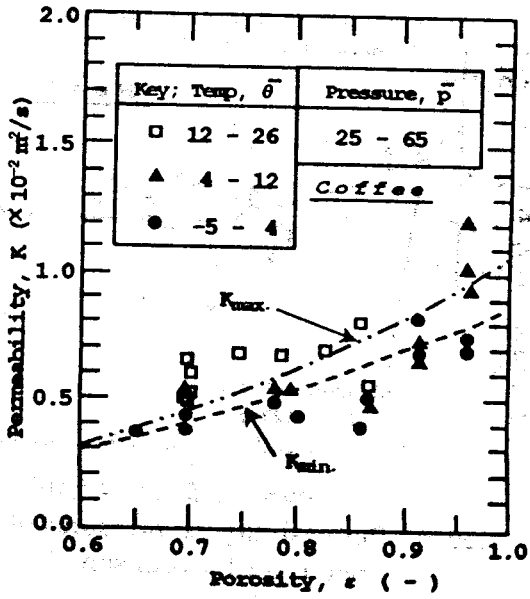Figure 8 Thermal conductivity results for
coffee solutions (Sagara(16))

Figure 9 Permeability vs. porosity for
coffee solutions (Sagara (16))

Raw beef

The relationship between thermal conductivity and the pressure of the dried layer is shown in Figure 6. Thermal conductivity λ^* plotted in this figure is determined by neglecting the heat absorbed by water vapor flowing through the dried layer. Harper (9) measured the thermal conductivity of completely freeze-dried foods using a steady state method and concluded that

Table 2 Thermal conductivity and permeability for mashed apple samples

Sample No. (time*) (min)	Sample Surface Temperature (°C) θ_s	Position of Sublimation Front from Sample Surface (mm)	Temperature** (°C) $\bar\theta$	Pressure** (Pa) $\bar p$	Thermal conductivity (W/m·K) λ	Permeability (×10⁻² m²/s) K
13 (19)	0	10.4 ~ 11.2	-13.6	36.7	0.13	0.40
14 (69)	10	11.9 ~ 12.9	-11.8	23.7	0.068	1.3
15 (75)	20	9.0 ~ 10.0	-6.6	24.0	0.073	1.5
16 (23)	30	10.1 ~ 11.6	0.8	33.5	0.12	0.43
17 (28)	40	9.9 ~ 11.6	8.5	46.2	0.11	0.50
18 (60)	50	10.2 ~ 11.8	9.1	25.8	0.070	1.4
19 (71)	60	9.4 ~ 10.0	14.5	27.6	0.073	1.4
20 (80)	70	9.1 ~ 10.0	19.7	29.0	0.072	1.6

* Ice crystal growing period
** Average value for the dried layer

Table 3 Numerical values of the constant used to calculate the permeability of beef sample by equation (5) (Sagara (17))

Constants	Numerical value used	Origin
r	58×10^{-6}, m	Mellor (15)
k'	2.5 , -	Mellor and Lovett (14)
τ	4.2 , -	Mellor (15)
δ_1	$3\pi/16$, -	Mellor and Lovett (14)
σ	4.6×10^{-10} , m	Kennard (18)
ε	0.64 , -	Harper (9)

the experimental data can be adequate-
ly correlated by an empirical equation.
A curve in Figure 6 was calculated by
applying the recommended values for
beef to his equation. Although effect of
the pressure on thermal conductivity
was not measured in this study as
described above, it was considered that
the thermal conductivity essentially had
a tendency to increase as the pressure
increase as shown in the curve.

Permeability vs. the pressure of the
dried layer relationship are shown in
Figure 7. Mellor and Lovett (14)
applied values of the structural
parameter to an equation derived on the
basis of collision theory (15) for the
permeability in terms of the mean free
path, giving K as in equation [5].

$$K = \frac{\varepsilon}{\tau} D_k \left[\frac{3}{32k'} \frac{2r}{\lambda} + \delta_1 \cdot (1 - e^{-2r/\lambda}) + e^{-2r/\lambda} \right] \qquad [5]$$

The values for K were in good
agreement with Mellor's (15)
theoretical curve based on a collision
theory and also with their experimental
data using completely freeze-dried
samples under steady-state conditions.
Table 3 shows the numerical values of
the constant applied to the equation (5).
As the drier layer temperature was
increased, permeability had a tendency
to increase at the surface temperature
ranging 30 to 80 °C and to decrease
from 80 to 100 °C. It was considered
that in this surface temperature range
the heat supplied across the dried layer
was dissipated as both sensible heat to
raise the temperature of the frozen
layer and latent of sublimation. Thus
the model applied over this temperature
range was found to provide invalid
values because the drying conditions
did not satisfy the assumption used in
the model as mentioned before.

Coffee solution

The result obtained in the present
studies has shown clearly that thermal
conductivity has been markedly
affected by solute concentration or the
porosity of the dried layer as shown in
Figure 8. Porosity was assessed from
cumulative composition using 0.625
specific volume for pure coffee soluble.
A linear relationship between thermal
conductivity and porosity was obtained
and the equation of a regression line
fitted to all of the data is also presented
in Figure 8.

The relationship between permeabi-
lity and porosity at various dried layer
temperatures is shown in Figure 9. The
curve of K_{max} in Figure 9 was
calculated from the maximum values of
temperature (26 °C) as well as pressure
(65Pa) applying structural parameters
obtained from equation (5). The
calculation method of K_{min} is the same
(-5 °C, 25Pa) as described for K_{max}.
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 had been of the dried layer.

Other food materials

Table 4 shows values of the thermal
conductivity and permeability for
several food materials obtained by
Sagara (10)'s model. According to the
Y. H. Ma et al. (12)'s suggestion
mentioned above, the drying rate of
minced beef was found to be limited by
heat transfer rate, such as mashed
apple, raw beef as well as coffee
solution. On the other hand, that of

Table 4 Thermal conductivity and permeability for several food materials

Material	Sample surface Temperature (°C) θ_s	Pressure in the chamber (Pa) P_s	Temperature* (°C) θ	Pressure* (Pa) $\bar{P}$	Thermal conductivity (W/m·K) λ	Permeability ($\times 10^{-2}$ m²/s) K	Reference
Sliced apple	-10~10	20~30	-17.7~-3.4	38.4~80.0	0.056~0.123	0.063~0.120	(obtained in this work)
Mashed apple(A)*	0~40	20~30	-13.6~-8.5	33.5~46.2	0.11~0.13	0.40~0.50	(obtained in this work)
Mashed apple(B)*	10~70	20~30	-11.8~19.7	23.7~29.0	0.068~0.073	1.3~1.6	(obtained in this work)
Beef	30~100	7~30	3.0~40.8	38.2~78.5	0.036~0.084	0.090~0.405	Sagara et al. (19)
Minced beef	40	2.7~13.3	7.3~10.3	-	0.050~0.069	0.13~0.24	Widodo and Tambunan
Coffee solution (6~30%)***	20~53	10~95	-5.3~14.8	-	0.062~0.172	0.340~1.220	Sagara and Hosokawa (
Coffee solution (29~45%)***	-7~71	7~12	-14.1~26.1	47.1~66.8	0.153~0.277	0.213~0.649	Sagara and Ichiba (21)
Coffee solution (10~36%)***	60	22~34	12.9~20.2	24.9~64.9	0.063~0.144	0.508~4.235	Ichiba (13)
Shrimp	30~50	7~133	4.2~21.2	53.6~263	0.038~0.086	0.031~0.120	Wenur (22)

*Average value for the dried layer **(A) Rapid freezing and (B) Slow Freezing
***Coffee solute concentration

shrimp was limited by water vapor transfer flowing through the dried layer, such as sliced apple. In this study, the surface temperature of the slice sample could not be set at more than 10 °C to maintain an original structure. However, as shown in Table 4, the surface temperature of shrimp was ranging from 30 to 50 °C. The result indicated that the transport properties of shrimp should be measured and investigated under lower surface temperature conditions in connection with the structural nature as well as operating parameters.

NOMENCLATURE

C_p = specific heat at constant pressure, J/(kg-K)

D_k = Knudsen diffusion coefficient, m²/s

ΔH = latent heat of sublimation of ice, J/kg

K = permeability, m²/s

k' = structural constant, -

l = thickness of slab, m

$\dot{m}$ = mass flux density (mass transfer rate), kg/(m²-s)

m = the fraction of water remaining, -

M = molecular weight, kg/mol

N = 1 (in radiant heating upon one surface), - ; 4 (in radiant heating upon double surfaces), -

p = pressure, Pa

$\dot{q}$ = heat flux (heat transfer rate), J/(m²s)

R = gas constant, J/(mol-K)

r = equivalent pore radius, m

T = absolute temperature, K

t = time, s

$X(t)$ = position of the sublimation front, -

Greek letters

a = constant defined by equation (3)

β = constant defined by equation (4)

δ_1 = roughness factor of pore, -

ε = porosity, -

θ = temperature, °C

λ = thermal conductivity, W/(m-K) (Equation (1))

ρ = density, kg/m³

τ = tortuosity factor, -

Subscripts

f   sublimation front

s   surface

w   water vapor

REFERENCES

Lusk, G., Karel, M. and Goldblith, S.A., 1964, Thermal conductivity of Some Freeze-Dried Fish, Food Technology, 18(10) pp.1625-1628

Massey, W. M. and Sunderland, J. E., 1967, Measurement of Thermal Conductivity during Freeze-drying of Beef, Food Technology, 21(3A) pp.90A-94A

Hoge, H.J. and Pilsworth, M.N., 1973, Freeze-Drying of Beef, J. of Food Science, 38 pp.841-848

Stuart, E.B. and Closset, G., 1971, Pore Size Effect in the Freeze-Drying Process, J. of Food Science, 36 pp.388-391

Bralsford, R., 1967, Freeze-Drying of Beef, J. of Food Technology, 2 pp.339-363

Gaffney, J.J. and Stephenson, K.Q., 1968, Apparent Thermal Conductivity during Freeze-Drying of a Food Model, Trans. of ASAE, 11(6) pp.874-880

Sandall, O.C., King , C.J. and Wilke, C.R., 1967, The Relation-ship Between Transport Properties and Rates of Freeze-Drying of Poultry Meat, AIChE J. 13(3) pp.428-438

Harper, J.C. and El Sahrigi, A.F., 1964, Thermal Conductivities of Gas-Filled Porous Solids, I&EC Fundamentals, 3 pp.318-324

Harper,J.C., 1962, Transport Properties

of Gases in Porous Media at Reduced Pressures with Reference to Freeze-Drying, AIChE J., 8(3) pp.298-302

Sagara, Y. and Hosokawa, A., 1982, Dry Layer Transport Properties and Freeze-Drying Characteristics of Coffee Solutions, Proc. Third Int. Drying Symposium IDS'82, Birmingham, pp.487-496

Bird, R.B., Stewart, W.E. and Lightfoot, E.N., 1960, Transport Phenomena, Wiley, pp.253-260, 508-513

Ma, Y.H. and Peltre, P.R., 1975, Freeze-Dehydration by Microwave Energy: Part 1 Theoretical Investigation, Part 2 Experimental Study, AIChE J., 21(2) pp.335-350

Ichiba, J., 1994, The Effect of Freezing Rate on Drying Characteristics of Granular Food Materials: Change in the Structure and Transport Properties, MD's Thesis, The University of Tokyo, pp.60-62

Mellor, J.D. and Lovett, D.A., Vacuum, Vol.18, p.625

Mellor, J.D., 1978, Fundamentals of Freeze-Drying, pp.94-128, Academic Press, London

Sagara, Y., Automatic Measurement System for Transport Properties of Food Samples Undergoing Sublimation Dehydration, Advances in Food Engineering, pp.111-124

Sagara, Y., 1986, Transport Properties Measurement of Food Sample Undergoing Sublimation Dehydration, Proc. Fifth Int. Drying Symposium IDS '86, Boston, pp.413-421

Kennard, E. H., 1938, Kinetic Theory of Gases, 149, McGrow-Hill

Sagara, Y., Kameoka, T. and Hosokawa, A., 1982, Measurement of Thermal Conductivity and Permeability of the Dried Layer during Freeze Drying of Beef, J. of Soci. Agr. Machinery, Japan 44(3)

Widodo, M. and A.H.Tambunan, 1996, Penentuan Nilai Konduktivitas Panas dan Permeabilitas Uap Air pada Lapisan Kering Daging Sapi Giling selama Proses Pengeringan Beku, Bul. Keteknikan Pert., Th.X No.2, pp.52-60

Sagara, Y. and Ichiba, J., 1994, Measurement of Transport Properties for the Dried Layer of Coffee Solution Undergoing Freeze Drying, Drying Technology, 12(5), pp.1081-1103

Wenur, F., 1997, Model Silindris Untuk Pengkajian Proses Pengeringan Beku Udang, Ph.D.Thesis, Institut Pertanian Bogor, Indonesia, p.58