Available online at www.sciencedirect.com
ScienceDirect
Journal of Food Engineering 81 (2007) 127–132
JOURNAL OF FOOD ENGINEERING
www.elsevier.com/locate/jfoodeng

Diffusive model with variable effective diffusivity considering shrinkage in thin layer drying of chitosan

Lucia M. Batista [a], Cezar A. da Rosa [b], Luiz A.A. Pinto [c,*]

[a] Food Engineering, Fundação, Universidade Federal do Rio Grande – FURG, P.O. Box 474, 96201900 – Rio Grande, RS, Brazil
[b] Chemical Engineering, Fundação, Universidade Federal do Rio Grande – FURG, P.O. Box 474, 96201900 – Rio Grande, RS, Brazil
[c] Department of Chemistry – Fundação, Universidade Federal do Rio Grande – FURG, P.O. Box 474, 96201900 – Rio Grande, RS, Brazil

Received 5 April 2005; received in revised form 23 August 2006; accepted 24 October 2006
Available online 14 December 2006

Abstract

In the thin layer drying of chitosan, a diffusive model considering the material volume change was used, due to the occurrence of shrinkage during the operation. The samples were placed in a rectangular tray with 4 mm of thickness, and inserted in the discontinuous dryer, with parallel air flow at 60 °C of temperature and air speed of 1.5 m/s. The sample shrinkage occurred in the thickness, and the linear shrinkage coefficient was constant. In the model, variable moisture effective diffusivity and equilibrium conditions at the material surface were considered. The dimensionless second order non linear partial differential equation, resulting from the model, was solved numerically by the finite differences technique. A good agreement between the numerical data of the average moisture content, obtained by the model, and the experimental data was observed.

Keywords: Chitosan; Shrinkage; Diffusive model; Drying

1. Introduction

Chitosan is a commercially available material, whose stability, chemical properties, and biocompatibility have led to many industrial applications. These include pharmaceutical, biomedical and food material and waste water treatment (Ayers & Hunt, 2001; Chen & Hwab, 1996). The cationic characteristic of the chitosan offers an opportunity to take advantage of its electrostatic interaction properties. Chitosan films are used in the separation of ethanol from water by evaporation, water purification and controlled release of pharmaceuticals (Srinivasa, Ramesh, Kumar, & Tharanathan, 2004). The drying operation is important in chitosan production since this step shall guarantee that the necessary moisture content for the product storage be reached (6–8% w.b.) without causing alterations in the material.

Study of drying in the food products processing has been used more and more aiming at the production of the dehydrated foods of good characteristics (Ibanoglu & Maskan, 2002; Márquez, Michelis, & Giner, 2006; Ramesh, Wolf, Tevini, & Jung, 2001; Teixeira & Tobinaga, 1998; Waananen & Okos, 1996). The physical and transport properties and the shrinkage of the material are also very important parameters for the formulation and resolution of physical–mathematical models that explain the mass and heat transfers along the drying operation (Fortes & Okos, 1980).

The theory of water migration by diffusion represented by the Fick's second law, expressed in terms of moisture content gradient, is largely used when studying drying of different food products, for presenting a good agreement between experimental and predicted values (Chirife, 1983).

The moisture effective diffusivity is an important transport property in food drying processes modeling, being a function of temperature and material moisture content.

* Corresponding author. Tel.: +55 53 233 8648; fax: +55 53 233 8745.
E-mail addresses: lucia@vetorialnet.com.br (L.M. Batista), eqmcezar@click21.com.br (C.A. da Rosa), dqmpinto@furg.br (L.A.A. Pinto).

0260-8774/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jfoodeng.2006.10.014

Notation

A	drying area (m^2)
D_{EF}^{S}	moisture effective diffusivity of the solid (m^2/s)
D_{EF}^{V}	volumetric moisture effective diffusivity (m^2/s)
Fo	number of Fourier (dimensionless)
L	sample thickness (m)
L_S	sample thickness of the dry solid (m)
m_{ss}	dry solid mass (kg_{dS})
t	time (s)
X	local moisture content of the sample (d.b.) (kg_{H2O}/kg_{dS})
X^*	dimensionless local moisture content of the sample (d.b.) (dimensionless)
$\bar{X}$	average moisture content of the sample (d.b.) (kg_{H2O}/kg_{dS})
X_C	critical moisture content of the sample (d.b.) (kg_{H2O}/kg_{dS})
X_E	equilibrium moisture content of the sample (d.b.) (kg_{H2O}/kg_{dS})
X_{TRANS}	transition moisture content of the sample (d.b.) (kg_{H2O}/kg_{dS})
Y	dimensionless free moisture content (dimensionless)

Greek letters

α	linear shrinkage coefficient (kg_{dS}/kg_{H2O})
α^*	dimensionless linear shrinkage coefficient (dimensionless)
ρ_{ds}	density of the dry solid (g/cm^3)
ξ	space coordinate (m)
ξ^*	dimensionless space coordinate (dimensionless)

However, due to the complex food composition and physical structure, accurate estimates of this property are difficult to obtain, thus leading to the need of experimental measurements, as reported by Vagenas and Karathanos (1993). According to these authors, when the parameter is considered to vary, it is calculated through the application of the slopes method.

For materials that present shrinkage, the use of Fick's second law solutions is not possible as integration domain is not constant. A model equation considering material shrinkage, for the local moisture content profile, was used by Kechaou and Roques (1989) and Bonazzi et al. (1997). The authors used this model in the study of the gel slabs drying, with 2.0 mm and 1.2 cm of thickness, respectively, determining the local profile of moisture content in function of the thickness, which was variable with time.

Viollaz and Suarez (1991) and Pinto and Tobinaga (1994) presented a diffusive model including shrinkage in the dimensionless form, considering the volumetric effective diffusivity constant and equilibrium at the material surface (Eq. (1)).

$$\left(\frac{\partial X^*}{\partial Fo}\right) = \frac{\partial}{\partial \xi^*}\left(\frac{1}{(1+\alpha^* X^*)^2}\frac{\partial X^*}{\partial \xi^*}\right) \quad (1)$$

Viollaz and Suarez (1991) used this procedure in the potato drying, while Pinto and Tobinaga (1994) used this model for the study of fish muscle drying.

Volume variation of food during drying is analyzed through the coefficient of linear shrinkage (α), that is related to the material thickness, similar to the equation of thermal expansion determination, as described in Pinto and Tobinaga (2006). The authors determined the linear shrinkage coefficient for fish muscle, which was practically constant during the constant rate period and the first phase of the falling rate of drying.

The aim of this work was to study the thin layer drying modeling of purified chitosan, in paste form, considering shrinkage along the process and to determine the physical and transport properties of this material.

2. Material and methods

The raw material used was purified chitosan obtained from shrimp residuals, in the Laboratory of Unit Operations/DQ/FURG.

Raw material characterization of moisture content and Nitrogen-total was performed according to analytical methods of AOAC (1995). The factor of correction of the analysis of Nitrogen-total for chitosan, (N-chitosan) was an 11.5 value. This factor is the relationship of present nitrogen in the chitin monomer.

Drying of chitosan was performed in thin layer, using a discontinuous tray dryer, having the tray a rectangular form (12 cm of width and 14 cm of length) with thickness of 4 mm. Air drying conditions were: temperature of 60 °C and air velocity of 1.5 m/s. Two replicates were run to verify the reproducibility of the results.

The determining of the sample mass was done through an electronic scale adapted to the drier with 0.01 g precision. Dry bulb temperatures before and after the tray and the wet bulb temperature at the dryer exit were measured by (copper–constantan) thermocouples, with precision of 1.0 °C. Air velocity was measured by an anemometer of 0.1 m/s of accuracy.

Measurements of mass and temperature were taken every 5 min, during the drying experiments. The samples were dried until constant weight, to obtain the dynamic equilibrium moisture content. Sample thickness was verified every 30 min, with the use of a digital caliper (MITUTOYO, model CD-6 CS).

Drying curves of dimensionless moisture content in function of the time and the drying rate in function of the material moisture content were used for the determination of the constant and the falling rate periods of the drying.

A linear fit for the thickness variation with moisture content was performed, according to Eq. (2), to calculate the linear shrinkage coefficient.

$$L = L_S(1 + \alpha X) \tag{2}$$

Moisture effective diffusivity values evaluated through slopes method (Eq. (3)), were adjusted as a function of the moisture, so that it could be used in the model.

$$D_{EFF} = \left[\frac{(dY/dt)_{exp}}{(dY/dF_o)_{Teo}}\right] L^2 \tag{3}$$

where, $(dY/dt)_{exp}$ is calculated from the plot of dimensionless free moisture content in function of time, obtained from drying experimental data, and $(dY/dFo)_{Teo}$ from the theoretical curve of the diffusion of moisture content, presented by Keey (1972).

A procedure suggested by Crank (1975) was used to analyze the shrinkage phenomenon during drying of purified chitosan. The continuity equation given by Eq. (4) is used for rectangular geometry, infinite slab, quasi-isothermal process, unidirectional transport and density of the sample during drying independent of the position.

$$\frac{\partial X}{\partial t} = \frac{\partial}{\partial \xi}\left(D^S_{EFF}\frac{\partial X}{\partial \xi}\right) \tag{4}$$

where ξ is considered along the diffusion path, and measured from the initial position of the sample, so that an increment of ξ includes an equal increment in the amount of dry solid, and as this remains constant, the integration domain is constant.

As the shrinkage was only considered in the normal direction, the effective diffusivity based on the dry solid mass can be written in function of the volumetric effective diffusivity, in the form of Eq. (5), according to Crank (1975):

$$D^S_{EFF} = D^V_{EFF}\left[\frac{\rho_b}{\rho_{ds}(1+X)}\right]^2 \tag{5}$$

Considering shrinkage only in the thickness, the definition of L and L_S is presented by Eqs. (6) and (7):

$$L = \frac{m_{ds}(1+X)}{A\rho_b} \tag{6}$$

$$L_s = \frac{m_{ds}}{A\rho_{ds}} \tag{7}$$

Substituting Eqs. (6) and (7) in Eq. (2), then Eq. (5) can also be written in the form of Eq. (8).

$$D^S_{EF} = D^V_{EF}\left[\frac{1}{(1+\alpha X)}\right]^2 \tag{8}$$

Substituting Eq. (8) into Eq. (4), in the dimensionless form, according to Pinto and Tobinaga (2006), Eq. (9), used for the falling rate period of the drying, was obtained.

$$\frac{\partial X^*}{\partial t/L_S^2} = \frac{\partial}{\partial \xi^*}\left[\frac{D^V_{EF}(X^*)}{(1+\alpha X)^2}\frac{\partial X^*}{\partial \xi^*}\right] \tag{9}$$

With the following initial and boundary conditions, considering equilibrium at the surface.

$$\text{initial}: t = 0 \quad 0 < \xi < 1.0 \Rightarrow X^* = 1.0$$

$$\text{boundary}: \xi^* = 0; \quad t > 0 \Rightarrow \left(\frac{\partial X^*}{\partial \xi^*}\right) = 0$$

$$\xi^* = 1.0; \quad t > 0 \Rightarrow X^* = \frac{X_E}{X_C} : \xi^* = 1;$$

$$t > 0 \Rightarrow X^* = \frac{X_E}{X_C}$$

The average moisture content is given by Eq. (10).

$$\bar{X}^*_{(t)} = \int_0^{1.0} X^* d\xi^* \tag{10}$$

where the dimensionless variables X^*, ξ^* and α^* are defined in Eqs. (11)–(13):

$$X^* = (X/X_C) \tag{11}$$

$$\xi^* = (\xi/L_{(S)}) \tag{12}$$

$$\alpha^* = \alpha X_C \tag{13}$$

The technique of finite differences and fourth order Runge–Kutta method with variable step were used, for local profile moisture content determination, and the Simpson's method was used to obtain the average moisture content profile.

3. Results and discussion

Raw material results of characterization of purified chitosan were N-chitosan equal to $9.1 \pm 1.0\%$.

Chitosan initial moisture content used for the drying experiments was of 8.8 ± 0.2 (dry basis). Dimensionless moisture content as a function of time and drying rate as a function of the moisture content (Figs. 1 and 2),

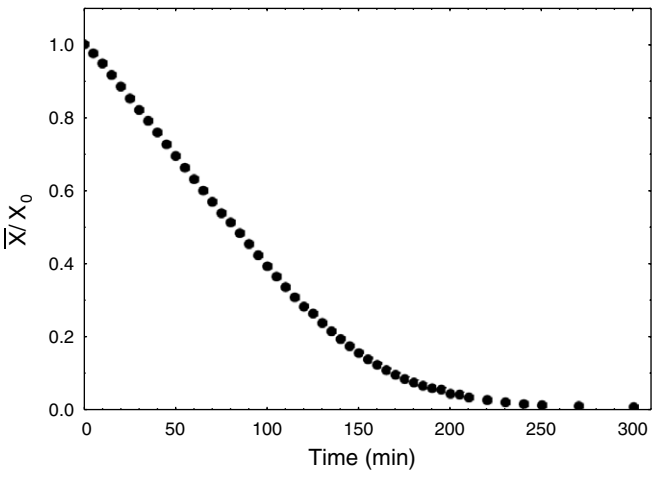

Fig. 1. Drying curve of the dimensionless moisture content as a function of time.

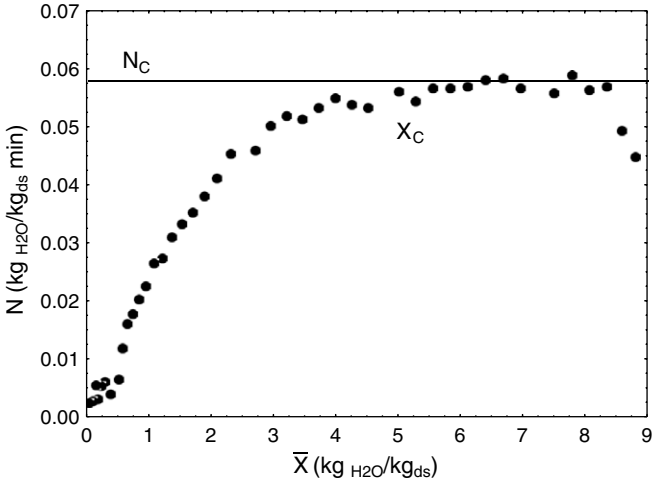

Fig. 2. Drying rate curve in function of the average moisture content.

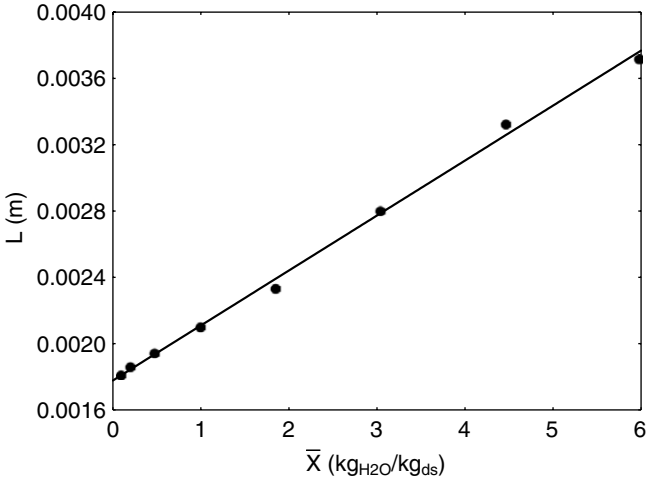

Fig. 4. Thickness of the samples in function of the moisture content.

respectively, show two different drying periods: the constant and falling rate periods.

The last point fitting the horizontal line in Fig. 2 corresponds to the critical moisture content (X_C), of 5.0 ± 0.5 (d.b.).

The falling rate period can be divided in two phases, the first and second falling rate periods, as can be seen in Fig. 3. The transition moisture content is where phase changes happen, it has $X_{TRANS} = 0.10$ (d.b.). Equilibrium moisture content (X_E=0.04 d.b.) was reached when the mass remained constant.

Experimental data of the thickness as a function of the moisture content (d.b.) were fitted by Eq. (2), where L_S was 0.00173 m. The data can be observed in Fig. 4. The equation used presented a correlation of 99.76%, and the obtained value of α was of 1.57. The linear shrinkage coefficient obtained in this work was very close to the one obtained by Viollaz and Suarez (1991), equal to 1.55, for the potato slabs.

The volumetric effective diffusivity was correlated with the dimensionless material moisture content, for the falling rate period, through a linear-exponential equation (Eq. (14)).

$$D_{EF}^{V}(X^*) = D_0 + aX^* \exp(bX^*) \tag{14}$$

where D_0 is the effective diffusivity of the dry solid (m^2/s), "a" is adjust parameter (m^2/s) and "b" is adjust parameter (dimensionless).

A good fit was reached, with a correlation coefficient of 0.996, obtained by non linear regression method, as presented in Fig. 5, and the values of the parameters are presented in Eq. (15).

$$D_{EF}^{V}(X^*) = 1.26 \times 10^{-11} + 1.52 \times 10^{-8} X^* \exp(-4.93X^*) \tag{15}$$

Fig. 6 presents the results of the solution of the diffusive model considering linear shrinkage, with variable volumetric effective diffusivity (Eq. (9)) given as the local profile of the dimensionless moisture content of the material, during the falling rate period, for different drying times.

The diffusive model considering linear shrinkage (Eq. (9)) represents well the mechanism of water migration of

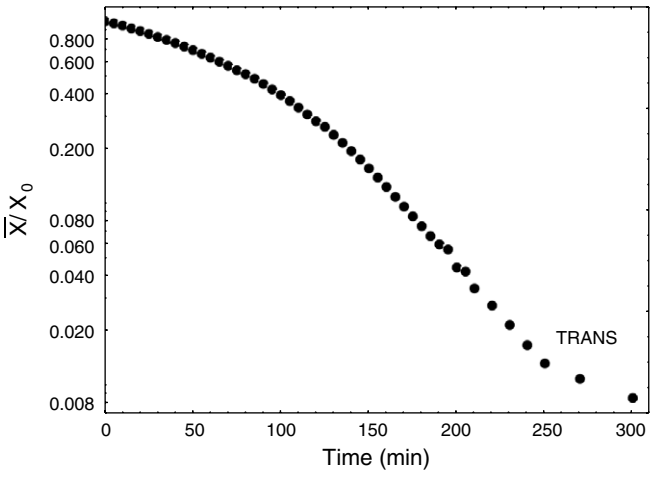

Fig. 3. Drying curve of the dimensionless moisture content as a function of time, in semi-log scale.

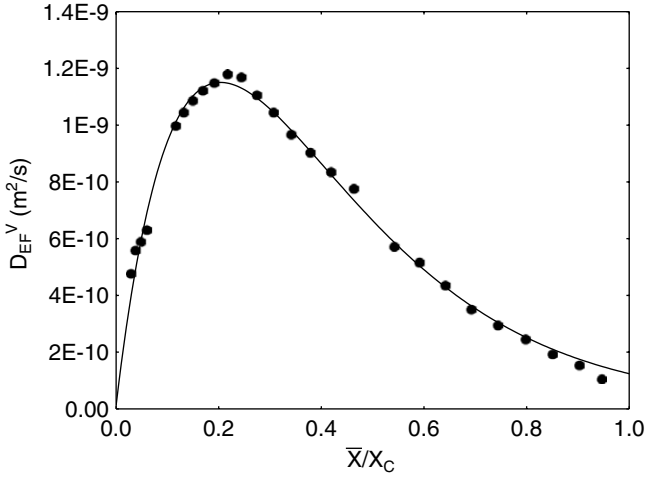

Fig. 5. Volumetric effective diffusivity as a function of the dimensionless moisture content.

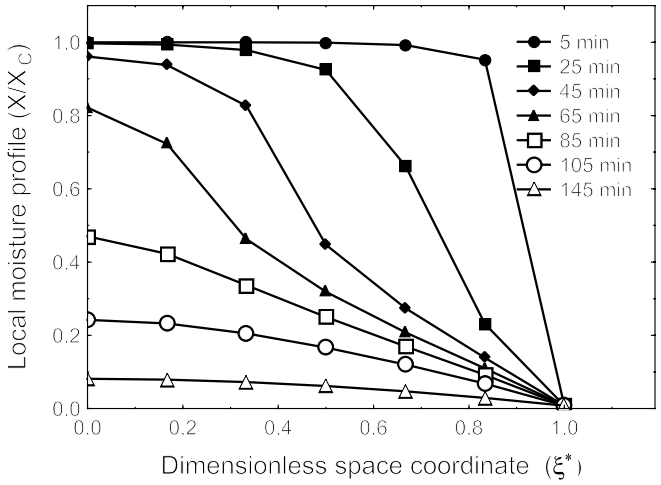

Fig. 6. Profile of local dimensionless moisture content of the material, for the falling rate period.

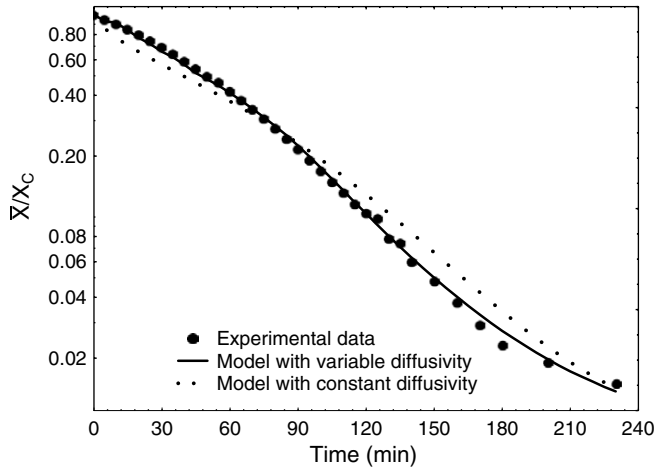

Fig. 7. Average moisture profile of the material, for the falling rate periods of drying; experimental data and the presented models.

the purified chitosan, in the falling rate period, as a good agreement with the experimental data (Fig. 7) was obtained. The solution of the diffusive model considering shrinkage with volumetric effective diffusivity as a function of the moisture content presented a better agreement with the experimental data than the diffusive model considering this transport parameter constant (Eq. (1)), as presented in Fig. 7.

4. Conclusion

The drying occurred during the constant rate period and mainly in the first phase of the falling rate period. It was observed that the transition moisture was close to the commercial moisture content of the chitosan. Thus, the second falling rate phase was neglected. A significant shrinkage took place in material thickness along the drying operation, presenting a linear behavior with material moisture content.

The diffusive model, considering shrinkage, presented a good agreement to the experimental data. The model considering the variable volumetric effective diffusivity presented better agreement with the average profile of the experimental data, when compared with the same model considering this parameter constant.

Acknowledgement

This work was supported by CAPES (Brazilian Agency for Improvement of Graduate Personnel), CNPq (National Council of Scientific and Technological Development) and FAPERGS (Fundation for Research Support from Rio Grande do Sul State).

References

Association of official Analytical Chemists (AOAC) (1995) (16th ed.). *Official methods of analysis* (Vol. 1). Arligton/USA: AOAC International.

Ayers, M. R., & Hunt, A. J. (2001). Synthesis and properties of chitosan–silica hybrid aerogels. *Journal of Non-Crystalline Solids, 285*, 123–127.

Bonazzi, C., Ropoche, A., & Michon, C. (1997). Moisture diffusion in gelatin slabs by modeling drying kinetics. *Drying Technology, 15*(6-8), 2045–2059.

Chen, R. H., & Hwab, H. D. (1996). Effect of molecular weight of chitosan with the same degree of deacetylation on the thermal, mechanical, and permeability properties of the prepared membrane. *Carbohydrate Polymers, 29*, 353–358.

Chirife, J. (1983). Fundamentals of the drying mechanism during air dehydration of foods. In A. Mujumdar (Ed.). *Advances in drying* (Vol. 3, pp. 73–102). Washington/New York/London: Hemisphere Publishing Corporation.

Crank, J. (1975). *The mathematics of diffusion* (2nd ed.). Great Britain, Oxford: Claredon Press, p. 414.

Fortes, M., & Okos, M. R. (1980). Drying theories: their bases and limitations as applied to food and grain. In A. Mujumdar (Ed.). *Advances in drying* (Vol. 1, pp. 119–154). Washington: Hemisphere Publishing Corporation.

Ibanoglu, S., & Maskan, M. (2002). Effect of cooking on the drying behaviour of tarhana dough, a wheat flour–yoghurt mixture. *Journal of Food Engineering, 54*, 119–123.

Kechaou, N., & Roques, M. (1989). A variable diffusivity model for drying deformable. In A. S. Mujumdar & M. Roques (Eds.), *Drying 89* (pp. 332–338). New York: Hemisphere Publishing Company.

Keey, R. B. (1972). *Drying: principles and practice. International series of monographs in chemical engineering*. Pergamon Press, p. 13.

Márquez, C. A., Michelis, A., & Giner, S. A. (2006). Drying kinetics of rose hip fruits (*Rosa eglanteria* L.). *Journal Food Engineering, 77*, 566–574.

Pinto, L. A. A., & Tobinaga, S. A (1994). Diffusional model with shrinkage during drying of fish muscles. In: 9th international drying symposium, Gold Coast, Australia. (Vol. B, pp. 1069–1076).

Pinto, L. A. A., & Tobinaga, S. (2006). Diffusive model with shrinkage in the thin layer drying of fish muscles. *Drying Technology, 25*(4), 509–516.

Ramesh, M. N., Wolf, W., Tevini, D., & Jung, G. (2001). Influence of processing on the drying of spice paprika. *Journal of Food Engineering, 49*, 63–72.

Srinivasa, P. C., Ramesh, M. N., Kumar, K. R., & Tharanathan, R. N. (2004). Properties of chitosan films prepared under different drying conditions. *Journal of Food Engineering., 63*(1), 79–85.

Teixeira, M., & Tobinaga, S. (1998). A diffusion model for describing water transport in round squid mantle during drying with

a moisture-dependent effective diffusivity. *Journal of Food Engineering, 36*, 169–181.

Vagenas, G. K., & Karathanos, V. T. (1993). Prediction of the effective moisture diffusivity in gelatinized food systems. *Journal of Food Engineering, 18*, 159–179.

Viollaz, P., & Suarez, C. (1991). Shrinkage effect on drying behavior of potato slabs. *Journal of Food Engineering., 13*, 103–114.

Waananen, K. M., & Okos, M. R. (1996). Effect of porosity on moisture diffusion during drying of pasta. *Journal of Food Engineering, 28*, 121–137.