SORPTION EQUILIBRIUM OF BRAZILIAN PINE (*ARAUCARIA ANGUSTIFOLIA*) SEEDS

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Abstract. *Araucaria angustifolia* belongs to family Araucariaceae, is the only economically important conifer species native to Brazil. The seeds of this tree, named pinhão, are consumed in the South and Southeast of Brazil. They are big in size (3-8 cm X 1-2 cm) weighing 6.5-8.5 g and have high nutritious value. They are consumed after cooked and posterior peeling, or they are used as a raw flour for regional dishes. Pinhão seeds can be considered as a source of starch, dietary fiber, Mg and Cu. However, the literature about nutritional and technological aspects of pinhão is very scarce and there are no report about moisture sorption models for this product. The seeds have a high humidity and a high water activity (higher than 80% dry basis and about 0.98 respectively) and they are contaminated easily by mushrooms during the stockpiling, hindering its commercialization. In this work, the moisture sorption isotherms of raw *Araucaria angustifolia* seeds were determined. The seeds were dried at 50° C to obtain samples with different moisture contents and stored in polythene bags kept in a refrigerator at 0° C for about 10 days to attain moisture uniformity. The seeds were allowed to equilibrate in the ambient condition for 6 h and it was determined the moisture content and the water activity at four temperatures (15, 25, 30 and 40° C). A non-linear least squares regression program was used to evaluate various moisture sorption models described in the literature. The experimental data was also used to determine the thermodynamic functions of pinhão, used to provide an understanding of the properties of water and energy requirements associated with the sorption behavior. Isosteric heat (differential enthalpies) was calculated through direct use of moisture isotherms by applying the Clausius-Clapeyron equation.

Keywords: Pinhão seeds, *Araucaria angustifolia*, Isotherms.

1. Introduction

Brazilian Pine (*Araucaria angustifolia*) belongs to the Araucariaceae family and is the only economically important conifer species native to Brazil (Zandavalli et al., 2004). Its geographical distribution includes Argentina and Brazil, where it is concentrated in the southermost states of Paraná, Santa Catarina and Rio Grande do Sul (Zandavalli et al., 2004). Native people in the South of Brazil usually consume the seeds of this tree, named pinhão. They are consumed after cooked and posterior peeling, or they are used as raw flour for regional dishes. Pinhão seeds are big in size (3-8 cm X 1-2 cm) weighing 6.5-8.5 g (Reitz et al., 1978) and can be considered as a source of starch, dietary fiber, magnesium and copper (Cordenunsi et al., 2004). Protein and lipid content are low (of about 3 and 1.3 respectively) (Cordenunsi et al., 2004; Kramer et al., 2004). The literature about nutritional and technological aspects of pinhão is very scarce and there are no reports about moisture sorption models for this product. The seeds have a high humidity and they are contaminated easily by mushrooms during the stockpiling, hindering its commercialization.

However, though attempts have been made to find a general isotherm equation, this has not yet been found because water activity depends on food composition and the interaction of the different constituents with water in thermodynamical equilibrium conditions (Welti-Chanes & Vergara, 1997). Numerous mathematical equations

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can be found in literature that describes water sorption isotherms. Nine of the equations are used in this work and are shown in Table 1.

The methods used for the determination of equilibrium moisture sorption isotherms of agricultural products can be classified into: (a) those in which the material is brought into equilibrium with air of fixed temperature and relative humidity and the moisture content of the material is measured (gravimetric method) and (b) those in which air is brought to equilibrium with material at a fixed temperature and moisture content and the relative humidity of the air are determined. Rao & Pfost (1978) concluded that the latter methods are simpler and faster. However the gravimetric technique has been recommended as the standard method (Speiss & Wolf, 1987).

The isosteric heat of sorption or differential enthalpy of sorption gives a measure of the water-solid binding strength. A rapid computational procedure, commonly used for its determination, is the application of the Clausius-Clapeyron equation to the sorption isotherms, at constant moisture content (McMinn & Magee, 2003).

The knowledge of the magnitude of the heat of sorption, at a specific moisture content, provides an indication of the state of the sorbed water and, hence, a measure of the physical, chemical and microbiological stability of the food material under given storage conditions. In addition, the variation in heat of sorption with moisture content, and magnitude relative to the heat of vaporization of pure water provides valuable data for energy consumption calculations and subsequent design of drying equipment and an understanding of the extent of the water-solid versus water-water interactions (McMinn & Magee, 2003).

Table 1. Nine commonly used moisture sorption isotherm models

Name of the equation	Equation	
GAB (Guggenheim-Anderson-de Boer) (Van den Berg, 1985)	$X = \dfrac{X_m.C.K.aw}{(1-K.aw)\times(1-K.aw+C.K.aw)}$	(1)
Helsey (Helsey, 1948)	$aw = \exp\left(-\dfrac{A}{X^B}\right)$	(2)
Peleg (Peleg, 1993)	$X = k_1.aw^{n_1} + k_2.aw^{n_2}$	(3)
Oswin (Lomauro et al., 1985)	$X = A.\left(\dfrac{aw}{1-aw}\right)^B$	(4)
Chung - Pfost (Chung & Pfost, 1967)	$\ln(aw) = -A.\exp(-B.X)$	(5)
Chen (Chen, 1971)	$aw = \exp\left(-\exp(k - C.\exp(B.X)\right)$	(6)
Henderson (Henderson, 1952)	$(1-aw) = \exp(A.X^B)$	(7)
Chirife (Castillo et al., 2003)	$X = \exp\left[A + B.\ln\left(C - \ln aw\right)\right]$	(8)
Smith (Smith, 1947)	$X = A + (B.\log(1-aw))$	(9)

X, equilibrium moisture content (kg kg⁻¹ dry solids); *aw*, water activity; X_m, monolayer moisture content (kg kg⁻¹ dry solids); A, B, C, K, k_1, k_2, n_1, n_2, k, are parameters of the equations.

The differential entropy (ΔS_d) of a material is proportional to the number of available sorption sites at a specific energy level (Madamba et al., 1996).

The objective of the present work was to obtain sorption isotherms at selected temperatures, to determine the best fit of selected sorption isotherm models, and to estimate the isosteric heat of sorption and the differential entropy for *Araucaria angustifolia* seeds (pinhão).

2. Materials and methods

Experiments were carried out at the Food Science and Technology Institute of Federal University of Rio Grande do Sul, as described below.

2.1. Experimental procedure

The *Araucaria angustifolia* seeds used in this study were purchased in a local market (Porto Alegre, Brazil) and stored at -20° C in polythene bags for a few months. For the experiments, the seeds of pinhão were defrozen and allowed at the ambient condition. Seeds used in this work have a size between 4.5-6.9 cm and 1.7-2.8 cm. Initial moisture content of the seeds was determined in a stove by 24 hours at 105° C (AOAC, 1990). Due to the high moisture content of pinhão and the high thermal resistance, the method described by Ajibola et al. (2003), with some modifications, was used to determine isotherms of desorption. Ajibola et al. (2003) dried seeds (cowpea) at 50° C to obtain samples with lower moisture content, and stored in polythene bags kept in a refrigerator at 0° C. The *Araucaria angustifolia* seeds were dried at 50°C in a bin drier for about 45 hours. From time to time, samples were taken off and stored in polythene bags and kept in a refrigerator at 0° C for about 10 days to reach uniform moisture. The seeds were allowed to equilibrate in the ambient condition for 6 h and the moisture content was determined and the water activity at four temperatures (15, 25, 30 and 40° C) was measured directly in a water activity analizator *AquaLab 3TE*. Desorption isotherms at these temperatures were determinate.

2.2. Data analysis

The experimental data obtained was fitted to nine moisture sorption isotherm models presented in Table 1, using the non-linear regression module of *Statistica 5.0* software (Statsoft, USA). The BET (Brunauer, Emmett & Teller, 1938) model was not tested because this model is used for *aw* < 0.5 and the *aw* experimental values obtained were out of this range. For all models the Quase-Newton method for optimization was used except for Henderson model (which use the Hooke-Jeeves method), Helsey and Chung models (which use the Hooke-Jeeves and Quase Newton method), Chen and Smith moldels (which use the Simplex method). To evaluate the fit quality of each model, the mean relative percent error (MRE) was used, which is defined by

$$MRE = \frac{100}{N} \sum_{i=1}^{N} \frac{\left| m_{ei} - m_{pi} \right|}{m_{ei}} \qquad (10)$$

where m_{ei} and m_{pi} are, respectively, the measured and predicted equilibrium moisture content in % (dry basis), equilibrium moisture content in % (db), and N is number of data points.

The mean relative percentage deviation modulus (MRE) is widely adopted throughout the literature to evaluate the quality of the fit of isotherm models. The lower values of MRE the better fit of the model and it is

generally considered that MRE values below 10% indicate an adequate fit for practical purposes (Viswanathan et al., 2003; Figueira et al., 2004).

2.3. Calculation of the isoteric heat of sorption and the differential entropy

The net isosteric heat of sorption can be determined from moisture sorption data using the following equation, which is derived from the Clausius-Clapeyron equation (Rizvi, 1986; Tsami, 1991):

$$\Delta h = -R \left[\frac{\partial \ln(aw)}{\partial (1/T)} \right]_X \tag{11}$$

and

$$\Delta h = \Delta H - \Delta H_{vap} \tag{12}$$

where aw is the water activity, Δh the net isosteric heat of sorption (kJ mol^{-1}), ΔH the isosteric heat of sorption (kJ mol^{-1}), ΔH_{vap} the heat of vaporization (kJ mol^{-1} water), R the universal gas constant (kJ mol^{-1} K^{-1}), X the equilibrium moisture content and T is the absolute temperature (K).

The net isosteric heat of sorption can be calculated from Eq.(11) by plotting $\ln(aw)$ versus 1/T for a specific moisture content of material and determining the slope which is equal to $-\Delta h/R$. This procedure is repeated for different moisture contents in order to determine the dependence of Δh on the moisture content. The net isosteric heats of sorption for different moisture content were calculated from Eq.(11) using a least-square analysis and the isotherm model that best describes the experimental sorption data for pinhão was used to determine the aw values for each moisture content . This procedure is based on the assumption that Δh is invariant with temperature and requires data of the sorption isotherms at more than two temperatures (Tsami, 1991).

The relationship between the isosteric heat (Δh) and the differential entropy (ΔS) of sorption is given by:

$$\left(\ln aw \right)_X = -\frac{\Delta h}{RT} + \frac{\Delta S}{R} \tag{13}$$

and, therefore, the differential entropy is obtained from the linear coefficient ($\Delta S/R$) of the straight obtained plotting $\ln(aw)$ versus 1/T for a specific moisture content of material (McMinn & Magee, 2003).

3. Results and discussion

3.1. Sorption isotherms

Araucaria angustifolia seeds have a high humidity and a high water activity, higher than 80% db and about 0.99, respectively. The desorption isotherms (experimental data) at 15, 25, 30 and 40° C are shown in Fig.1. The range of water activity was 0,46 < aw < 0,99 and it was not possible to obtain lower values of aw with this procedure. The values shown are the arithmetic media of two experimental results. The standard deviation for the equilibrium moisture content (kg kg^{-1} dry solids) of each experimental point was within the range of 0.001-0.031. As expected, the equilibrium moisture content (EMC) decreased with decrease in water activity (aw) at constant temperature.
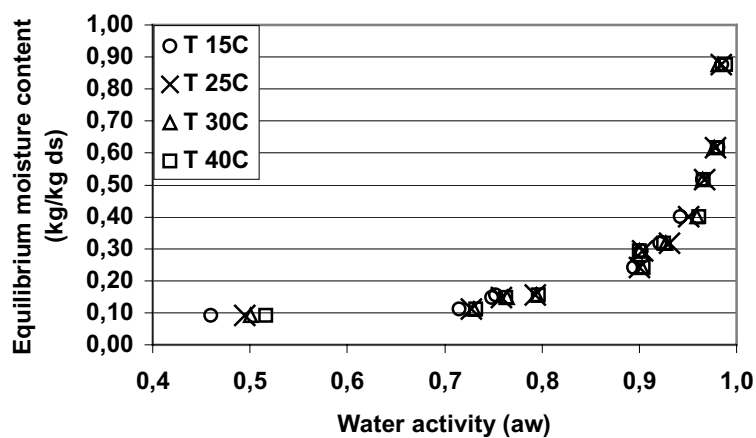
Fig. 1. Experimental values of equilibrium moisture (dry basis), as a function of water activity for pinhão at different temperatures.

The parameters for the sorption models for pinhão are shown in Table 2, together with the mean relative percentage error (MRE). The analysis of this table indicates that the Chirife model best describes the experimental desorption data for pinhão throughout the range of temperature studied, followed by the Helsey model. The Chirife model gives MRE values ranging from 5.47% and 8.79% (average value 7.19%); the Helsey model ranging from 6.62% to 10.72% (average value 8.73%) and the Oswin model gives an average MRE value of 9.47%. The Chirife model was the only to give MRE values lower than 10% for all temperatures. Comparison between experimental data and Chirife model for each temperature are shown in Figs. 2-5.

Table 2. Estimated values of coefficients and mean relative percent error (MRE) obtained for sorption models applied to experimental desorption data for pinhão

| Model	Constant	15 °C	25 °C	30 °C	40 °C	Average
GAB	X_m	0.0325	0.0266	0.0243	0.0316	
	C	169768	606437	476460	270867	
	K	0.9732	0.9832	0.9882	0.9730	
	r^2	0.963	0.975	0.956	0.986	
	MRE (%)	**11.85**	**14.15**	**18.46**	**9.41**	**13.47**
Helsey	A	0.0106	0.0122	0.0139	0.0088	
	B	1.7342	1.5286	1.4057	1.8514	
	r^2	0.974	0.989	0.970	0.988	
	MRE (%)	**7.96**	**6.62**	**10.72**	**9.61**	**8.73**
Peleg	k_1	0.5348	0.3774	2.2809	0.3696	
	k_2	17.799	1.4040	0.3837	0.8033	
	n_1	4.8883	3.3960	81.679	3.3471	
	n_2	254.72	65.342	3.5232	44.257	
	r^2	0.970	0.982	0.973	0.982	
	MRE (%)	**17.59**	**12.78**	**13.49**	**12.98**	**14.21**
Oswin	A	0.0792	0.0620	0.0531	0.0839	
	B	0.5564	0.6300	0.6854	0.5228	
	r^2	0.974	0.988	0.967	0.990	
	MRE (%)	**9.04**	**7.71**	**12.43**	**8.72**	**9.47**
Chung-Pfost	A	0.6690	0.5898	0.5815	0.5810	
	B	5.4108	5.2261	5.1691	5.2677	
	r^2	0.894	0.877	0.848	0.928	
	MRE (%)	**25.40**	**27.16**	**28.12**	**23.40**	**26.02**
Chen	k	-0.0145	-0.0154	-0.0187	-0.0096	
	C	1.0949	0.8800	0.9306	0.7906	
	B	8.5179	8.0493	8.6419	7.1729	
	r^2	0.983	0.986	0.985	0.981	
	MRE (%)	**14.21**	**13.56**	**12.70**	**15.57**	**14.01**
Henderson	A	-4.8608	-4.6541	-4.5232	-4.9950	
	B	0.5892	0.5119	0.4813	0.5932	
	r^2	0.954	0.963	0.938	0.985	
	MRE (%)	**16.55**	**19.92**	**22.88**	**11.78**	**17.78**
Chirife	A	-2.4977	-2.6188	-2.5261	-2.7625	
	B	-0.5093	-0.5271	-0.4622	-0.6483	
	C	-0.00449	-0.00695	-0.01329	0.00663	
	r^2	0.9751	0.9935	0.9859	0.9913	
	MRE (%)	**8.79**	**5.47**	**7.15**	**7.36**	**7.19**
Smith	A	-0.1310	-0.1634	-0.1649	-0.1589	
	B	-0.4634	-0.4834	-0.4866	-0.4739	
	r^2	0.913	0.896	0.866	0.944	
	MRE (%)	**21.69**	**24.59**	**25.17**	**20.38**	**22.96**
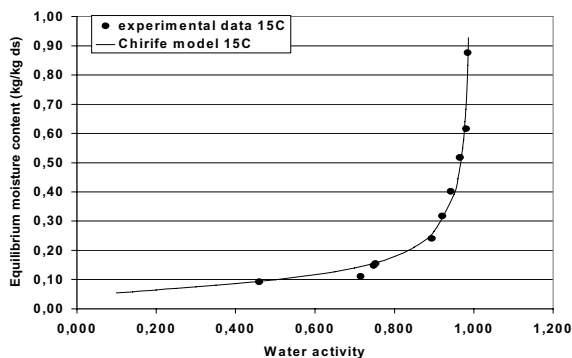
Fig. 2. Predicted moisture sorption isotherms of pinhão at 15° C using Chirife model and experimental data.
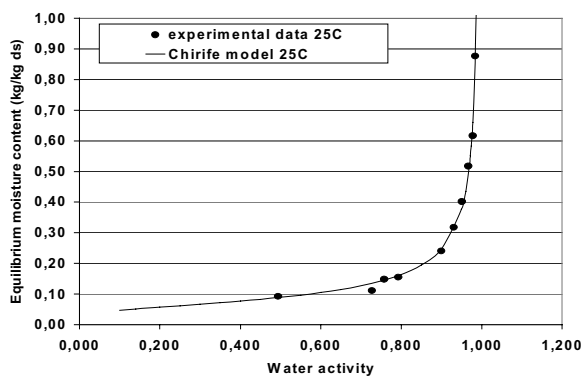

Fig. 3. Predicted moisture sorption isotherms of pinhão at 25° C using Chirife model and experimental data
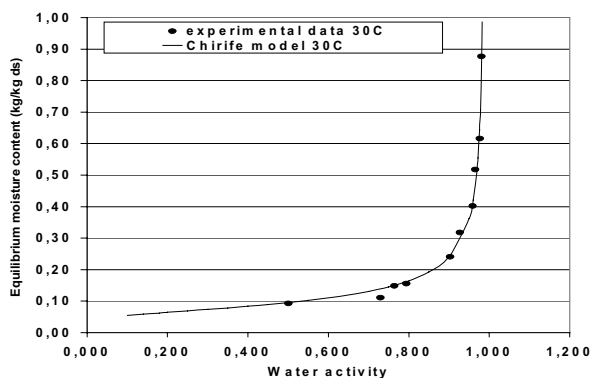

Fig. 4. Predicted moisture sorption isotherms of pinhão at 30° C using Chirife model and experimental data.
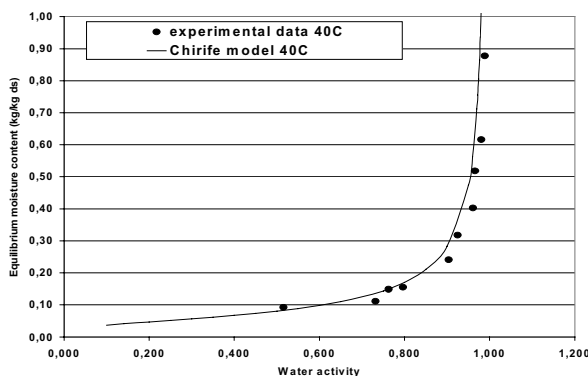
Fig. 5. Predicted moisture sorption isotherms of pinhão at 40° C using Chirife model and experimental data

3.2. Isoteric heat of sorption and differential entropy

The isosteric heats of sorption of pinhão were calculated by applying the Clausius-Clapeyron equation to the experimental equilibrium isotherm data. The Chirife model, that best describes the experimental sorption data for pinhão, was previously used to determine the *aw* values for each moisture content. The model was also used for *aw*<0.5 (out of the experimental range) to observe the behavior of the isosteric heat at low moisture content. Fig. 6 shows the results obtained. The isosteric heat has a strong dependence on moisture content, as the energy required for sorption increases at low equilibrium moisture contents. Isosteric heats of sorption are high at low moisture contents (<0,15 kg kg^{-1} ds) and decrease rapidly with an increase in material moisture content.
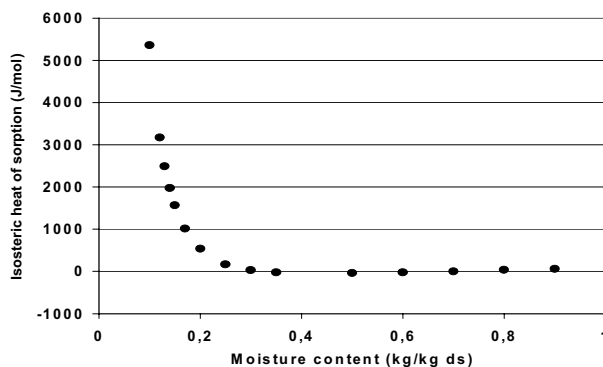

Fig. 6. Isosteric heat of sorption of pinhão as a function of equilibrium moisture content.

The ΔS values for sorption at given moisture content were calculated by linear regression using eq 16. It was assumed that, at a specific moisture content, Δh and ΔS did not vary with temperature (Aguerre et al., 1986). Results are shown in Fig.7. The differential entropy also displays a strong dependence on moisture content.
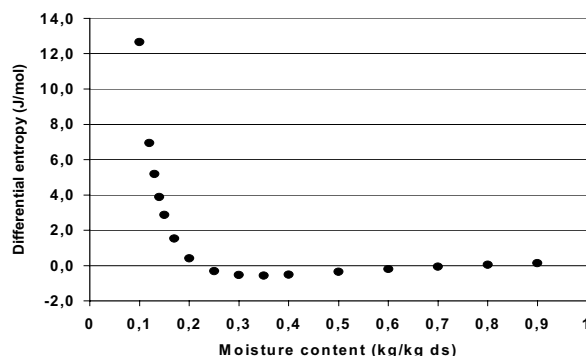
Fig. 7. Differential entropy of pinhão as a function of equilibrium moisture content.

4. Conclusions

Araucaria angustofalia seeds (pinhão) are consumed in the South of Brazil and can be considered as a source of starch, dietary fiber, magnesium and copper. The literature about technological aspects of this product is very scarce. Pinhão have a high humidity (higher than 80% db) and water activity (of about 0.98) that difficult its commercialization. The results shown that temperature has little effect on the sorption behaviour of pinhão. The water activity decreases with increasing temperature at constant equilibrium moisture content. Within the temperature (15 to 40º C) and water activity (*aw*>0.460) ranges investigated the Chirife model was found to best represent the experimental data. The net isosteric heat of sorption was calculated using the Clausius-Clapeyron equation and it decreased with increase moisture content and the trend became asymptotic as the moisture content of about 0.3 kg/kg ds was approached. The differential entropy also decreased with increase moisture content with an exponential trend similar to that of isosteric heat. Moisture isotherms of pinhão using the gravimetric method are under study in our laboratory to be compared with these results.

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