Original Article

DRYING OF PINEAPPLE SLICES *IN NATURA* AND PRE-OSMODEHYDRATED IN INVERTED SUGAR

SECAGEM DE FATIAS DE ABACAXI IN NATURA E PRÉ-DESIDRATADAS OSMOTICAMENTE EM AÇÚCAR INVERTIDO

Pedro Amorim BERBERT[1]; Marcia Terezinha Ramos de OLIVEIRA[2]; Ana Paula MARTINAZZO[3]

1. Professor, Ph.D.; Agricultural Engineering Laboratory, Northern Rio de Janeiro State University – UENF, Campos dos Goytacazes, RJ, Brasil. pberbert@uenf.br; 2. Postdoctoral Researcher, Northern Rio de Janeiro State University – UENF, Campos dos Goytacazes, RJ, Brasil; 3. Professor, D.Sc., Department of Agribusiness, Federal University of Rio de Janeiro – UFF, Volta Redonda, RJ, Brasil.

ABSTRACT: This research describes the drying kinetics and compares the convective drying rates of *in natura* and osmodehydrated pineapple slices in inverted sugar. The effective moisture diffusivity during air drying was estimated using Fick's second law of diffusion. The suitability of a theoretical liquid-diffusion model and seven semi-theoretical mathematical models for use in describing the experimental drying curves was also evaluated. Goodness of fit between experimental and predicted values was based on the root mean square error, mean absolute percentage error, mean bias error, agreement index, residual plot analysis and the principle of parsimony. Osmotic dehydration was conducted in 155, 310, and 465 mL L^{-1} osmotic solutions, at 40 and 50 ºC for 2 h at 60 rpm. Convective drying was performed in a tray cabinet dryer using heated ambient air at 60 ºC and 1.15 m s^{-1}. Osmotic pretreatment facilitated water removal during the first hours of drying, a trend that was reversed towards the end of the process for samples osmodehydrated at the highest solution concentration. The effect of the osmotic pretreatments on drying rate was negligible at 40 °C, but at 50 °C the rate of moisture removal was more intense for samples *in natura* and osmodehydrated at the lowest solution concentration. Effective moisture diffusivity increased with temperature and solution concentration. The single-exponential, three-parameter semi-theoretical drying model gave the best predictions of the drying curves of pineapple slices both *in natura* and pre-osmodehydrated in inverted sugar.

KEYWORDS: *Ananas comosus* (L) Merrill. Dewatering-impregnation. Drying rate. Error analysis. Fruit dehydration. Mathematical modeling.

INTRODUCTION

Mathematical models employed to describe fruit drying have been widely investigated in the area of pre-processing agricultural products either to elucidate the physical mechanisms involved in the process or simply to describe the kinetics of drying. There are studies that address the topic from theoretical models of drying, which employ partial differential equations to describe the processes of energy and mass transfer that occur within these products. Besides the mechanisms of internal transfer, the mechanisms of external transfer that occur in various types of convective dryers must also be considered.

The use of osmotic dehydration as a preliminary step in convective drying of fruits has been the subject of several studies. This combination of methods allows for the generation of dehydrated products that retain sensory and nutritional characteristics that more closely resemble those observed in fruit *in natura* (FORNI et al., 1997; QUEIROZ et al., 2007). Osmotic dehydration is the immersion of fruit, whole or sliced, in concentrated solutions of one or more types of solute, usually sugars. Among the solutes used in the osmotic dehydration of fruits that replace the use of concentrated sucrose solutions are maltodextrin, maltose, mannitol and sorbitol. In contrast, despite all the advantages related to its use, there are relatively few studies on the osmotic dehydration of fruit using an inverted sugar solution as the osmotic agent. Inverted sugar syrup is obtained by the hydrolysis of sucrose solutions, and the degree of solution inversion represents the intensity of the breakdown of the molecules into two constituent monosaccharides: glucose and fructose (DIONELLO et al., 2007).

Knowledge of the effect of osmotic pretreatment on the drying rate by convection can assist in establishing the best operating conditions of this combined system for fruit preservation. Moreover, the drying characteristics of any product, including the evaluation of mathematical models that best describe the process, are important in selection and development of equipment as well as calculation of operating costs. Therefore, the objective of this study was to investigate the drying

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kinetics and the rate of convective drying of pineapple slices, both *in natura* and pre-osmodehydrated in diluted solutions of inverted sugar, as well as to assess the suitability of a theoretical liquid-diffusion model and of seven semi-theoretical mathematical models to describe the experimental drying curves.

MATERIALS AND METHODS*

*Nomenclature and meaning of mathematical and Greek symbols and subscripts are given in Appendix 1.

Sample preparation, osmotic dehydration, and convective drying

Fifty pineapples (*Ananas comosus* (L.) Merrill) of the *Pérola* variety supplied by producers in the north and northwest regions of Rio de Janeiro state were used. The crop was harvested when the fruit cluster centers were yellow (subgroup "painted"). Only fruit with a mass between 1.2 and 1.5 kg (Class 2) were selected, which, after transport to the laboratory, were stored in chambers at 10 ºC and were removed only to conduct the experiment when more than 50% of the clusters were completely yellow (subgroup "yellow").

Once the crowns were removed, the fruit was washed in tap water and immersed in neutral commercial detergent for hygienization at 1% for 15 min and submerged in chlorinated water for sanitization (8-10 ppm active chlorine) for 10 min. After this procedure, the fruit was rinsed with distilled water and then manually cut into slices or rings with a mean thickness of 10 mm. Immediately after, four samples were cut from each slice in the shape of an arc (Figure 1).

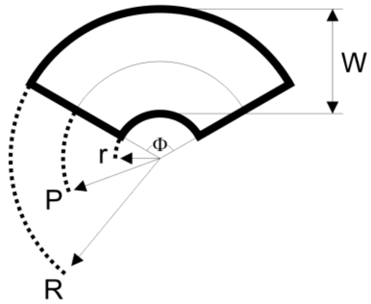

Figure 1. Arc-shaped pineapple sample.

The samples were then subjected to bleaching by exposing them to water vapor for 1 min followed by immediate transfer to plastic bags so that the samples could be cooled in an ice bath for 1 min. Subsequently, the samples were immersed in 1% ascorbic acid for 5 min to avoid non-enzymatic browning. The process of osmotic dehydration was conducted with the use of benchtop shakers containing B. Braun Biotech International incubator chambers (model Certomat U/HK) using three 500 mL beakers in each shaker and employing a fruit:syrup ratio of 1:10 (by mass).

The type of osmotic agent used was inverted sugar syrup (brand name Gludex 216 provided by Dulcini Food – São Paulo, Brazil), with an inversion rate higher than 90% and density of 1,290 g L^{-1}. The samples were dehydrated in diluted solutions with concentrations of 155, 310 and 465 mL of inverted sugar per liter of distilled water. In this experiment, two temperature levels for the solution were examined (40 °C and 50 °C), with a shaking speed of 60 rpm and 2 h immersion time. Apart from the tests that included a prior dehydration stage by immersion-impregnation, in which the samples were subsequently dried by convection, an additional treatment was used, without pre-osmodehydration. In this treatment, the *in natura* samples were also bleached and immersed in a solution of ascorbic acid before drying.

Convective drying was performed using a tray dryer prototype capable of providing controlled conditions of temperature and drying air flow. The drying chamber consisted of three trays of 0.50 x 0.62 m, which were constructed of galvanized steel mesh and arranged horizontally to provide tangential airflow. Convection drying was performed by arranging the samples on small trays (0.15 x 0.15 m) with perforated bases, which were constructed from aluminum mesh and then placed on top of the trays for convective drying. Drying was performed at 60 °C and at a drying air velocity of 1.15 m s^{-1}.

The water content determination throughout the drying process was performed by gravimetry. The samples were weighed at time 0 as well as at 15, 45, 75 and 120 min and at 60 min intervals after 120 min until the end of the drying process. Drying was stopped when the samples reached water content between 15-18% w.b. Water content was determined before the drying process (i.e., at the end of pre-osmotic dehydration) and after the drying process using a vacuum oven at 70 °C for 24 h.

Theoretical and semi-theoretical mathematical drying models

The Fick's second law of diffusion will be used to describe the movement of moisture by liquid diffusion as the principal mass transfer mechanism during convective drying. Assuming that the medium is isotropic, the diffusion coefficient is constant and the volume shrinkage is negligible, Fick's second law in three-dimensional space can be written as:

$$\frac{\partial M}{\partial t} = D_{eff} \nabla^2 M \qquad (1)$$

If D_{eff} is assumed to depend on position in the product, or on moisture content or temperature, then Equation 1 may be replaced by

$$\frac{\partial M}{\partial t} = \nabla\left[D_{eff}\left(\nabla M\right)\right] \qquad (2)$$

In order to solve any model such as those given by Equations 1 and 2 an appropriate geometric shape must be assumed for the approximate representation of the individual sample, i.e., slab, cylinder or sphere. In the case of one-dimensional diffusion in a medium bounded by two parallel planes (infinite slab) considered so thin that effectively all the mass transfer occurs through the plane faces and a negligible amount through the edges, Crank (1975) proposed Equation 3 as solution for Equation 1:

$$\frac{M_t - M_e}{M_0 - M_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-D_{eff}(2n+1)^2 \pi^2 \frac{t}{4L^2}\right] \qquad (3)$$

The Fourier series on the right-hand side of Equation (3) can be evaluated for each individual case, but for any degree of accuracy a large number of terms are involved (BECKER; SALLANS, 1955). Decision on how many terms of Equation (3) should be used is based on a preliminary analysis of the value of the Fourier number of diffusion which, for an infinite slab, is given by $Fo = D_{eff}\, t/L^2$. According to PARTI (1993) the terms of the infinite Fourier series decrease very rapidly and for Fo > 0.1 only the first term needs to be used. It has also been observed that for long drying times, MR < 0.6, Equation (3) simplifies to a limiting form of the diffusion equation given by Equation (4) (MADAMBA et al., 1996; SANKAT et al., 1996; NIETO et al., 1998). The moisture ratio (MR) is defined as $MR = [(M_t – M_e)/(M_0 – M_e)]$. Equation (4) should be used with caution when the aforementioned conditions for simplification of Equation (3) do not apply (HEBBAR; RASTOGI, 2001; PARK et al., 2002).

$$\frac{M_t - M_e}{M_0 - M_e} = \frac{8}{\pi^2} \exp\left[-D_{eff} \pi^2 \frac{t}{4L^2}\right] \qquad (4)$$

Effective moisture diffusivity was estimated for each data set by using Microsoft Excel™ solver add-in. Solver is a nonlinear optimization method that uses the generalized reduced gradient (GRG) method of iteration to identify unknown variables by minimizing the sum of squared errors. In the present work the target function selected to be minimized consisted of the sum of the squared differences between experimental and estimated moisture ratios.

Although numerical solutions of differential equations in drying have been proposed for various geometries, semi-theoretical and empirical equations have also been used to predict kinetics in drying of agricultural products as well as to provide subsidies for the development of more efficient and adequate dryers for each type of product. In this work, besides the theoretical approach, the experimental data from convective drying were also fitted to seven mathematical models of drying (Table 1) usually reported in the literature.

Table 1. Thin-layer drying models.

Model number	Model name	Equation
1	Lewis	$MR = \exp(-k_0 t)$
2	Simple-exponential, two-parameter	$MR = a \exp(-k_0 t)$
3	Simple-exponential, three-parameter	$MR = a \exp(-k_0 t) + c$
4	Double-exponential, two-parameter	$MR = a \exp(-k_0 t) + (1 - a) \exp(-k_0 a t)$
5	Double-exponential, three-parameter	$MR = a \exp(-k_0 t) + (1 - a) \exp(-k_0 b t)$
6	Double-exponential, four-parameter	$MR = a \exp(-k_0 t) + b \exp(-k_1 t)$
7	Triple-exponential, six-parameter	$MR = a \exp(-k_0 t) + b \exp(-k_1 t) + c \exp(-k_2 t)$

The statistical design was completely randomized in a factorial 3 x 2 arrangement (sucrose concentration x temperature dehydration), with an additional control treatment (without pre-osmodehydration), each with three replicates, which totaled 21 experimental units. In the statistical data analysis, an adjustment was made for the variables moisture ratio and drying time for the nonlinear models described in Table 1 using the Gauss Newton procedure implemented in the program STATISTICA (2008). The degree of suitability of the models used to describe the phenomenon studied was evaluated through the calculation with following statistical parameters and according to the following criteria: 1) the lowest variation interval of the root mean squared error (RMSE) (GUNHAN et al., 2005), 2) mean absolute percentage error (η) (MUNDADA et al., 2010) less than 25%, 3) the lower range of average bias (ξ) (GUNHAN et al., 2005) and 4) fit index (δ) (WILLMOTT, 1982) in the 0.99-1.00 range. Moreover, the choice of appropriate models was based on the analysis of error dispersion, and taking into account the principle of parsimony (LARK, 2001). The coefficient of multiple determination or the multiple correlation coefficient squared R^2 will only be used as a complementary criterion in the evaluation of model performance. According to some authors (WILMOTT, 1982; KOBAYASHI; SALAM, 2000; HARMEL et al., 2010; RITTER; MUÑOZ-CARPENA, 2013) the main problem arising from choosing R^2, or tests of its statistical significance, as a quantitative measure of goodness-of-fit is misleading because the magnitude of R^2 is not consistently related to the accuracy of prediction.

RESULTS AND DISCUSSION

Kinetics of pineapple drying *in natura* and pre-dehydrated by immersion-impregnation

The change in moisture ratio of *in natura* and osmodehydrated pineapple slices in inverted sugar at 40 and 50 °C during air drying at 60 °C is graphically presented in Figures 2 and 3, respectively. It can be seen in Figure 2 that the drying characteristics of all treatments were similar during the first 5 h of the process. However, for the remainder of the drying process, the drying characteristics of the treatments were noticeably different. The reduction in MR of pineapple rings pre-dehydrated at 465 mL L^{-1} was less pronounced as compared to that observed in the other treatments. *In natura* samples dried to an intermediate MR, whereas samples submitted to treatments 155 and 310 mL L^{-1} had a more pronounced rate of reduction in MR against time. The MR for each treatment remained nearly constant towards the end of the drying. Nieto et al. (2001) observed a similar behavior when comparing the drying curves, at 60 °C, of *in natura* and osmotically dehydrated mango in a 39.5% w/w glucose aqueous solution.

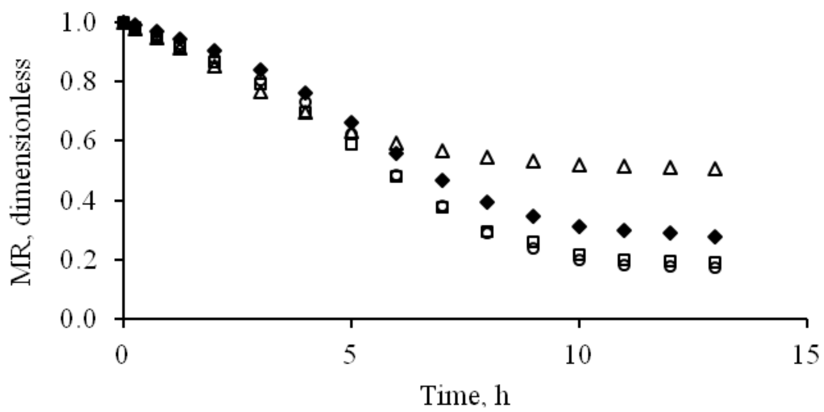

Figure 2. Moisture ratio of *in natura* (◆) and osmodehydrated pineapple slices at 40 °C during convective air drying at 60 °C and indicated values of inverted sugar solution concentration. ○, 155 mL L^{-1}; □, 310 mL L^{-1}; △, 465 mL L^{-1}.

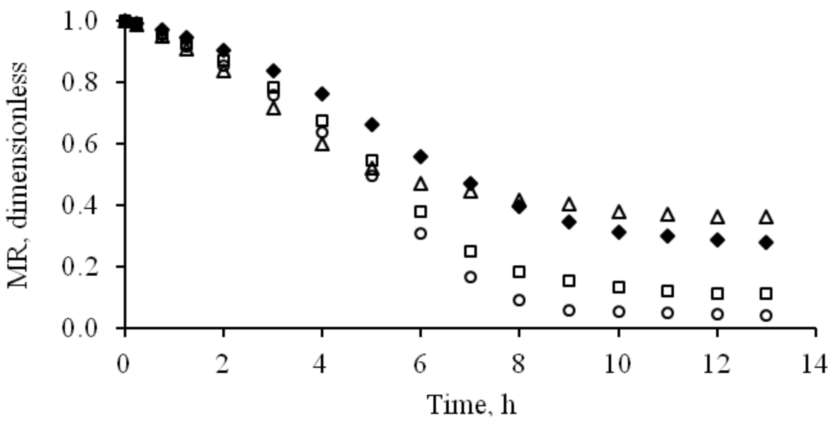

Figure 3. Moisture ratio of *in natura* (◆) and osmodehydrated pineapple slices at 50 °C during convective air drying at 60 °C and indicated values of inverted sugar solution concentration. ○, 155 mL L^{-1}; □, 310 mL L^{-1}; △, 465 mL L^{-1}.

Drying characteristics of the samples dried at 50 °C were somewhat different from those observed at 40 °C. Figure 3 shows that the drying characteristics of all treatments were similar during the first 2 h of the process. From 3 to 6 h of drying, fresh samples presented a consistently lower reduction in MR as compared to the osmodehydrated samples. However, after 6 h of drying, the lower the inverted solution concentration used to partially dehydrate the pineapple slices, the higher the moisture ratio. A similar trend was noted by An et al. (2013) in the convective air drying, at 70 °C, of cherry tomatoes pre-osmodehydrated in 50 and 70 °Brix sucrose solutions. As was the case with the osmotic pre-treatment at 40 °C, at approximately 6 h of drying, the pineapple rings pre-dehydrated at 50 °C in the 465 mL L^{-1} solution also showed a reduction in the rate of moisture reduction, attaining the highest value of MR at the end of the drying process. Osmotic pre-dehydration at 50 °C required 50 to 60% of the drying time needed to attain the same moisture ratio when the samples were dehydrated at 40 °C.

The behavior observed in the present work concerning the drying curves of pre-dehydrated pineapple slices in the 465 mL L^{-1} solution might have arisen from specific changes in mass transfer mechanisms governing moisture removal, as confirmed by the sudden change in the slopes of these curves after 6 h of drying. It is relevant to note that the total soluble solids (TSS) employed in our work were lower (up to 20 °Brix) than values normally found in literature, 50 to 70 °Brix (LOMBARD et al., 2008; BOTHA et al., 2012; SILVA et al., 2014), which may have produced some structural deformation in the sample particular to this treatment. The drying of fruit samples is generally followed by shrinkage, and its intensity depends on the pretreatment. The more concentrated a sugar solution is, the higher the sample volume reduction. The use of heat disrupts the fruit matrix, probably changing the porosity and hence the transport properties of the cell wall. A more significant volume reduction associated with a higher solute uptake may have produced a higher level of occlusion of the intercellular spaces available for water or vapor removal, thus reducing the rate of change in MR associated with the drying of pre-treated samples in the 465 mL L^{-1} solution.

Figures 4 and 5 present the change in drying rate of fresh and pre-osmodehydrated pineapple slices in inverted sugar at 40 and 50 °C, respectively, during air drying at 60 °C. There was no evidence of a constant drying rate at the given experimental conditions, which suggests that liquid diffusion is the principal mechanism governing mass transfer during convective drying of pineapple rings.

Figure 4 illustrates that there is a negligible effect of the osmotic pretreatments at 40 °C on the drying rate. Higher drying rates at the onset of the *in natura* sample drying are associated with its higher initial moisture content as compared to the pre-dehydrated samples. In all treatments, variation of drying rate with respect to moisture content can be represented by two linear functions with $R^2 > 0.95$, one representing an initial falling rate with a higher slope, followed by a second slower falling rate period. These findings are in accordance with results reported by Nicoleti et al. (2001) and Madamba (2003).

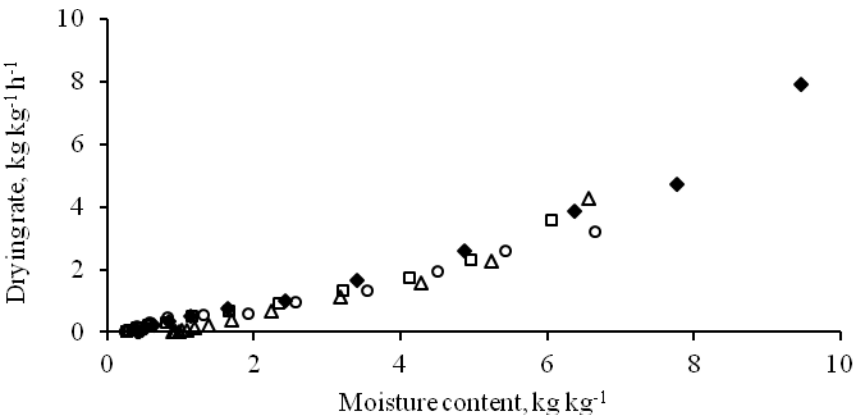

Figure 4. Drying rate for fresh (◆) and osmodehydrated pineapple slices in inverted sugar at 40 °C and indicated values of solution concentration. ○, 155 mL L^{-1}; □, 310 mL L^{-1}; △, 465 mL L^{-1}.

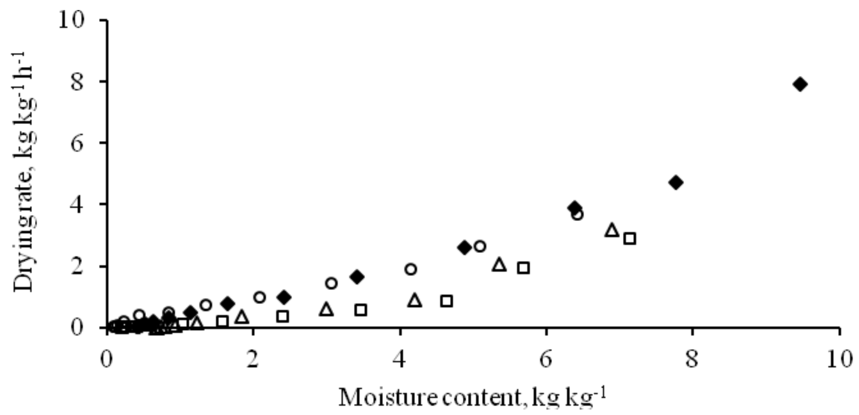

Figure 5. Drying rate for fresh (◆) and osmodehydrated pineapple slices in inverted sugar at 50 °C and indicated values of solution concentration. ○, 155 mL L^{-1}; □, 310 mL L^{-1}; △, 465 mL L^{-1}.

Variation in drying rate against moisture content of fresh and pre-osmodehydrated pineapple slices in inverted sugar at 50 °C (Figure 5) can be divided in two groups, which is an indication of the effect of osmotic solution temperature on the drying characteristics of the arcs of pineapple rings. The rate of moisture removal was more intense for samples *in natura* and pre-osmodehydrated in 155 mL L^{-1} inverted sugar solution. This occurred because the low osmotic potential (11 °Brix) of the 155 mL L^{-1} diluted solution was close to the TSS of the fresh fruit (9 °Brix). The drying rates of samples pre-osmodehydrated in 310 and 465 mL L^{-1} solutions did not differ substantially and were always lower than the previously mentioned treatments. Thus, the higher the concentration, the greater the number of glucose and fructose molecules in the solution. These molecules penetrate into the tissues of the superficial layer of the fruit, imbuing them more intensively to hinder the removal of water from their interior, thus reducing the drying rate.

Even if the drying of pre-osmodehydrated products is slower, there is the advantage of the impregnation of solids and the consequent reduction in the permeability of the tissues of the superficial layer of the fruit, as well as the reduction of the apparent diffusivity of the water, both of which act as beneficial factors in maintaining the stability of dehydrated fruit during storage. As a pretreatment, the effects of osmotic dehydration are mainly related to the improvement of some nutritional, sensory and functional properties of the product. Published reports show that parameters, such as color, flavor and texture of fruits and vegetables susceptible to air drying, vacuum drying or lyophilization, were improved when a prior stage of osmotic dehydration was used (SILVEIRA et al., 1996; TORREGGIANI; BERTHOLO, 2001; QUEIROZ et al., 2007; KEK, 2013; MEDEIROS, 2016).

Effective moisture diffusivity

The influence of solution concentration on effective moisture diffusivity during convective drying of *in natura* and osmodehydrated pineapple slices at 40 and 50 °C is shown in Figure 6. Cubic functions fitted to the experimental data presented in Figure 6 resulted in correlation coefficients close to unity. D_{eff} was found to increase with temperature at each value of concentration of the osmotic solution in the range studied. Saputra (2001) quoted that the higher the temperature the higher the solubility of the sugar and the higher the osmotic pressure of the osmotic agent used. Temperature has an effect on the membrane permeability by making it more permeable to the water coming out of the product. Higher values of D_{eff} associated with higher drying-air temperatures have been also observed for young coconut strips (MADAMBA, 2003), cubes of papaya (FERNANDES et al., 2006) and litchi (JANJAI et al., 2010).

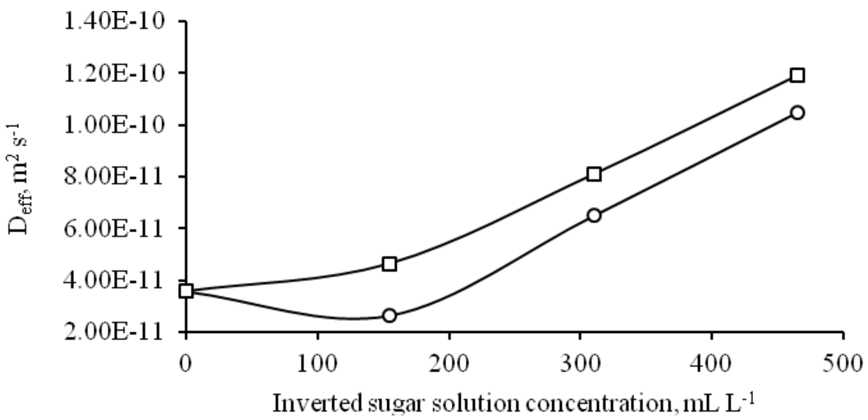

Figure 6. Effective moisture diffusivity of *in natura* and osmodehydrated pineapple slices in inverted sugar during convective air drying at 60 °C and indicated values of temperature of the osmotic solution concentration. ○, 40 °C; □, 50 °C.

In agreement with the literature data on osmotic dehydration of fruits (RODRIGUES; FERNANDES, 2007), the effective moisture diffusivity of osmodehydrated pineapple slices increased with solution concentration. Prinzivalli et al. (2006) showed that this phenomenon is caused by a significant texture loss in conjunction with a partial or complete breakdown of the sample tissue associated with the osmotic pre-treatment. As pointed out by Rodrigues and Fernandes (2007), when the cell wall membranes are disrupted the water diffusion within the fruit tissue becomes easier and the effective water diffusivity increases as shown in Figure 6. Notwithstanding, D_{eff} of the *in natura* sample during convective drying was always smaller than the values obtained with pre-osmodehydrated slices but that submitted to the 155 mL L^{-1} at 40 °C pre-treatment. This might be due to the fact that in this pre-treatment the diluted solution at a lower temperature has no osmotic potential to cause a significant change in cell wall membranes, favoring solute uptake to the detriment of water loss, thus reducing moisture diffusivity.

Figure 6 also reveals that the influence of the osmotic solution concentration on the effective moisture diffusivity during convective drying is stronger than the influence of the temperature of the solution. Values of D_{eff} reported herein lie within the general range observed for food (10^{-11} to 10^{-9} m^2 s^{-1}), as affected by temperature, pre-treatment, variety and composition of the material (MADAMBA, 2003).

Evaluation of the degree of suitability of the theoretical and semi-theoretical models to the drying curves

Table 2 shows the statistical parameter values (RMSE, η, ξ and δ), and R^2, used to evaluate the suitability of the theoretical diffusion model given by Equation 4 and the seven semi-theoretical mathematical models presented in Table 1 to the experimental data of convection drying at 60 °C of pineapple ring arcs pre-dehydrated by immersion-impregnation at 40 to 50 ºC as well as the results of drying *in natura* samples (i.e., those that did not undergone pre-osmodehydration).

Compared to the semi-theoretical models, the simulation provided by the theoretical diffusion model (Equation 4) was unsatisfactory as indicated by the largest RMSE and average bias (ξ) intervals of variation, mean absolute percentage error (η) of 10.64% to a disappointing extreme interval value of 46.39%, and the lowest values of fit index. These results indicate that the diffusion model given by Equation 4 cannot be considered a good predictor of the thin-layer drying behavior of pineapple ring arcs *in natura* and pre-dehydrated by immersion-impregnation. Explanations for this behavior results from misleading assumptions made in the use of the analytical solution of second Fick's law, Equation 3, which was obtained by considering constant slab thickness, uniform initial moisture distribution within the pineapple ring arcs, assumption that the surface is at its equilibrium moisture content, neglection of temperature gradients in the sample and the supposition that all the diffusing moisture leaves the sample through the plane faces and a negligible amount through the edges.

Table 2. Values of error parameters (RMSE, η, ξ and δ), and R^2, used to investigate the goodness-of-fit of the theoretical diffusion model given by equation 4 and the seven mathematical drying models presented in Table 1, in the description of the convective drying, at 60 ºC, of *in natura* and osmodehydrated *Pérola* pineapple slices in inverted sugar solutions of 155, 310 e 465 mL L^{-1} at 40 and 50 ºC for 2 h.

Model number	Error parameter	Osmotic dehydration at 40 ºC			Osmotic dehydration at 50 ºC			Fruit *in natura*
		Inverted sugar solution concentration (mL L^{-1})						
		155	310	465	155	310	465	
1	R^2	89.45	93.11	98.55	88.36	92.09	92.09	93.15
	RMSE	0.05	0.09	0.04	0.12	0.08	0.08	0.09
	η	5.59	31.48	10.63	36.87	13.67	18.17	20.10
	ξ	-0.01	-0.01	-0.01	-0.02	-0.02	-0.01	-0.02
	δ	0.97	0.98	1.00	0.96	0.98	0.99	0.98
2	R^2	91.59	95.04	98.88	91.25	94.49	96.77	95.39
	RMSE	0.05	0.08	0.03	0.10	0.07	0.06	0.07
	η	5.06	26.45	10.59	31.53	11.15	13.61	15.58
	ξ	0.00	0.01	0.00	0.01	0.00	0.01	0.01
	δ	0.98	0.99	1.00	0.98	0.99	0.99	0.99
3	R^2	94.99	98.77	98.95	97.02	97.49	97.75	97.04
	RMSE	0.04	0.04	0.03	0.06	0.04	0.05	0.06
	η	4.07	13.15	8.72	17.68	8.06	13.73	14.82
	ξ	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	δ	0.99	1.00	1.00	0.99	0.99	0.99	0.99
4	R^2	89.45	99.19	98.55	88.36	92.09	95.10	93.07
	RMSE	0.05	0.03	0.04	0.12	0.08	0.08	0.09
	η	5.59	10.28	10.63	36.87	13.67	18.17	20.53
	ξ	-0.01	0.01	-0.01	-0.02	-0.02	-0.01	-0.02
	δ	0.97	1.00	1.00	0.96	0.98	0.99	0.98
5	R^2	97.57	99.41	99.22	96.40	96.95	99.48	96.16
	RMSE	0.02	0.03	0.03	0.07	0.05	0.02	0.07
	η	2.81	8.19	11.04	19.82	8.77	7.73	16.71
	ξ	0.00	0.01	0.00	-0.01	-0.01	0.00	-0.02
	δ	0.99	1.00	1.00	0.99	0.99	1.00	0.99
6	R^2	97.77	95.04	99.15	91.25	94.49	96.77	96.16
	RMSE	0.02	0.08	0.03	0.10	0.07	0.06	0.07
	η	2.75	26.45	5.95	31.53	11.15	13.61	15.58
	ξ	0.00	0.01	0.00	0.01	0.00	0.01	0.01
	δ	0.99	0.99	1.00	0.98	0.99	0.99	0.99
7	R^2	91.59	95.04	99.95	91.25	94.49	96.77	95.39
	RMSE	0.05	0.08	0.01	0.10	0.07	0.06	0.07
	η	5.06	26.45	1.56	31.53	11.15	13.61	15.58
	ξ	0.00	0.01	0.00	0.01	0.00	0.01	0.01
	δ	0.98	0.99	1.00	0.98	0.99	0.99	0.99
Eqn.4	R^2	82.79	94.16	97.07	85.05	85.02	95.77	91.29
	RMSE	0.12	0.14	0.07	0.24	0.17	0.10	0.20
	η	12.35	35.49	10.64	46.39	32.80	17.38	45.37
	ξ	-0.07	0.02	-0.02	0.09	0.02	-0.03	0.07
	δ	0.81	0.93	0.98	0.64	0.74	0.96	0.81

From the results presented in Table 2, it can be argued that none of these assumptions were fully attained. Besides, it remains to be verified if the difference between the one-term solution of Equation 4 is significantly different of the series solution of Equation 3 with higher order terms, although there are evidences that this difference is less than 5% for long drying times (BROOKER et al., 1992). Fortes and Okos (1980) arrived at the conclusion that even when one accepts the fact that diffusion equations can fit experimental values for some solids, there remains the problem of their physical validity for it has been furnishing wrong predictions and misinterpretation of experimental results. They even state that the probable reason for its acceptance is the logarithmic behavior of the solution of the diffusion equations, resembling experimental drying curves.

Considering now the semi-theoretical models (Table 1), one of the significant facts demonstrated by the data presented in Table 2 refers to the similarity in performance of some pairs of models, with regard to evenness of the statistical parameters evaluated. As such, it is observed that Models 1 (Lewis) and 4 (double exponential of two parameters) showed almost identical numerical values for R^2, RMSE, η, ξ and δ, except for a treatment in which the samples were pre-dehydrated at 40 °C in a 310 mL L^{-1} solution. The drying constants and constants of the mathematical models obtained for each treatment are presented in Table 3.

Considering the coefficient of determination R^2 as a complementary criterion for comparing the suitability of various models, it is observed that only Models 1 and 4, which had been considered equivalent, did not fit the drying experimental data according to the established criteria. For the other models evaluated, in general and despite minor differences, the highest R^2 values occurred for drying of samples pre-dehydrated at 40 °C, with decreasing values for samples pre-dehydrated at 50 °C as well as for those dried without osmotic pretreatment. The lowest ranges of the root mean square error (Table 2) were obtained for Model 3 [or simple exponential of three-parameter ($0.03 \leq \text{RMSE} \leq 0.06$)] and 5 [or double exponential of three-parameter ($0.02 \leq \text{RMSE} \leq 0.07$)]. These models showed the lowest mean absolute percentage error interval, where $4.07 \leq \eta \leq 17.68$ (Model 3) and $2.81 \leq \eta \leq 19.82$ (Model 5), respectively. Therefore, considering only the three statistical parameters evaluated, these two models were those that best fit the description of the experimental drying curves of pineapple ring arcs *in natura* and pre-dehydrated by immersion-impregnation.

Table 3. Drying constants (k_0, k_1 e k_2) and constants of the mathematical models (a, b, and c) presented in Table 1, in the description of the convective drying, at 60 ºC, of *in natura* and osmodehydrated *Pérola* pineapple slices in inverted sugar solutions of 155, 310 e 465 mL L^{-1} at 40 and 50 ºC for 2 h.

Model number	Constants	Osmotic dehydration at 40 ºC			Osmotic dehydration at 50 ºC			Fruit *in natura*
		Inverted sugar solution concentration (mL L^{-1})						
		155	310	465	155	310	465	
1	k_0	0.0801	0.1663	0.1871	0.1494	0.1134	0.2088	0.1306
2	k_0	0.0903	0.1859	0.1967	0.1715	0.1285	0.2321	0.1475
	a	1.0391	1.0960	1.0432	1.1171	1.0842	1.0921	1.1064
3	k_0	0.0006	0.0424	0.2138	0.0064	0.0055	0.1489	0.0751
	a	131.7077	2.9407	1.0168	16.5785	15.7638	1.3537	1.6028
	c	-130.6751	-1.8976	0.0344	-15.5189	-14.7213	-0.2889	-0.5320
4	k_0	0.0801	0.2894	0.1871	0.1494	0.1134	0.2088	70.2984
	a	1.0000	2.0982	1.0000	1.0000	1.0000	1.0000	0.0018
5	k_0	0.2574	0.3964	1.9078	0.0038	0.0045	0.8441	0.0324
	a	-99.9532	-134.6715	-0.1179	2.9916	2.9648	-0.7894	5.1641
	b	0.9898	0.9918	0.1110	-9.7347	-6.5606	0.4000	0.5340
6	k_0	0.2703	0.1859	0.2037	0.1715	0.1285	0.2321	0.1475
	k_1	0.2595	0.1859	-0.5606	0.1715	0.1285	0.2321	0.1475
	a	-26.0109	0.5416	1.0509	0.3100	0.2547	0.1918	0.5306
	b	26.9950	0.5544	0.0000	0.8071	0.8295	0.9003	0.5758
7	k_0	0.0903	0.1859	0.5036	0.1715	0.1285	0.2321	0.1475
	k_1	0.0903	0.1859	0.4837	0.1715	0.1285	0.2321	0.1475
	k_2	0.0903	0.1859	-0.0247	0.1715	0.1285	0.2321	0.1475
	a	0.0573	0.1773	-20.9143	0.5756	0.2124	0.2188	0.3906
	b	0.4710	0.5424	21.8142	0.3873	0.5204	0.4285	0.4607
	c	0.5107	0.3763	0.0891	0.1542	0.3514	0.4448	0.2551

According to Gunhan et al. (2005), the most accurate model is one that has a mean bias ξ close to zero. Of the two models considered appropriate in the representation of the drying curves, only Model 3 [or simple exponential model of three parameters on which the MR = a exp($-k_0$t) +c] showed zero bias for all treatments, allowing it to be considered the model which describes the drying of pineapple ring arcs *in natura* and osmotically pre-dehydrated pineapple with greater accuracy. However, the variation interval of the average bias for Model 5 ($-0.02 \leq \xi \leq 0.01$) was also very small and close to zero, which indicated that the ξ values obtained were not sufficient to disqualify this model in predicting the drying curves. Furthermore, the comparison between the experimental and estimated curves indicated that the two models sometimes underestimate and sometimes overestimate the process, albeit with reduced intensity. This result was corroborated by the values of the fit index, which varied in the range $0.99 \leq \delta \leq 1.00$, showing that the two models had similar performance in describing the drying curve of ring arcs of both *in natura* and osmotically pre-dehydrated pineapples.

Figure 7 shows the experimental data and the drying curve obtained by the simple exponential model of three parameters for pineapple ring arcs osmotically pre-dehydrated at 40 °C in a solution of inverted sugar at 465 mL L^{-1}. Similar performances of the two models (3 and 5) were observed for all other treatments.

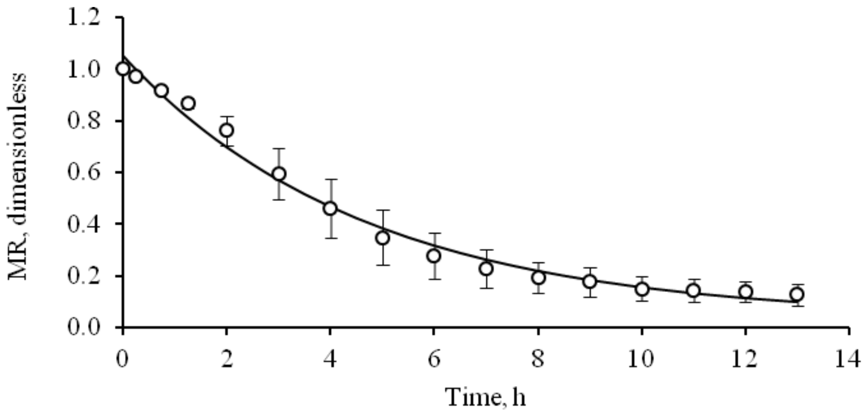

Figure 7. Moisture ratio vs. time (experimental values, ○, and drying curve predicted by the three parameter, single exponential model) for convective drying, at 60 ºC, for pineapple slices osmodehydrated at 40 ºC in 465 mL L^{-1} inverted sugar solution.

However, drying models can only be considered satisfactory if, in the description of the experimental drying curves, the residues obtained are solely due to random errors of measurement of the variables involved. If any functional relationship is observed between residues and estimated values of the moisture ratio, or the drying time, it can be inferred that the model is inappropriate, indicating that the parameters employed in its development are insufficient to explain the variation of experimental data.

In all treatments the residues were randomly above and below zero, denoting that there were no functional relationships between the residues and drying time and moisture ratio. This result indicates that there were no interference by non defined variables in the measured values of moisture ratio. Similar results obtained with Model 5 also revealed its adequacy in describing the drying curves.

Of the eight models evaluated in this study only semi-theoretical Models 3 (single-exponential, three-parameter) and 5 (double-exponential, three-parameter) can be considered adequate in the description of the convective drying, at 60 ºC, of *in natura* and osmodehydrated pineapple slices in inverted sugar solutions at 40 and 50 ºC, and may be employed with confidence in drying simulation software as well as in dryer design. However, when different mathematical models are capable of describing the same physical phenomenon with different levels of complexity, the principle of parsimony should be considered. This principle states that one should not multiply entities unnecessarily in parametric model fitting, or make further assumptions than are needed, and in general that one should use no more complex a model or representation of reality than absolutely necessary (LARK, 2001). Thus, considering the principle of parsimony, the model that was chosen to describe the drying of *in natura* and pre-osmodehydrated pineapple slices for the conditions examined in this study is the single-exponential, three-parameter model.

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RESUMO: O trabalho descreve a cinética de secagem e compara as taxas de secagem por convecção de fatias de abacaxi *in natura* e pré-desidratadas osmoticamente em açúcar invertido. A difusividade efetiva da água no interior do produto durante a secagem foi calculada empregando-se a Segunda Lei de Fick. Avalia, também, o grau de adequação de um modelo teórico de difusão de liquido e de sete modelos semi-teóricos na descrição das curvas experimentais de secagem. A desidratação osmótica foi realizada empregando-se soluções a 155, 310 e 465 mL L^{-1}, a 40 e 50 ºC, sob agitação a 60 rpm e tempo de imersão de 2 h. A secagem por convecção foi feita em secador do tipo gabinete com bandejas, com ar à 60 ºC e 1,15 m s^{-1}. O grau de ajuste dos modelos foi avaliado por meio da raiz do erro quadrático médio, do erro percentual absoluto médio, do viés médio, do índice de ajuste, pela análise da dispersão de resíduos e aplicando-se o princípio da parcimônia. O pré-tratamento osmótico facilitou a remoção de água durante as primeiras horas de secagem, comportamento que se reverteu ao final do processo para amostras desidratadas na solução mais concentrada. O efeito do pré-tratamento osmótico sobre a taxa de secagem foi desprezível a 40 ºC, no entanto, a 50 ºC, a taxa de remoção de água foi mais intensa para amostras *in natura* e pré-desidratadas nas soluções de menor concentração. A difusividade efetiva aumentou em função de aumentos na temperatura e na concentração da solução. O modelo exponencial simples de três parâmetros foi o que melhor descreveu as curvas de secagem por convecção de fatias de abacaxi *in natura* e pré-desidratadas osmoticamente em açúcar invertido

PALAVRAS-CHAVE: *Ananas comosus* (L.) Merrill. Desidratação-impregnação. Taxa de secagem. Análise de erro. Desidratação de frutas. Modelagem matemática.

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APPENDIX I

Nomenclature

D	diffusion coefficient, $m^2 s^{-1}$
i	ith measurement of moisture ratio at a given experimental run
k	drying constant or drying coefficient, s^{-1}
L	half thickness of an infinite slab, m
M	moisture content, kg water / kg dry matter
M_0	initial moisture content, kg water /kg dry matter
M_e	equilibrium moisture content, kg water /kg dry matter
M_t	moisture content at any time t, kg water /kg dry matter
MR	moisture ratio, dimensionless
$\overline{MR}$	mean moisture ratio, dimensionless
N	number of experimental measurements of moisture ratio at a given experimental run
n	integer number of the infinite series, n = 1, 2, 3, . . .
p	mean radius of an arc-shaped pineapple sample, m

R	outer radius of an arc-shaped pineapple sample, m
r	inner radius of an arc-shaped pineapple sample, m
R^2	coefficient of multiple determination or the multiple correlation coefficient squared
RMSE	root mean squared error
t	time of drying, h
W	width of an arc-shaped pineapple sample, m
w.b.	wet basis

Greek symbols

δ	fit index, dimensionless
Φ	internal angle of an arc-shaped pineapple sample, degree
η	mean absolute percentage error, %
ξ	average bias, dimensionless
∇	operator $\frac{\partial}{\partial x}+\frac{\partial}{\partial y}+\frac{\partial}{\partial z}$

Subscripts

0	initial value
0 and 1	subscript of the drying constant k
a, b and c	coefficient of a semi-theoretical model
e	equilibrium
eff	effective
est	value estimated by the model
exp	experimental value
t	at time t