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Determination of thermo-physical properties of freeze-dried foodstuffs

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The thermo-physical properties of some important foodstuffs have been estimated and are correlated with temperature and pressure using semi-empirical technique. For determination of thermal conductivities (k) of paneer and mango samples, 'Uniformly Retreating Ice Front' (URIF) model has been used at two different methods of freezing conditions i.e. conventional slow freezing and rapid cryogenic freezing. In all the cases, linear equation expressing k as dependent variable with chamber pressure (P) [ranging from 0.003 to 0.05 mbar] and average temperature of dried layer (T) [ranging from 275 to 295 K] as independent variables has been established. The heat capacity, C_p of different freeze-dried foodstuffs have been determined experimentally using 'Differential Scanning Calorimeter' for a wide range of temperature at specific values of moisture content of practical significance. The equations of the best fit curves are also presented, enabling one to estimate the heat capacity value for freeze dried foodstuff (with specified moisture content) at any temperature within the range of 258 to 319 K.

Keywords: Thermal conductivity, URIF model, Heat capacity, Freeze dried foodstuffs

IPC Code: A23L1/00, A23L1/025

Determination of thermo-physical properties *viz*. the thermal conductivity and the heat capacity of the freeze-dried layer is of utmost importance for their subsequent application in the prediction and analysis of internal heat transfer rate through the dried layer for the material undergoing freeze-drying. It has been observed by different researchers that the effective thermal conductivity in the dried layer (k) of the material undergoing freeze drying depends significantly on the temperature of the dried layer of the material, total pressure in the drying chamber and with the type of gas present in the dried layer. The first investigation on k was systematically carried out by Harper & Tappel[1,2]. Saravacos *et al.*[3,4] and Triebes & King[5] have reported that the thermal conductivity values of the freeze-dried material is higher at higher relative humidity of the surrounding gas. Sandall *et al.*[6] also determined the transport properties of freeze-dried foodstuffs *viz*. poultry meat under specific conditions of freeze-drying. However, no general correlation between transport properties and process variables was established. In a review, King[7] has shown that at very low pressure, k for freeze-dried pear assumes an asymptotic value that is independent of the surrounding gas. However, at higher pressure although k takes a new higher asymptotic value, this is profoundly dependent on the nature of the gas present. An explanation for such behavior has been thoroughly discussed[7].

In the present work, k has been determined using Uniformly Retreating Ice Front (URIF) model presented by King[7] for two foodstuffs *viz*. paneer and mango under two methods of freezing conditions i.e. conventional slow freezing and rapid freezing using liquid nitrogen at various operating conditions of chamber pressures (P) and shell (radiant heat source) temperatures. For all the cases, linear equation expressing k as dependent variable with chamber pressure (P) and average temperature (T) of dried layer of the foodstuff as independent variables has been established using semi-empirical approach. The heat capacity, C_p of different freeze-dried foodstuffs have been determined experimentally using standard instrument for a wide range of temperature at specific values of moisture content of practical significance. The equation of the best-fit curves are also presented, enabling one to estimate the heat capacity value for freeze-dried foodstuff at any temperature within the temperature range of 258 to 319 K.

Experimental Procedure

The freeze-drying of paneer and mango was conducted in a cylindrical shell having a diameter of

0.340 m and of 0.360 m length and heated electrically on the outer shell surface to transmit radiant heat required to freeze dry the food stuff. The cylindrical shell was connected to a vacuum pump having a capacity of 8.33 dm^3/s and capable of evacuating the shell up to 0.001 mbar pressure.

Two methods of freezing were employed, (i) conventional slow freezing using a refrigeration unit capable of maintaining a temperature as low as 223 K and (ii) rapid cryogenic freezing using liquid N_2 (boiling point 77 K). Pre-frozen foodstuff in the form of rectangular parallelepiped was kept in a thermocol container exposing only one surface while the other five surfaces were kept insulated and was mounted on a balance capable of measuring weight from 0.01 to 600 g. The temperature of the radiant heat source was preset and vacuum was applied to the shell after inserting the weighing balance holding the sample kept in the container. The temperatures of the radiator surface, top (dried) surface of the material and frozen layer of the material (probe inserted at the center point of the material) were recorded using three RTDs. The pressure of the drying chamber was measured using a pirani gauge. Primary stage of freeze-drying proceeded via sublimation of ice crystals and generated a dried layer above the frozen layer. The resulting vapour escaped through the dried layer to the surface, countercurrent to the heat flow. The vapour then diffused through the chamber and was finally collected upon the condenser where water vapour de-sublimed as ice. The primary drying stage came to an end when all the ice crystals were sublimed. The schematic diagram of one-dimensional experimental model is shown in Fig. 1.

Freeze-drying experiments were carried out at different controlled shell temperatures and chamber pressures. The paneer and mango samples were conventionally or cryogenically frozen and only the top surface was available for heat and mass transfer (Table 1).

Results and Discussion

Thermal conductivity of paneer

The thermal conductivity of freeze-dried foodstuffs was determined using URIF model of King[7], which can mathematically be expressed as:

$$A = \frac{4kM_{\mathrm{W}}V_{\mathrm{W}}}{\Delta H_{\mathrm{S}}L^2}B - \frac{2}{L}\frac{k}{h_{\mathrm{e}}} \qquad \ldots (1)$$

where, $A = 1 - x$ and $B = (T_{\mathrm{e}} - T_{\mathrm{f}})/(-dx/dt)$. The term x is defined as the fraction of the initial moisture remaining in the sample and is calculated as the ratio of the difference between the initial moisture content and weight loss for a given time span to the initial moisture. The loss in weight of the sample with respect to time during drying was recorded. The data thus obtained have been used to determine the values

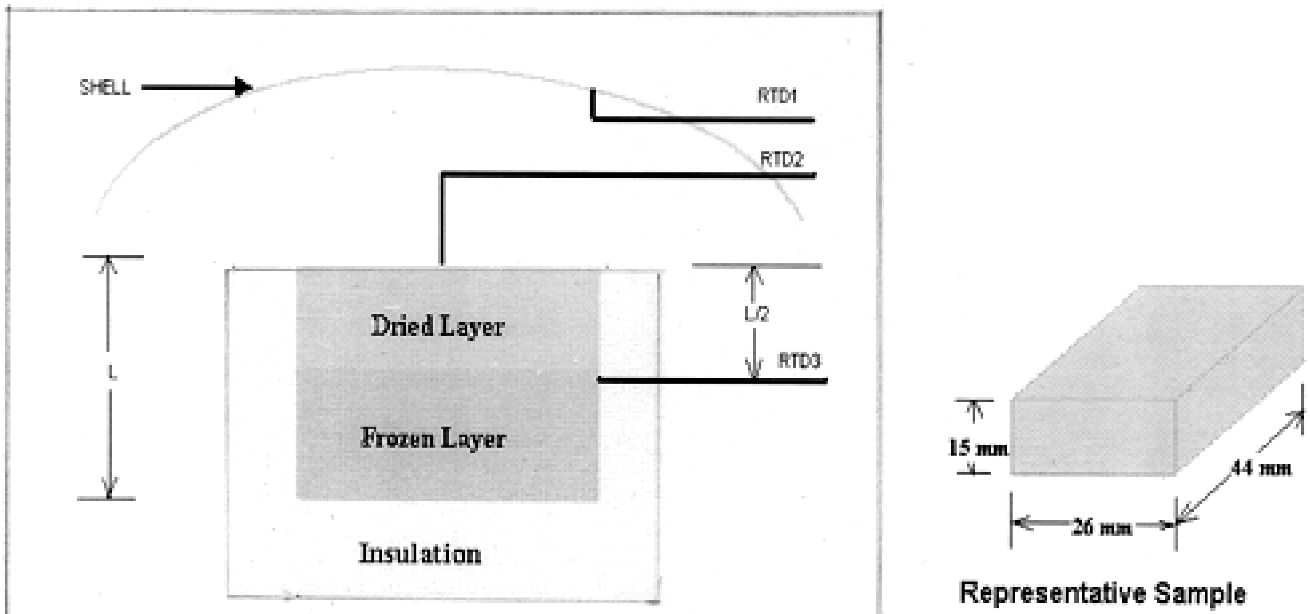

Fig. 1—Schematic diagram of one-dimensional experimental model

Table 1—Typical experimental results of one-dimensional freeze-drying on paneer (conventional freezing) for determination of thermal conductivity of dried layer
[Average (set) shell temperature= 308 K; Average chamber pressure=0.0041mbar; Sample size=44×26×15 mm; freezing procedure:conventional]

Time (Min)	Shell temperature [T_e] (K)	Dried surface temperature [T] (K)	Center temperature [T_f] (K)	Weight of material + container [g]	Chamber pressure [P] [mbar]
0.0	308	258.0	257.1	23.70	0.0400
30.0	308	279.6	257.3	23.26	0.0043
60.0	308	282.1	259.2	22.70	0.0042
90.0	308	284.2	260.7	22.22	0.0042
150.0	308	287.1	262.4	21.40	0.0043
210.0	308	289.3	263.3	20.64	0.0041
270.0	308	291.4	264.0	19.90	0.0041
330.0	308	293.0	264.6	19.22	0.0040
390.0	308	294.4	265.3	18.60	0.0040
450.0	308	295.6	266.3	18.02	0.0045
510.0	308	296.7	267.9	17.44	0.0047
570.0	308	297.7	270.1	16.90	0.0041
630.0	308	298.6	273.2	16.39	0.0040
690.0	308	299.4	278.2	15.89	0.0041
750.0	308	299.9	284.7	15.50	0.0041

of A and B. The total moisture present in the foodstuff has been determined using Mettler LJ16 moisture analyzer.

In order to determine k from the slope of Eq. (1), a plot containing A as ordinate and B as abscissa has been made at different experimental conditions and plotted on same figure. Three representative plots of such findings have been shown in Fig. 2 for conventionally frozen paneer. The best-fit straight line was obtained by least square technique and from the slope of the straight line the value of the thermal conductivity has been computed using Eq. (1).

In a similar manner, the terms A and B are plotted against each other for cryogenically frozen paneer under different operating conditions of chamber pressure and shell temperatures as shown in Fig. 3.

It is observed from the Fig. 3 that the slope is steeper for run at 308 K shell temperature and 0.013857 mbar chamber pressure. This indicates that thermal conductivity of the freeze-dried layer is high at higher values of chamber pressure. A close inspection of the straight lines for runs at 313 and 302 K clearly indicates that the thermal conductivity of the dried layer of the foodstuff increases with increase in both shell temperature and chamber pressure.

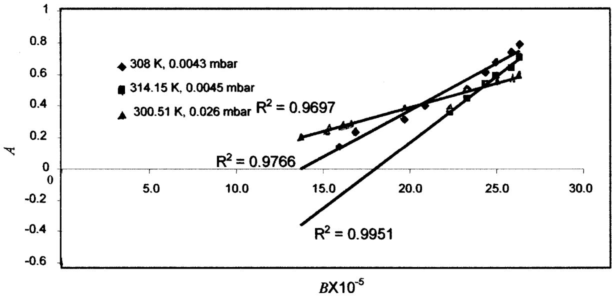

Fig. 2—Plot of A versus B under different set of operating conditions for conventionally frozen (slow freezing) paneer

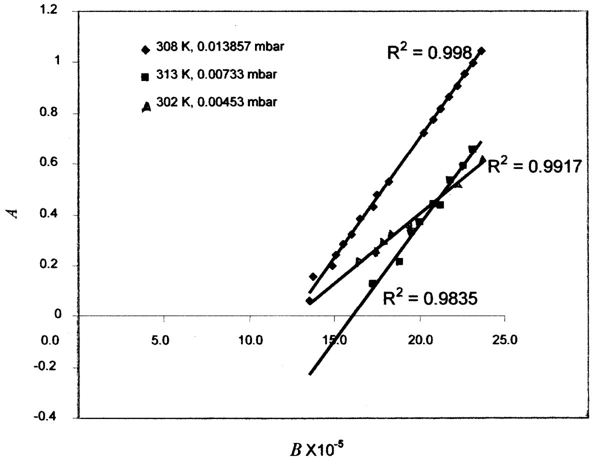

Fig. 3—Plot of A versus B under different set of operating conditions for cryogenically frozen (Liquid N_2 dipped, rapid freezing) paneer

Thermal conductivity of mango

The thermal conductivity of mango was estimated following the same procedure as described in previous section and the data thus obtained were plotted in Fig. 4.

It is evident from the comparison between runs at 308 and 309 K that the thermal conductivity is quite sensitive to chamber pressure. However, a comparison between runs conducted at 315 and 309 K clearly indicates that an increase in shell temperature enhances the thermal conductivity of the freeze-dried material.

From Fig. 5 it is evident that the thermal conductivity of the dried layer of cryogenically freeze-dried mango increases with increase in both chamber pressure and shell temperature. However, a close inspection on the above family of straight lines indicates that the thermal conductivity is more sensitive to chamber pressure rather than shell temperature.

The calculated values of the thermal conductivities for paneer and mango under different operating conditions are summarized and presented in Tables 2 and 3, respectively. It should be noted that the final moisture contents of the dried foodstuffs (*viz.* paneer and mango) are 5.0 wt%.

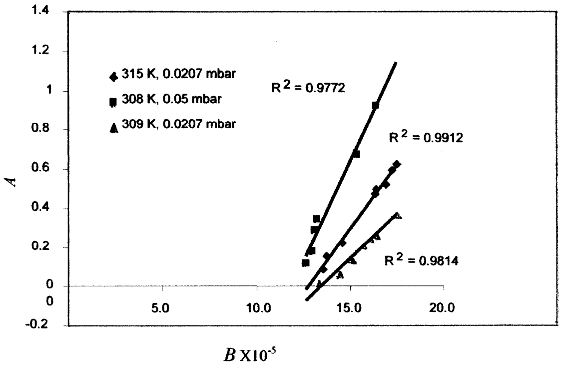

Fig. 4—Plot of *A* versus *B* under different set of operating conditions for conventionally frozen (slow freezing) mango

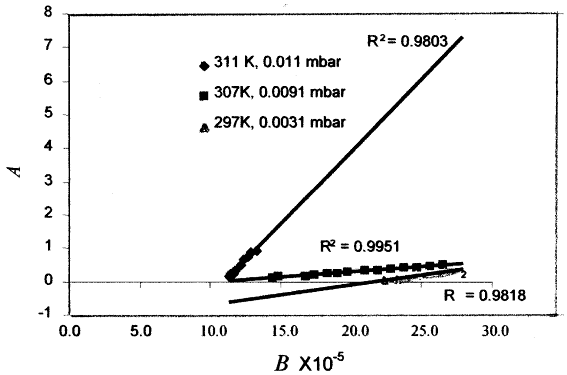

Fig. 5—Plot of *A* versus *B* under different set of operating conditions for cryogenically frozen (Liquid N_2 dipped, rapid freezing) mango

Correlation of thermal conductivities of the dried layer of freeze-dried foodstuffs

It is assumed that the thermal conductivity of freeze-dried foodstuffs vary linearly with dried layer

Table 2— Thermal conductivity of freeze-dried paneer at different operating conditions

Freezing method	Radiator temperature (K)	Chamber pressure (mbar)	Dimension ×10^9 (m^3)	Average temperature of dried layer (K)	Thermal conductivity (W/m.K)
Normal	308.0	0.00572	44×26×15	290.98	3.826E-02
Normal	308.0	0.0043	44×26×15	292.38	2.634E-02
Normal	314.0	0.0045	44×26×15	288.0	4.26E-02
Normal	300.51	0.026	90×40×15	278.83	4.646E-02
Liquid N_2	308.0	0.013857	42×26×15	283.73	4.301E-02
Liquid N_2	313.0	0.00733	43×26×14	291.0	3.8193E-02
Liquid N_2	302.0	0.00453	44×26×15	288.53	2.858E-02

Table 3—Thermal conductivity of freeze-dried mango at different operating conditions

Freezing method	Radiator temperature (K)	Chamber pressure (mbar)	Dimension ×10^9 (m^3)	Average temperature of dried layer (K)	Thermal conductivity (W/m.K)
Normal	315.0	0.0207	44×26×15	279.45	3.91 E-02
Normal	308.0	0.05	42×25×15	285.70	3.82 E-02
Normal	309.0	0.0207	42×25×15	295.1	4.1 E-02
Liquid N_2	311.0	0.011	41×23×13	290.0	7.04 E-02
Liquid N_2	297.0	0.0031	40×23×15	275.5	9.84 E-03
Liquid N_2	307.0	0.0091	41×23×15	278.5	2.327 E-02

average temperature (T) and chamber pressure (P). Mathematically this can be represented as follows:

$$k = a + b\,T + c\,P \qquad \ldots (2)$$

where, a, b, and c are constants for a particular material and specific mode of freezing. Based on the model equation, the thermal conductivity data (Tables 2 & 3) of the dried layer of paneer and mango for two different modes of freezing (i.e., conventional and cryogenic modes) were correlated with temperature and pressure using linear regression technique of POLYMATH software. The coefficients thus obtained are presented in Table 4.

Specific heat of freeze dried food stuffs

In order to solve the energy balance equation of the dried layer to find the unsteady state temperature profile during freeze-drying, the heat capacity of the dried layer must be known. Therefore, determination of heat capacity C_p of the dried layer is of utmost importance.

The moisture content and other physical properties of the foodstuffs are given in Tables 5 and 6 whereas Table 7 presents values of heat capacity for different freeze-dried foodstuffs at various temperatures obtained by differential calorimetric method (Model: DSC 204 F1 Phoenix). Graphical representation of the results is shown for different foodstuffs and corresponding best-fit curve representing data sets are calculated using regression analysis. The equation of the best-fit curves are also presented, enabling one to estimate the heat capacity value for freeze-dried foodstuff at any temperature within the temperature range of 258 K to 319 K.

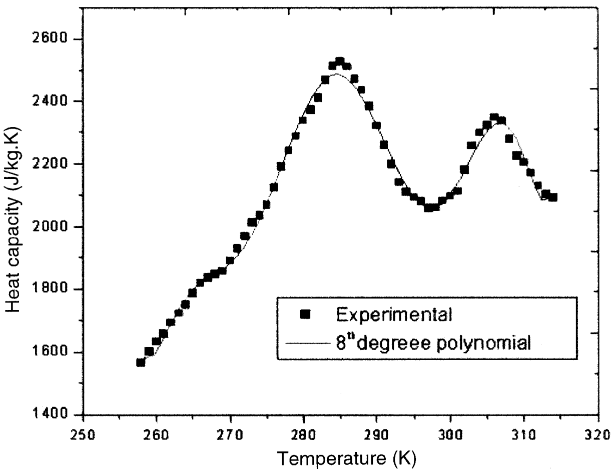

Fig. 6—Plot of heat capacity with temperature for hilsa fish

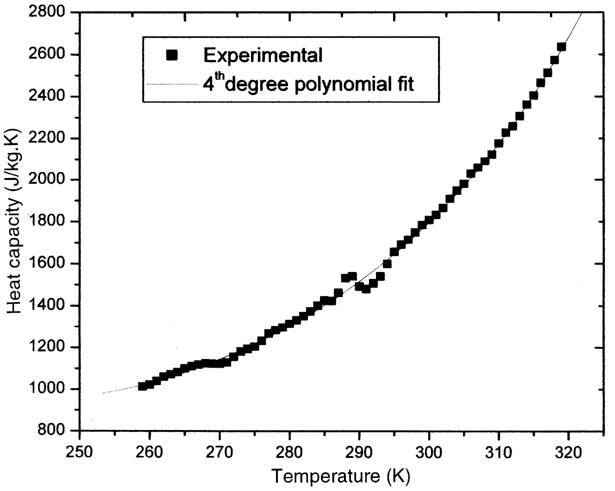

Fig. 7—Plot of heat capacity with temperature for lamb liver

Table 4— Values of constants of Eq. (5) for correlating thermal conductivities

S No.	Material	Type of freezing	*a*	*b*	*c*	Variance
1.	Paneer	Normal refrigeration	1.02425	-0.00348596	4.95751	2.64291×10^{-30}
		Liquid nitrogen dipping	0.371545	0.001035153	2.24339	3.94171×10^{-29}
2.	Mango	Normal refrigeration	0.0173383	7.31722×10^{-5}	0.0413714	3.0824×10^{-30}
		Liquid nitrogen dipping	-1.11048	0.00406419	0.20624	9.67277×10^{-31}

Table 5—Moisture content of freeze-dried foodstuffs used as representative sample for determination of heat capacity

Sample name	Moisture content (%)	Temperature of experiment (K)
Hilsa fish	5.01	378
Paneer	6.09	378
Goat lever	5.01	378
Prawn	4.95	378

Table 6—Typical values of true density, bulk density and porosity of various freeze-dried foodstuffs

Sample	True density $\times10^{-3}$ (kg / m^3)	Bulk density $\times10^{-3}$ (kg / m^3)	Porosity (%)
Paneer	1.893	0.563	70.47
Prawn	0.343771	0.212493	61.78002
Hilsa fish	1.139341	0.751373	51.6345

Table 7—Heat capacity of different freeze-dried foodstuffs at various temperatures

Temp. (K)	Paneer	Lamb liver	Prawn	Hilsa fish	Temp. (K)	Paneer	Lamb liver	Prawn	Hilsa fish
	Heat capacity$\times 10^{-3}$ (J/(Kg . k)								
258	1.40414	1.00052	0.92453	1.56219	289	2.469	1.54185	1.26123	2.38447
259	1.42813	1.01306	0.93061	1.6006	290	2.34564	1.49272	1.24152	2.3205
260	1.45313	1.0225	0.93808	1.63225	291	2.20728	1.47985	1.24697	2.26019
261	1.47252	1.04017	0.96324	1.65689	292	2.10174	1.50685	1.25718	2.19925
262	1.50016	1.06057	0.99236	1.69219	293	1.99696	1.54057	1.27165	2.1419
263	1.52272	1.07185	1.00988	1.72128	294	1.8677	1.59958	1.27906	2.11108
264	1.54137	1.08259	1.01604	1.75065	295	1.74886	1.6567	1.3211	2.0934
265	1.56267	1.0997	1.03517	1.78704	296	1.64637	1.69132	1.31338	2.07995
266	1.59156	1.11133	1.05787	1.81818	297	1.5469	1.71486	1.28279	2.05727
267	1.61104	1.118	1.07188	1.83468	298	1.47946	1.74921	1.33887	2.06049
268	1.63591	1.12495	1.08734	1.84597	299	1.44024	1.78386	1.37795	2.08281
269	1.65066	1.12232	1.09536	1.85555	300	1.42505	1.80872	1.35313	2.09843
270	1.67302	1.12219	1.11765	1.88914	301	1.44783	1.83246	1.35296	2.11221
271	1.69941	1.12851	1.12196	1.92755	302	1.52811	1.86546	1.36146	2.18113
272	1.72623	1.15543	1.12176	1.96855	303	1.64092	1.90968	1.36013	2.2573
273	1.75802	1.18093	1.14531	2.01243	304	1.75612	1.94928	1.42281	2.29769
274	1.78561	1.19353	1.15289	2.03489	305	1.85576	1.98171	1.44356	2.32173
275	1.82246	1.2037	1.15626	2.06885	306	1.94757	2.0301	1.41993	2.35024
276	1.87035	1.23191	1.16131	2.12373	307	2.00249	2.0607	1.43337	2.33735
277	1.92883	1.26618	1.18199	2.19244	308	2.03674	2.09148	1.46933	2.27684
278	1.97155	1.28347	1.18763	2.24296	309	2.07383	2.12339	1.49934	2.22533
279	1.9857	1.29662	1.1852	2.28646	310	2.11223	2.17735	1.49857	2.20535
280	2.00453	1.31364	1.20178	2.33934	311	2.0816	2.22834	1.48975	2.17183
281	2.04546	1.33153	1.21565	2.37379	312	1.99485	2.25928	1.48931	2.13163
282	2.10394	1.35171	1.22396	2.41127	313	1.89978	2.30705	1.50436	2.10415
283	2.17771	1.37466	1.26105	2.46711	314	1.83124	2.36236	1.51905	2.0923
284	2.25486	1.40115	1.23306	2.51238	315	1.78115	2.40536	1.54986	2.07963
285	2.32463	1.42595	1.17513	2.52698	316	1.75055	2.46604	1.58918	2.07403
286	2.37528	1.42422	1.19469	2.50909	317	1.72925	2.51311	1.60478	2.10447
287	2.44212	1.46259	1.24038	2.47091	318	1.73674	2.57407	1.63529	2.20518
288	2.49471	1.53236	1.27825	2.43614	319	1.76487	2.63677	1.64144	2.31572

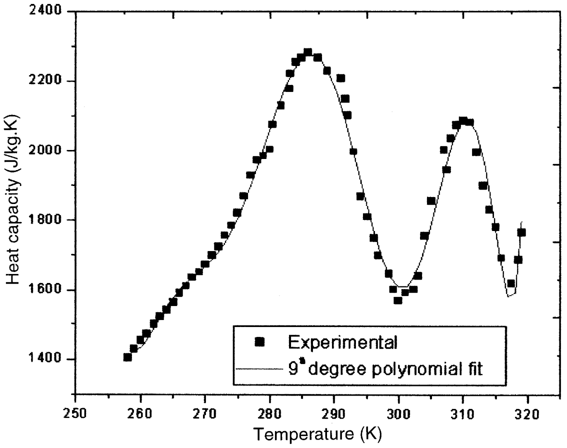

Fig. 8—Plot of heat capacity with temperature for paneer

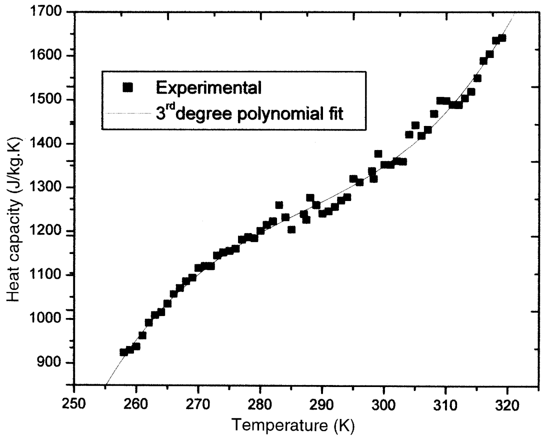

Fig. 9—Plot of heat capacity with temperature for prawn

Correlation between heat capacity and temperature

The heat capacity values of freeze-dried hilsa fish, lamb liver, paneer and prawn have been plotted (Figs 6-9) against temperature according to the data presented in Table 7. For different freeze dried food materials different degrees of polynomial curves have been found to fit the experimental data satisfactorily (Table 8).

Table 8—Values of coefficients of polynomial equations for correlating heat capacity of freeze dried substances with temperature

Sample	F_0	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	
Hilsa fish	1.08723E12	-3.06838E10	3.78562E8	-2.66677E6	1.173207E4	-0.330067E2	0.05799	-5.81766E-5	2.55133E-8	
	R-Square(COD)=0.9923, N=57, P=<0.0001									
Lamb liver	Q_0	Q_1	Q_2	Q_3	Q_4					
	2.31167994E5	-3.3426058E3	1.828306E1	-4.481E-2	4.1696E-5					
	R-Square (COD)=0.99808,N=61,P=<0.0001									
Paneer	N_0	N_1	N_2	N_3	N_4	N_5	N_6	N_7	N_8	N_9
	-3.86134E12	1.24474E11	-1.7814E9	1.48552E7	-7.954872E4	2.836743E2	-6.7366E-1	1.03E-3-	9.1286E-7	3.60124E-10
	R-Square (COD)=0.98319, N=62, P=<0.0001									
Prawn	J_0	J_1	J_2	J_3						
	-1.293744074E5	1.35172791E3	-4.6864E0	5.44384E-3						
	R-Square (COD)=0.99165, N=62, P=<0.0001									

For freeze dried hilsa fish:

$$C_{\mathrm{pH}} = F_0 + F_1 T + F_2 T^2 + F_3 T^3 + F_4 T^4 + F_5 T^5 + F_6 T^6 + F_7 T^7 + F_8 T^8 \qquad \ldots (3)$$

For freeze dried liver:

$$C_{\mathrm{pL}} = Q_0 + Q_1 T + Q_2 T^2 + Q_3 T^3 + Q_4 T^4 \qquad \ldots (4)$$

For freeze dried paneer:

$$C_{\mathrm{pP}} = N_0 + N_1 T + N_2 T^2 + N_3 T^3 + N_4 T^4 + N_5 T^5 + N_6 T^6 + N_7 T^7 + N_8 T^8 + N_9 T^9 \qquad \ldots (5)$$

For freeze dried prawn:

$$C_{\mathrm{pPR}} = J_0 + J_1 T + J_2 T^2 + J_3 T^3 \qquad \ldots (6)$$

The coefficients of the polynomial expressions have been determined using best curve fitting method using ORIGIN software and are presented in Table 8 along with statistical fit parameters.

Conclusion

The thermal conductivity and heat capacity data of freeze dried materials vary widely with temperature, pressure, moisture content as well as freezing condition. Therefore, it is very difficult to derive any general correlation for these properties. Here, correlations of thermal conductivities in linear form and heat capacities in polynomial form have been developed which could satisfactorily be used for those particular substances. From the nature of the best fit correlating curves it is advisable not to use the simulated equations beyond the range of experimental values.

Acknowledgement

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Nomenclature

a,b,c	=	Constants used in Eq. (2)
A	=	Term used in Eq. (1), dimensionless
B	=	Term used in Eq. (1), K. s
C_{pH}	=	Specific heat of freeze-dried hilsa fish, J/ (kg .K)
C_{pL}	=	Specific heat of freeze-dried lamb liver, J/ (kg .K)
C_{pP}	=	Specific heat of freeze-dried paneer, J/ (kg .K)
C_{pPR}	=	Specific heat of freeze-dried prawn, J/ (kg. K)
F_0, F_1, F_2, F_3, F_4, F_5, F_6, F_7, F_8	=	Constants used in Eq. (3)
h_{e}	=	Heat transfer coefficient external to the material being dried, W/m^2. K
h_{I}	=	Internal heat transfer coefficient, within the material being dried, W/m^2. K
ΔH_{S}	=	Latent heat of sublimation of ice (J/kg)
J_0, J_1, J_2, J_3	=	Constants used in Eq. (6)
k	=	Thermal conductivity of the dry layer, W/m.K
L	=	Thickness of foodstuff sample
ΔL	=	Thickness of the dried layer at any time during drying
M_{W}	=	Molecular weight of water
N_0, N_1, N_2, N_3, N_4, N_5, N_6, N_7, N_8, N_9	=	Constants used in Eq. (5)

P = Chamber pressure, mbar

Q_0 , Q_1 , Q_2 , Q_3 , Q_4 = Constants used in Eq. (4)

t = Time, s

T = Temperature of the dried material, K

T_e = Temperature of the heat source, K

T_f = Temperature of the sublimation front, K

V_W = Volume of the material occupied by unit weight of water initially

X = Fraction of the initial moisture remaining in the sample

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