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KINETICS AND MASS TRANSFER DURING ATMOSPHERIC FREEZE DRYING OF RED PEPPER

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Abstract: Drying is applied for moisture removal to allow safe and extended storage. Red pepper (*Capsicum annum)* samples were heat pump dried in fluidized bed at different air temperatures. A slightly modified solution of the diffusion equation was used to describe the kinetics and drying rates of red-pepper. The model well described the low and medium temperature drying processes. The determined effective mass diffusivities varied from 0.7831 to 4.0201×10^{-9} m^2/s and increased consistently with drying air temperature. The mass diffusivity was correlated to temperature by linear regression with coefficient of determination equal to 0.999 and negligible standard error.

Keywords: Fick´s law, effective mass diffusivity, models, property, quality

INTRODUCTION

The mankind has long been concerned with food supply and with the possibilities to extend its availability out-of-season. Drying is among the oldest preservation methods. The principle is to reduce the raw material moisture content and water activity to levels where the activity of spoiling agents is minimized. A properly dried product can be safely stored for a long time at nearly ambient conditions (Alves-Filho and Strømmen, 1996).

The advantage of drying as a preservation process is a relatively low cost for storage and handling of lighter dried products. However, conventional dryers have the drawback of high energy utilization, which must be addressed due to the current uncertainty of energy supply and the expectation of higher costs. Also, the recent increase in health awareness by consumers is generating a demand for higher product quality. Therefore, the new challenges for researchers and the industries are to develop new energy efficient technologies to produce enhanced quality products (Alves-Filho, 2002).

Conventional vacuum freeze dryer is used for heat sensitive materials such as pharmaceuticals and foods. The products have superior quality compared to those obtained by similar but higher temperature dryers (Song and Kim 2003, Shishehgarha et al., 2002). The disadvantages of these dryers are either long residence time or high energy consumption. To overcome drawbacks of conventional dryers research have been directed to combine low temperature drying with energy efficient heat pump technologies. A properly designed heat pump dryer uses only a fraction of the energy required by conventional convective and vacuum freeze dryers. Heat pump drying is currently industrially applied but research is continuously needed to assist in new product development, to improve performance and to increase dryer's throughput (Alves-Filho and Strømmen, 1997).

Red pepper (*Capsicum annum)* is among the products with quality dependency on drying conditions. The dried pepper fruit has been converted to powder since ancient times. Presently the dried ripped fruits are ground and used as food condiment and color ingredients (Simal et al., 2005). The color depends on capsaicin or carotenoid contents in the pepper fruit. Then, the color and spice-flavor are the product major quality attributes. The drying of pepper is done by traditional solar exposure of the material and hot air dryers. Usually, the product properties are non-uniform and the quality is reduced due to temperature variation or over-heating.

Modeling kinetics is important to control the drying conditions to attain specified quality attributes. Also, modeling is an essential tool to design new dryers and to improve performance of existing equipment. Drying kinetics correlations for different conditions are necessary to enhance the quality of the product and to reduce energy consumption (Mujumdar and Alves-Filho, 2003).

Diffusion models for kinetics for hot air drying of red peppers have been studied (Sanjuán et al., 2003, Mulet et al., 2005). India, a large producer and exporter of spices, has contributed with several publications on drying of red chili pepper at temperatures range of 45 to 65°C (Arora et.al., 2006). However, the authors are unaware of any report specific on heat pump atmospheric freeze drying of red peppers.

Therefore, this paper describes experiments on atmospheric heat pump drying of red peppers. The objectives are to study the effect of air temperature on drying kinetics and product quality, to correlate moisture content with time and mass diffusivity with temperature. The additional goals are to study the behavior of the drying rate curves and to quantify the cumulative water removal, which are linked to dryer capacity.

Equations for kinetics and drying rates

Atmospheric freeze drying process is advantageously applied for heat sensitive materials (Alves-Filho and Roos, 2006). Sublimation can proceed with minimum material depletion while keeping the structure stable during the process. However, atmospheric freeze drying is highly unsteady state process that is complex due to continuous change in transport properties as the material dries. This is related to internal and external resistances that ultimately affect the mass and heat exchange between air and product. Thus, these resistances are related to the convective boundary layer past the solid and the internal diffusion within the drying material. The transport mechanisms act simultaneously and may be described by

$$\frac{\partial x}{\partial \tau} = D_e \cdot \left(\nabla^2 x + \delta \cdot \nabla^2 t\right) \tag{1}$$

A common assumption is that the drying air enters, removes moisture of the bed of wet particles and leaves the chamber at the same wet bulb temperature as in the inlet. This is often verified in practice since atmospheric freeze drying of initially high moisture material occurs at nearly adiabatic conditions. Thus, for Cartesian coordinates Equation (1) simplifies to

$$\frac{\partial x}{\partial t} = r^2 \cdot O_d \cdot \nabla^2 x \tag{2}$$

The Fick´s second law usually holds for atmospheric freeze drying kinetics with slight modification to incorporate effects of initial material heating or cooling periods. For drying vegetable cubes at equilibrium in the solid-air interface and with specified boundary and initial conditions, the solution for Equation (2) is

$$x = \frac{8 \cdot [(x_o - x_e]}{\pi^2} \cdot \sum_{i=1}^{\infty} \frac{1}{n^2} \exp\left[-n^2 \cdot O_d (\tau - \tau_f)\right] + x_e \tag{3}$$

Where τ_f is the heating and cooling time factor and O_d is the ratio of mass diffusivity to cube half thickness squared. Then, the O_d and De account for the different contributions of the external and internal resistances (Alves-Filho, 2002).

Now, the moisture ratio is given by

$$xR = \frac{x - x_e}{x_o - x_e} = \sum_{i=1}^{\infty} \frac{8}{(\pi n)^2} \exp\left[-n^2 \cdot O_d (\tau - \tau_f)\right] \tag{4}$$

The specific drying rate is

$$N = \frac{8 \cdot [(x_o - x_e]}{\pi^2} \sum_{i=1}^{\infty} -O_d \cdot \exp\left[-n^2 (\tau - \tau_f)\right] \tag{5}$$

The cumulative water removal during drying is

$$M_w = \Gamma \cdot \int_0^{\tau_f} \left(\frac{8 \cdot [(x_o - x_e]}{\pi^2} \cdot \sum_{i=1}^{\infty} -O_d \cdot \exp\left[-n^2 (\tau - \tau_f)\right] \right) \cdot d\tau \tag{6}$$

where Γ is the ratio of the total load of dry matter to the particle surface area.

Table 1. Test conditions

Run	t,°C	x_o, %db	x_f, %db	τ, hr
1	−10	27.78	0.75	18.00
2	-5	27.78	0.11	23.89
3	-3	27.78	0.32	25.42
4	20	27.78	0.31	4.92

Even though vegetables are normally highly hygroscopic the O_d ratio may account for several drying periods. In such materials the drying rate drops sharply initially and slowdown progressively as internal mass transfer resistance increases. Also, the internal resistance increases as the surface moisture is removed and the drying front deepens inside the material. Therefore, the drying potential tends to zero as the material moisture approaches equilibrium with the surrounding air.

MATERIALS AND METHODS

Raw material and sample preparation

Fresh red peppers (*Capsicum annuum*) acquired locally were cleaned by removing residues (10.3% weight) and frozen at -25°C. Then, the freezing-room temperature was increased to -5°C to avoid pulp deformation and water loss when the frozen pepper was cut into $5x10^{-3}$ m side cubes. The batch volume used for each trial was 2 liters.

Heat pump dryer and drying tests

The red pepper drying experiments were done using a heat pump dryer with the samples placed inside a transparent cylindrical chamber with diameter of 0.25 m and height 0.5 m as illustrated in Fig. 1. The air flow was controlled in the range of 1.5 and 2.5 m/s to well fluidize the bed of samples. The different process variables such as the inlet and outlet of each component were logged and continuously recorded in files using a data acquisition system (Fluke hydra).

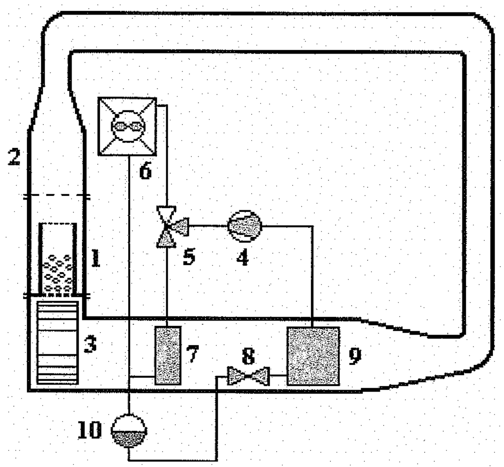

Fig. 1. Sketch of the heat pump dryer. 1: transparent drying chamber, 2: external drying chamber, 3: blower, 4: compressor, 5: three-way valve, 6: external condenser, 7: internal condenser, 8: throttling valve, 9: evaporator, 10: liquid receiver

The freezing point of fresh red pepper was determined in order to ensure that the atmospheric freeze drying trials were carried out without structural collapse. Following that, the freezing and above freezing drying air temperature was established as -3, -5, -10 and 20°C. The air velocity was kept constant during the process by a frequency inverter (Hitachi, HFC-VWS). Drying kinetics were determined taking samples at regular time intervals and measuring the moisture content.

Details on dryer, instrumentation and measurement procedures are described elsewhere (Alves-Filho, 2002).

Quality parameters

The red pepper final quality can be related to dried product color and bulk density. These parameters were measured during drying to study the possible effect of operating conditions.

A spectrocolorimeter type X–Rite 948 (CIE 1964, 10° observer and illuminant D_{65}) was used to determine the color components, L, a and b. These components are measured in color coordinates that characterize white/black (L), red/green (a) and yellow/blue (b).

The rehydration ability of pepper cubes was obtained at different temperatures and soaking times. The procedure is to pour a mass of dried samples into a screen-holder and immerse it into water bath at specific temperatures and time intervals. The selected temperatures were 20 °C and 90°C and soaking times were 30, 60, 180 and 300 seconds. The mass of the dried and wet samples were measured in triplicates and average value was determined for each test.

The bulk density was also measured by standard mass-volume method for each run prior and after drying. The bulk density is the ratio of mass to the volume of sample including the voids.

DISCUSSION OF RESULTS

The Equations (3) to (6) were correlated to experimental data and the coefficients were obtained based on minimization of the sum of squares of the residuals between the predicted and observed data. It should be noted that the temperature is the variable while the particle size and initial moisture contents are the same for all runs.

Equation (3) was used to fit the experimental drying data and the O_d ratio and effective diffusivities were determined for each run as given in Table 2.

Table 2. Equation (3) constants for all runs

Run	O_d, s^{-1}	$D_e \cdot 10^{-9}$, m^2/s	τ_f, hr
1	0.490	0.7813	0.580
2	0.860	1.4931	0.325
3	0.960	1.6667	0.098
4	2.834	4.9201	0.090

Equation (3) was used to obtain the drying curves and the results and measured data points are plotted in Figs 2-5. It is clear from the figures that the moisture decreases as the air temperature increases. The plots show a good agreement between predicted and experimental data and indicate that the curves tend asymptotically to the equilibrium moisture content.

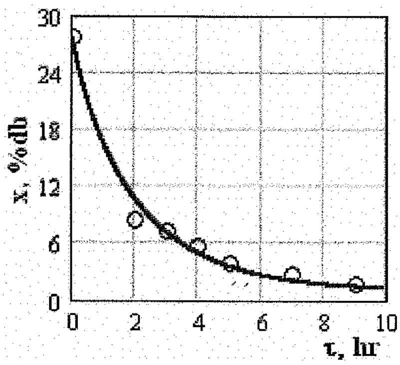

Fig. 2. Moisture content versus drying time for run 1

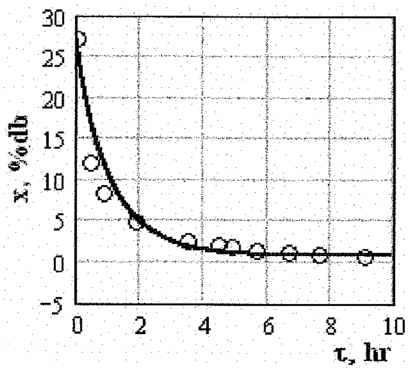

Fig. 3. Moisture content versus drying time for run 2

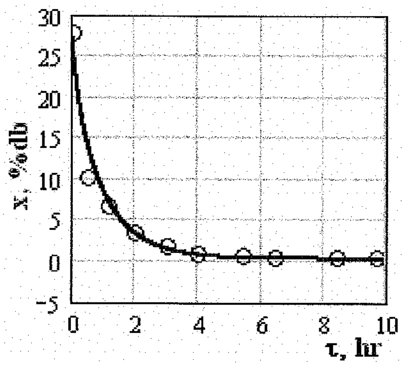

Fig. 4. Moisture content versus drying time for run 3

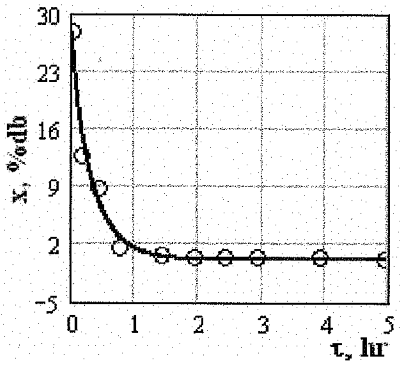

Fig. 5. Moisture content versus drying time for run 4

Equation (4) was used with constants in Table 2 to determine the moisture ratio and the plots for runs 1 and 4 are shown in Figures 6 and 7. It is evident that the drying rate depends on air temperature. This is indicated by the slope of the line of moisture ratio versus time. As expected, the moisture removal rate for run 4, dried at 20°C, is much higher than for run 1 freeze dried at -10°C. The other runs presented similar behavior.

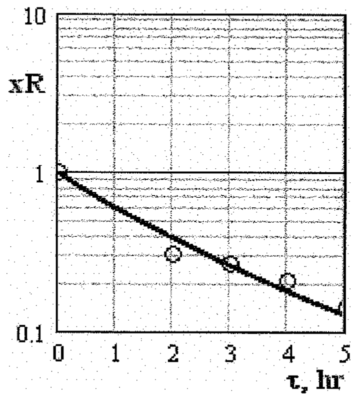

Fig. 6. Moisture ratio versus drying time for run 1

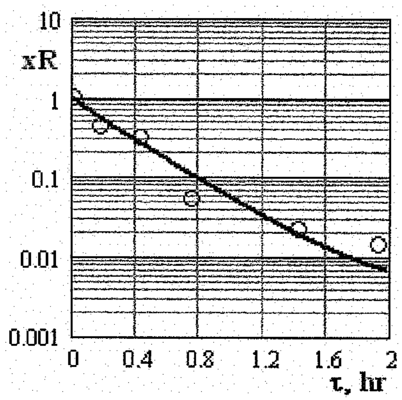

Fig. 7. Moisture ratio versus drying time for run 4

Equation (5) with the proper constants was used to compute the drying rates and the plots for all runs are presented in Figures 8-11. The drying rate curves are similar for all tests. The plots show that the rates increase as the temperature rises. This is also indicated by the increasing values of O_d ratio and effective diffusivities with the temperature as shown in Table 2. The O_d ratio for run 4 dried at 20°C is 5.8 times the value for run 1 dried at -10°C. The cumulative water removed for each run was obtained using Equation (6). These values together with total drying time, average drying rate and equilibrium moisture content obtained by desorption isotherms are given in Table 3 for all runs.

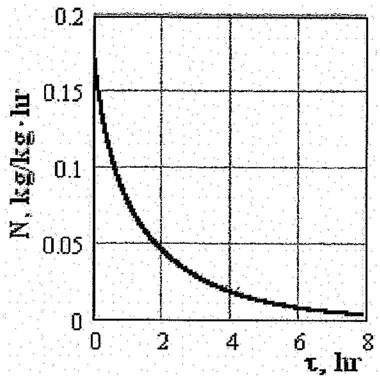

Fig. 8. Specific drying rate versus drying time for run 1

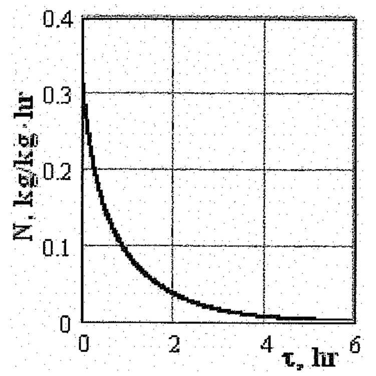

Fig. 9. Specific drying rate versus drying time for run 2

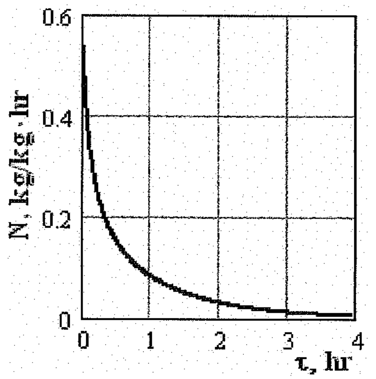

Fig. 10. Specific drying rate versus drying time for run 3

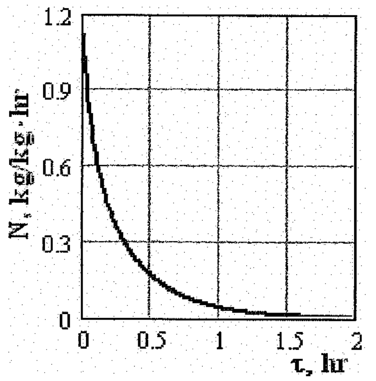

Fig. 11. Specific drying rate versus drying time for run 4

Table 3. Drying parameters to control the process and avoid over drying and energy losses

Run	1	2	3	4
M_w, g	213	221	220	220
$\Delta\tau$, hr	18.00	23.81	25.42	4.92
x_e, g/g	0.98	0.98	0.098	0.030
N_{avg}, g/hr	25.06	49.11	57.89	157.14

A first look in the drying curves may give the impression that the water removal and the drying time are similar for the runs (except for run 4). However, there is a striking difference in the mass transfer due to air temperature. When further calculation is done with Equation (6) it indicates that 98% of the moisture is removed at much shorter time than the $\Delta\tau$ used in the tests and shown in Table 2. The times for 98% water removal were 8.5, 4.5, 3.8 and 1.4 hours for runs 1, 2, 3 and 4, respectively. Using this time the average drying rates were calculated and are given in Table 3. Considering run 1 as the reference point, the average drying rates are 1.96, 2.31 and 6.27 times higher as temperature is increased from -10°C to -5, -3 and 20°C. The modeling was useful to indicate that all samples were over dried. Therefore, the drying process should have been stopped much earlier. Of course, in laboratory scale tests doubling the drying time just double the energy use in the order of a few hundreds of kilowatt-hours. However, in a full production industrial plant this over drying period would be equivalent to high unnecessary operation costs and to huge amounts of energy lost.

Once consistent values of the effective diffusivities are obtained the next step is to identify their relationship with the drying air temperature. A linear regression was used to correlate D_e with T as follows

$$D_e = -3.562\cdot10^{-8} + 1.383\cdot10^{-10}\cdot T \qquad (7)$$

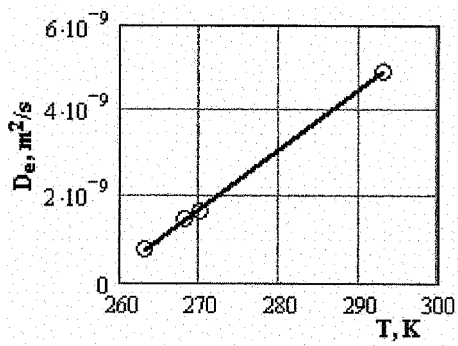

Fig. 12. Plot of the effective diffusivity versus drying air temperature for all runs. Solid line: Equation (7) and circles: test measurements

Equation (7) well describes the effective diffusivity as shown in the plot in Fig. 12. This is also confirmed by the determination coefficient with value equal to 0.999 and the standard error of $5.494 x 10^{-11}$.

The color measurements are presented in Table 4. It is observed that runs 1 and 2 have about the same brightness that is close to the raw material. The brightness of runs 1 and 2 was lower than for runs 3 and 4 dried at higher temperatures. Also, run 1 was more yellow than runs 3 and 4 while run 2 was pale yellow. However, the best color attribute was for run 4 dried at 20°C, which was slightly yellow with predominance of a sharp red color similar but more intense than the raw red pepper.

Table 4. Quality parameters for all runs and raw material

Run	ρ_b	Color components		
		L	a	b
1	97.6	30.38	33.4375	31.13
2	131.6	30.43	27.41	25.36
3	177.0	37.10	28.36	27.28
4	161.4	37.69	37.14	25.04
Raw	436.1	27.47	36.35	28.97

The dried red pepper bulk density was measured and the results are presented in Table 4. It indicates that ρ_b increases as the air temperature rises except for run 4. If -10°C is taken as the reference, the bulk density increased from 1 to 1.35, 1.82 and 1.65 times as the temperature increased from -10°C to -5, -3 and 20°C. The lightest and heaviest dried samples were for run 1 and run 3 with bulk densities equal to 97.9 and 177.0 kg/m^3 while the raw material had 436.1 kg/m^3.

Table 5. Rehydration for all runs by immersion during 60 sec in water at two temperatures

t_{im}, °C \ Run	1	2	3	4
20	2.0	2.5	1.9	1.7
90	2.5	3.0	2.6	2.1

The measurements on rehydration by immersion of dried samples into water bath at 20 and 90°C during 1 minute are presented in Table 5. It is evident that the rehydration is higher when the samples are immersed into hot than into cold water. When immersed into water at 20°C the rehydration varied from 1.7 to 2.5 times the mass of the dried samples. The lowest value was for run 4 dried at 20°C and the highest value was for run 2 dried at -5°C.

For immersion into 90° water the rehydration ranged between 2.1 to 3.0 times the mass of dried samples. The rehydration behavior was similar to the previous water temperature and again the lowest and highest values were for runs 4 and 2, respectively.

CONCLUSIONS

The trials on atmospheric heat pump drying of red pepper cubes were performed successfully. The obtained correlations well described the moisture content with drying time. The relationship between effective mass diffusivity and temperature was established for all tests with high determination coefficient and negligible standard error.

The drying rates and the cumulative water removal were in good agreement with the test data. These parameters provide essential information concerned to the best time to halt the drying process. This will have huge impact in the operation cost and energy savings in an industrial plant.

The dryer capacity increases with the air temperature and the desired red color is attained at highest test temperature. Thus, evaporation temperature such as 20°C may be successfully used to intensify the red color in the dried pepper, to reduce drying time and costs compared to sublimation temperatures.

However, when a lighter dried product and high rehydration are desired sublimation temperature is recommended. The reason is that the lowest bulk density was for -10°C and the highest rehydration was for the run dried at -5°C. Fortunately, sublimation can be easily combined with evaporation to improve the dryer capacity as well as enhance product quality dictated by optimum color, density and rehydration attributes.

NOMENCLATURE

a	color coordinate	
b	color coordinate	
D_e	effective mass diffusivity	m^2/s
L	color coordinate	
M	cumulative water removal	kg
N	specific drying rate	kg/kg·hr
n	coefficient 1, 2, ... ∞	
O_d	inverse drying time	hr^{-1}
r	particle thickness	m
T	absolute temperature	K
t	temperature	°C
x	moisture content	%db
xR	moisture ratio	

Greek letters

δ	thermal factor	kg/kg·K
Γ	ratio of dry matter to surface area	kg/m^2
ρ	density	kg/m^3

τ	time	hr
τ_f	heating and cooling time factor	s

Subscripts

avg	average
b	bulk
e	equilibrium
f	final
im	immersion
o	initial
w	water

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REFERENCES

Alves-Filho, O. and Y.H. Roos (2006), Advances in multi-purpose drying operations with phase and state transitions, Drying Technology, Vol. 24, No. 3, pp. 383-396.

Alves-Filho, O. (2002), Combined innovative heat pump drying technologies and new cold extrusion techniques for production of instant foods, Drying Technology, Vol. 20, No. 8, pp. 1541-1557.

Alves-Filho, O. and I. Strømmen (1997), Simulation model of heat pump dryer for fruits and roots, Drying Technology, Vol. 15, No. 5, pp. 1369-1398.

Alves-Filho, O. and I. Strømmen (1996), The application of heat pump in drying of biomaterials, Drying Technology, Vol. 14, No. 9, pp. 2061-2091.

Arora, S., S. Bharti and V.K. Sehgal (2006), Convective drying kinetics of red chillies, Drying Technology, Vol. 24, No. 3, pp. 189-193.

Mujumdar, A.S. and O. Alves-Filho (2003), Drying research-current state and future trends, CD-ROM Proceedings, 2nd Nordic Drying Conference (NDC'02), Copenhagen, Denmark, June 25-27, 2003, ISBN 82-594-2550-5.

Mulet, A., M. Blasco, J. García-Reverter, J.V. García-Pérez (2005), Drying kinetics of Curcuma longa Rhizomes, Journal of Food Science, Vol. 70, No. 5, pp. 318-323.

Sanjuán, N., M. Lozano, P. García-Pascual and A. Mulet (2003), Dehydration kinetics of red pepper (Capsicum annuum L var Jaranda), J. Sci. Food Agric., Vol. 83, pp. 697–701.

Shishehgarha F., J. Makhlouf and C. Ratti (2002), Freeze-drying characteristics of strawberries, Drying Technology, Vol. 20, No. 1, pp. 131-145.

Simal, S., M.C. Garau, A. Femenia and C. Rosselló (2005), Drying of red pepper (Capsicum Anuum): water desorption and quality, International Journal of Food Engineering, Vol. 1, No. 4, Article 1.

Song, C.S. and C.J. Kim (2003), Freeze-drying of Skim milk in a cylinder container, Drying Technology, Vol. 21, No. 9, pp. 1811-1838.