

INFLUENCE OF COOKING IN SORPTION ISOTHERMS OF *PINHÃO* (*ARAUCARIA ANGUSTIFOLIA* SEEDS)

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Abstract -- The seeds of *Araucaria angustifolia*, commonly known as *pinhão*, are widely consumed in both Southern and Southeastern Brazil due to their high nutritious value. Moisture desorption isotherms of cooked *pinhão* were determined at 15, 25, 30 and 40 °C and modeled using well know isotherm models. Results show that Chirife model most appropriately represents the experimental data as reported previously for raw *pinhão*. The differential enthalpy was calculated and decreased as moisture content increased, becoming almost constant at 0.3 kg water kg⁻¹ dry solids. Values, for each moisture content, were smaller than those reported for raw *pinhão*. The enthalpy-entropy compensation theory was applied to desorption isotherms providing the isokinetic temperature (401 ± 17 K). It was found that the desorption process investigated was enthalpy controlled as previously reported for raw *pinhão*.

Keywords -- *Pinhão*, *Araucaria angustifolia*, seed, sorption isotherms, thermodynamic properties, enthalpy-entropy compensation.

I. INTRODUCTION

Brazilian Pine (*Araucaria angustifolia*) belongs to the Araucariaceae family and is the most economically important native conifer species in Brazil (Zandavalli *et al.*, 2004). It is found in both Argentina and Brazil, stretching from southern states of Paraná, Santa Catarina and Rio Grande do Sul in Brazil to northern Argentina. People in the south of Brazil usually consume the seeds of this tree - known as *pinhão* - after being cooked and peeled. *Pinhão* is considered a source of starch, dietary fiber, magnesium and copper and its intake produces a low glycemic index (Cordenunsi *et al.*, 2004). *Pinhão* is a seasonal product, which is produced from April to August. Since the seeds have a high moisture content, they can be easily contaminated by fungi during the stockpiling, hindering its commercialization. Nutritional and technological aspects of *pinhão* are scarcely found in scientific literature. We have previously reported desorption isotherms of raw *pinhão* (Cladera-Olivera *et al.*, 2008) showing that temperature has little effect on the desorption behaviour and the Chirife model was found to best represent the experimental data.

The *pinhão* seeds can also be used to produce flour, after being cooked, peeled, dried and grinded. Cladera-Olivera *et al.* (2009) have reported the adsorption isotherms, for temperatures between 10 and 40°C, and ap-

plied the enthalpy-entropy compensation theory for *pinhão* flour. The authors found that the Chirife model was the most appropriate to describe the isotherms and that the adsorption processes was enthalpy controlled.

Another important and promising use that can be given to *pinhão* seeds is the use of its starch. The seeds have a starch content around 35% (wet basis) which can be easily extracted. Recently, Thys *et al.* (2010) presented the sorption isotherms for *pinhão* starch at temperatures ranged from 10 to 40°C and found that Peleg model most appropriately represents the experimental data and that the adsorption process investigated was spontaneous and enthalpy-controlled.

The sorption isotherms describe the relationship between water activity (equilibrium relative humidity) and the equilibrium moisture content of a given food at constant temperature; these represent an extremely valuable tool for food scientists and technologists since it can be used to predict potential changes in food stability, for storing method determination, packaging and ingredients selection, design and optimization of drying equipment. Several mathematical equations can be found in literature describing water sorption isotherms and nine of these equations are used in this work.

Thermodynamics is one of the approaches used in order to understand the properties of water and calculate energy requirements associated with heat and mass transfer in biological systems. Some thermodynamic functions employed in the analysis of sorption behavior in biological systems include the total heat of sorption, differential enthalpy, differential entropy and enthalpy-entropy compensation, which are calculated from sorption isotherms. The total heat of sorption (ΔH) is the total energy required to transfer water molecules from vapor state into a solid surface or vice-versa. It is useful, for example, in predictive drying models and in the design of drying equipment (Fasina, 2006). The isosteric heat of sorption or differential enthalpy (Δh) is the total heat of sorption minus the latent heat of vaporization for water and is a measure of the water-solid binding strength (McMinn and Magee, 2003). This is an important property which is employed for both design work and qualitative understanding of the water state on the food surface (Tolaba *et al.*, 2004). The differential entropy (Δs) of a material is proportional to the number of available sorption sites at a specific energy level (Madamba *et al.*, 1996). Gibbs free energy (ΔG) may be an indicative of the affinity of sorbents for water and provides a criterion to whether water sorption occurs as

a spontaneous process or not (Telis *et al.* 2000; Apostolopoulos and Gilbert, 1990).

Enthalpy-entropy compensation theory (or isokinetic theory) is used to evaluate physical and chemical phenomena such as sorption reactions. The theory states, in order to minimize free energy changes due to these phenomena, that: (i) the compensation (by changing Δh or Δs) arises from the nature of the interaction between the solute and solvent causing the reaction and (ii) the relationship between the enthalpy and entropy for a specific reaction is linear (Labuza, 1980; Madamba *et al.*, 1996). Ferro-Fontan *et al.* (1982) suggested the existence of a linear relationship between enthalpy and entropy for water sorption in some foods, which is confirmed by several other authors (Madamba *et al.*, 1996; Telis *et al.*, 2000; McMinn and Magee, 2003; Fasina, 2006).

The objectives of the present work are: (1) obtain desorption isotherms of cooked *pinhão* at selected temperatures by using mathematical models described in literature; (2) determine some thermodynamic functions (differential enthalpy and entropy); (3) evaluate the application of the enthalpy-entropy compensation theory and (4) compare the results obtained with the results available in the literature for raw *pinhão* in order to evaluate the effect of cooking in desorption process.

II. MATERIALS AND METHODS

A. Experimental procedure

Materials

The chemicals were from Quimex (São Paulo, SP, Brazil), Nuclear (Diadema, SP, Brazil) and Vetec (Duque de Caxias, RJ, Brazil).

The *Araucaria angustifolia* seeds used in this study were purchased at a local market (Porto Alegre, RS, Brazil) in 2005. The seeds were cleaned with abundant water, dried at ambient conditions for 24-48 h, selected and stored at 5° C in polythene bags until used, for a maximum period of 10 days. The *pinhão* seeds are cooked in autoclave for 50 min at 120°C before peeled.

Proximate composition

Proximate composition (moisture, protein, fat, ash, crude fiber, starch), total acidity and pH of cooked *pinhão* were determined. The total protein content was determined by the Kjeldahl method according to the method 979.09 of AOAC (1990), using a Tecator digester (Perstorp Analytical Co., Sweden). The conversion factor used was %N x 5.75 (Cladera-Olivera *et al.*, 2008). Ash was determined by incineration in a muffle furnace (Temco, Iowa, USA) at 550° C (method 923.03 of AOAC, 1990). Crude fiber was determined as ash after acidic and basic digestion according to the Method 962.09 of AOAC (1990). Lipids were extracted in a Soxhlet extractor (Tecnal, Piracicaba, SP, Brazil) with petroleum ether during 6 hours without acid digestion and were determined gravimetrically. Starch was determined by direct acid hydrolysis and by determining the amount of glucose in filtrate with Lane-Eynon volumetric method (Pearson, 1975).

Moisture content was calculated through the weight loss of a 10 g sample after heated in a conventional oven at 105°C (Biomatic 303, Porto Alegre, RS, Brazil) until attaining constant weight. Water activity (at 25° C) was determined in a water activity instrument (*AquaLab 3TE-Decagon*, Pullman, WA, USA). For pH analysis, 10 g of the sample were mixed with 75 mL of water at 25° C and the pH was measured after 1 hour with a digital pH-meter (Quimis Q-400M, São Paulo, Brazil). Total acidity was determined with 0.1 N sodium hydroxide titration, by using phenolphthalein as indicator, according to the Method 942.15 (AOAC, 1990) and expressed as mL of NaOH 0.1 N g⁻¹. Analyses were carried out in triplicate and results were expressed as average value ± standard deviation in percentage and in wet basis (wb).

Desorption isotherms

The desorption isotherms were determined by taking samples with different moisture content and measuring their water activity and their moisture content (Benado and Rizvi, 1985; Fasina, 2006) as described previously for raw *pinhão* (Cladera-Olivera *et al.*, 2008). The initial moisture content of cooked *pinhão* was about 80% dry basis (db).

In order to obtain samples with different moisture contents, the cooked seeds (with coat) were dried at 50°C in a bin drier (Ajibola *et al.*, 2003) during different times. From time to time, samples were taken off and stored in polythene bags (the final time of dryer was 50 hours) obtaining twelve samples with different moisture levels. The samples were kept in a refrigerator at 0° C for 10 days to reach uniform moisture (Ajibola *et al.*, 2003) and avoiding microbial activity. After this time, samples were allowed to equilibrate in the ambient condition for 6 hours (Ajibola *et al.*, 2003) in the bags and rapidly peeled and sliced. Immediately, a water activity instrument (*AquaLab 3TE-Decagon*, Pullman, WA), with user-selectable internal temperature control, was used to measure the water activity (equilibrium relative humidity) of the samples. Measures were carried out at four temperatures (15, 25, 30 and 40° C). The instrument uses the chilled-mirror dewpoint technique to measure the aw of a sample. In an instrument that uses the dewpoint technique, the sample is equilibrated with the headspace of a sealed chamber that contains a mirror and a means of detecting condensation on the mirror. At equilibrium, the relative humidity of the air in the chamber is the same as the water activity of the sample (Decagon Devices, 2003). Moisture content was also determined in each sample as described before, obtaining the equilibrium moisture content, expressed as kg water kg⁻¹ dry solids (ds). Water activity/moisture sorption analysis was carried out in duplicate. Equilibrium moisture content and water activity were taken as the average of the two moisture contents and water activities for each sample.

B. Data analysis

Isotherm models

The experimental data for the desorption isotherms 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, Tulsa, OK, USA). Regressions were repeated with various initial estimated values both above and below those that had been calculated to confirm that convergence has been reached (Peleg, 1993). The Brunauer-Emmett-Teller (BET) model (Park *et al.*, 2002), commonly used to fit isotherms, was not tested because this model is used for $aw < 0.5$ and aw experimental values obtained were almost out of this range. The goodness of fit of the different models was evaluated with the coefficient determination (r^2) and the mean relative deviation modulus (MRD). MRD has been widely adopted throughout the literature to evaluate the accuracy of the fit of isotherm models and is defined by:

$$MRD = \frac{100}{N} \sum_{i=1}^N \frac{|X_{ei} - X_{pi}|}{X_{ei}} \quad (1)$$

where X_{ei} and X_{pi} are, respectively, the measured and predicted equilibrium moisture content (kg water kg⁻¹ dry solids) and N is the number of data points. The lower the values of MRD the better fit of the model and MRD values below 10% generally indicate an adequate fit for practical purposes (Lomauro *et al.*, 1985).

Calculation of the isosteric heat (differential enthalpy) of desorption and the differential entropy

The differential enthalpy and entropy of sorption can be determined from moisture sorption data by using the following equation (Fasina *et al.*, 1997; 1999)

$$(\ln aw)_x = -\frac{\Delta h}{RT} + \frac{\Delta s}{R} \quad (2)$$

where aw represents the water activity, Δh the differential enthalpy of sorption (J mol⁻¹), Δs the differential entropy (J mol⁻¹ K⁻¹), R the universal gas constant (J mol⁻¹ K⁻¹), X the equilibrium moisture content (kg water kg⁻¹ dry solids) and T the absolute temperature (K).

The total heat of sorption ΔH (J mol⁻¹) can be obtained from the following equation:

$$\Delta H = \Delta h + \Delta H_{vap} \quad (3)$$

where ΔH_{vap} is the latent heat of vaporization of free water (J mol⁻¹).

The differential enthalpy of sorption (Δh) was calculated with basis on Eq. (2), where $\ln(aw)$ was plotted versus $1/T$ for a certain moisture content thus determining the slope of the curve, which is equal to $-\Delta h/R$; the differential entropy is obtained from the linear coefficient ($\Delta s/R$) of the straight (McMinn and Magee, 2003). The model that best describes the experimental sorption data for cooked *pinhão* was used to determine the aw value for each moisture content.

Enthalpy-entropy compensation theory (isokinetic theory) Ferro-Fontan *et al.* (1982) suggested the existence of a linear relationship between enthalpy and entropy for water sorption in some foods and this is confirmed by several other authors (Madamba *et al.*, 1996; Telis *et al.*, 2000; McMinn and Magee, 2003; Fasina, 2006). The isokinetic temperature, evaluated from the slope of the straight, represents the temperature at which all reactions in series proceed at the same rate (Heyrovsky, 1970). The compensation theory proposes a linear relationship between Δh and Δs (Leffler and Grunwald, 1963; Telis *et al.*, 2000; McMinn *et al.*, 2005):

$$\Delta h = T_\beta \Delta s + \Delta G_\beta \quad (4)$$

where T_β (K) is the isokinetic temperature and ΔG_β (J mol⁻¹) is the free energy at T_β and these values were obtained by linear regression. From a thermodynamic viewpoint, the free energy change (ΔG) can be used as an indicative of the sorbent affinity for water, hence providing a criterion as to whether water sorption is a spontaneous ($\Delta G < 0$) or non-spontaneous ($\Delta G > 0$) process (Apostolopoulos and Gilbert, 1990).

As proposed by Krug *et al.* (1976a, 1976b) a statistical analysis test can be used to corroborate the compensation theory, by comparing T_β with the harmonic mean

Table 1. Sorption isotherm models used in this work.

Name of the equation	Equation
BET (Brunauer <i>et al.</i> , 1938)	$\frac{aw}{(1-aw)X} = \frac{1}{X_m \cdot C} + \frac{(C-1)aw}{X_m \cdot C}$
GAB (Guggenheim-Anderson-de Boer) (Van den Berg, 1985)	$X = \frac{X_m \cdot C \cdot K \cdot aw}{(1 - K \cdot aw) \times (1 - K \cdot aw + C \cdot K \cdot aw)}$
Halsey (Halsey, 1948)	$aw = \exp\left(-\frac{A}{X^B}\right)$
Peleg (Peleg, 1993)	$X = k_1 \cdot aw^{n_1} + k_2 \cdot aw^{n_2}$
Oswin (Lomauro <i>et al.</i> , 1985)	$X = A \left(\frac{aw}{1-aw}\right)^B$
Chung – Pfof (Chung and Pfof, 1967)	$\ln(aw) = -A \cdot \exp(-B \cdot X)$
Henderson (Henderson, 1952)	$(1-aw) = \exp(A \cdot X^B)$
Chirife (Castillo <i>et al.</i> , 2003)	$X = \exp[A + B \cdot \ln(C - \ln aw)]$
Smith (Smith, 1947)	$X = A + (B \cdot \log(1-aw))$

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

temperature, defined as:

$$T_{hm} = \frac{n}{\sum_1^n (1/T)} \quad (5)$$

where n is the total number of isotherms used.

The compensation theory only applies if $T_\beta \neq T_{hm}$. An approximate $(1-\alpha)100\%$ confidence interval for T_β may be calculated from the following equation (Bertoin *et al.*, 1996; Telis *et al.*, 2000):

$$T_\beta = T_\beta \pm t_{m-2, \alpha/2} \sqrt{\text{Var}(T_\beta)} \quad (6)$$

where:

$$T_\beta = \frac{\sum (\Delta h - \overline{\Delta h})(\Delta s - \overline{\Delta s})}{\sum (\Delta s - \overline{\Delta s})^2} \quad (7)$$

and

$$\text{Var}(T_\beta) = \frac{\sum (\Delta h - \overline{\Delta h} - T_\beta \cdot \Delta s)^2}{(m-2) \cdot \sum (\Delta s - \overline{\Delta s})^2} \quad (8)$$

where m is the number of $(\Delta h, \Delta s)$ data pairs, $\overline{\Delta h}$ the average enthalpy, $\overline{\Delta s}$ the average entropy and $\overline{\Delta G_\beta}$ the average free energy.

III. RESULTS AND DISCUSSION

A. Proximate composition

Moisture represents $50.8 \pm 0.1\%$ of the fresh weight of cooked *pinhão* and the seed has a very high water activity, 0.984 ± 0.004 (at 25°C). Starch is the second main compound with $36.8 \pm 0.3\%$ (wb). *Pinhão* starch can be easily isolated by treatment with water under mild conditions, without addition of any additive (Cordenusi *et al.*, 2004; Thys *et al.*, 2008), and its properties suggest various new applications (Bello-Perez *et al.*, 2006). Other compounds were (wb): protein, $2.7 \pm 0.1\%$; crude fibre, $1.6 \pm 0.2\%$; lipid $1.11 \pm 0.03\%$ and ash $1.74 \pm 0.05\%$. These results were similar to those found for raw *pinhão* by Cladera-Olivera *et al.* (2008), and for raw and cooked *pinhão* by Cordenusi *et al.* (2004) Total acidity was 3.5 ± 0.1 mL of 0.1N NaOH g^{-1} and pH 4.8 ± 0.3 . As a result of cooking, the white seeds become brown on the surface due to the migration of some tinted compounds present in the seed coat (Cordenusi *et al.*, 2004).

B. Desorption isotherms

Figure 1 shows the experimental values of equilibrium moisture content of cooked *pinhão* as a function of water activities at different temperatures.

The standard deviation for the equilibrium moisture content of each experimental point was within the range of 0.001-0.015 (kg water kg^{-1} dry solids) and for the water activity 0.003-0.021. The range of water activity was $0.425 < a_w < 0.999$ and it was not possible to obtain lower values of a_w with this procedure, due to the high resistance to mass transfer of the coat seed.

As expected, the equilibrium moisture content decreased with decrease in water activity at constant temperature. This may be due to the fact that vapour pres-

sure of water present in foods increases with the umidity of the surroundings (Shivhare *et al.*, 2004).

The analysis of Fig. 1 also indicates that, in the range of the temperature used (between 15 and 40°C), the desorption isotherms of cooked *pinhão* were close to each other at different temperatures and results were similar to those found for raw *pinhão* by Cladera-Olivera *et al.* (2008). Since cooked *pinhão* is rich in starch and protein, these components affect the sorption data considerably, because protein and starch are macromolecules rich in polar sites such as $-\text{OH}$ and $-\text{H}$ groups, which behave as active (polar) sorptions centers (Erbas *et al.*, 2005).

The sorption relationships detailed in Table 1 were fitted to the experimental data. The parameters for desorption models for cooked *pinhão* are shown in Table 2, together with the mean relative deviation modulus (MRD).

As can be observed, Chirife model best describes the experimental data throughout the range of temperature studied, followed by the GAB model. The Chirife model gives MRD values ranging from 5.33% to 7.18% (average value 5.94%) and the GAB model ranging from 7.50% to 10.22% (average value 8.40%). The Chirife model was the only to give MRD values lower than 10% for all temperatures as described previously for raw *pinhão* (Cladera-Olivera *et al.*, 2008). This model also was the best to describe adsorption isotherms of *pinhão* flour (Cladera-Olivera *et al.*, 2009). For *pinhão* starch between 10 to 40°C , Thys *et al.* (2010) found that the Peleg model was the best to represent the experimental data but it was observed that other models also fitted well (Chung-Pfost, GAB, Henderson, BET and Chirife, in this order).

From GAB equation it is possible to evaluate the monolayer moisture content values (X_m) of foods. This is an important parameter in food storage and deterioration. The values of monolayer moisture content of cooked *pinhão* determined with GAB model can also be observed in Table 2 and are in the acceptable range for food products. Labuza (1984) indicated 10% (db) as the maximum monolayer moisture content for foods. Values of X_m for cooked *pinhão* were higher than values for raw *pinhão* for each temperature (Cladera-Olivera *et al.*, 2008) probably due to the gelatinization of starch.

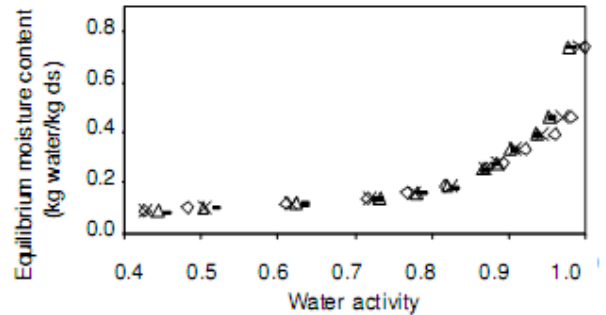


Figure 1. Experimental values of equilibrium moisture content (dry basis) as a function of water activity for cooked *pinhão* at different temperatures (\diamond 15°C ; \times 25°C ; Δ 30°C ; \square 40°C).

Table 2. Estimated values of coefficients and mean relative deviation modulus (MRD) obtained for selected sorption models applied to experimental desorption data for cooked *pinhão*.

Model	Constant	Temperature				Mean
		15 ° C	25 ° C	30 ° C	40 ° C	
GAB	X_m	0.0425	0.0435	0.0398	0.0394	
	C	369143	848860	936573	687180	
	K	0.9392	0.9455	0.9660	0.9699	
	r^2	0.968	0.983	0.989	0.988	
	MRD (%)	10.22	7.50	7.69	8.20	8.40
Halsey	A	0.0004	0.0036	0.0135	0.0160	
	B	4.0253	2.5810	1.6813	1.5751	
	r^2	0.830	0.928	0.988	0.988	
	MRD (%)	27.13	17.49	5.24	5.31	13.79
Peleg		NC	NC	NC	NC	
Oswin	A	0.1513	0.1209	0.0866	0.0817	
	B	0.2377	0.3729	0.5649	0.6016	
	r^2	0.924	0.971	0.994	0.993	
	MRD (%)	25.55	14.60	6.45	7.24	13.46
Chung-Pfost	A	1.6800	1.0603	0.8594	0.8288	
	B	9.8890	7.3140	6.0181	5.8054	
	r^2	0.989	0.966	0.898	0.790	
	MRD (%)	9.43	17.79	27.05	27.40	20.42
Henderson	A	-9.4835	-6.4874	-4.7867	-4.5842	
	B	1.1075	0.8542	0.6407	0.6142	
	r^2	0.991	0.988	0.974	0.970	
	MRD (%)	7.88	10.70	15.15	15.73	12.37
Chirife	A	-2.4064	-2.5429	-2.6246	-2.6305	
	B	-0.5099	-0.6223	-0.6401	-0.6378	
	C	0.0155	0.0207	0.0044	0.0003	
	r^2	0.988	0.989	0.994	0.994	
MRD (%)	7.18	5.90	5.33	5.36	5.94	
Smith	A	0.0265	-0.0352	-0.0870	-0.0967	
	B	-0.2457	-0.3434	-0.4312	-0.4481	
	r^2	0.989	0.980	0.925	0.916	
	MRD (%)	7.38	13.64	23.32	23.89	17.05

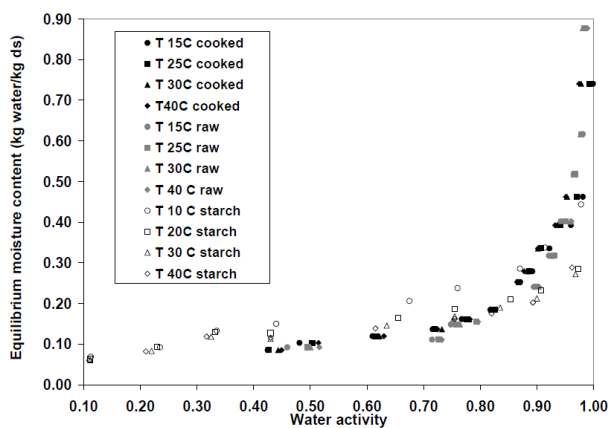


Figure 2. Comparison between isotherms of cooked *pinhão* (this work), raw *pinhão* (Cladera-Olivera *et al.*, 2008), and starch *pinhão* (Thys *et al.*, 2010) at different temperatures.

As reported by Bello-Pérez *et al.* (2006) *pinhão* starch has higher swelling, solubility and granule size than corn starch and that this starch source can be an alternative for food formulation where high moisture contents are required.

Figure 2 shows isotherms of cooked *pinhão* together with isotherms of raw *pinhão* (Cladera-Olivera *et al.*, 2008) and isolated starch *pinhão* (Thys *et al.*, 2010) ob

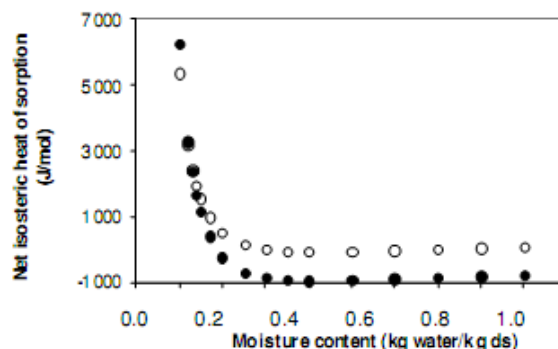


Figure 3. Differential enthalpy of desorption cooked (●) *pinhão* and raw (○) *pinhão* (Cladera-Olivera *et al.*, 2008) and as a function of equilibrium moisture content.

tained in previously works, for the sack of fully appreciating of these related substances. Isotherms of starch *pinhão* were obtained using the gravimetric method and aw values below 0.4 also were studied.

C. Isosteric heat of sorption (differential enthalpy) and differential entropy

The differential enthalpies of desorption of cooked *pinhão* were calculated by applying Eq. (2). The Chirife model, which best describes the experimental desorption data, has previously been used to determine aw val-

ues for each equilibrium moisture content. Values of a_w between 0.1 and 0.4 were extrapolated from the model. Figure 3 shows the results obtained together with results previously reported for raw *pinhão* (Cladera-Olivera *et al.*, 2008) where the differential enthalpy of desorption was plotted against the equilibrium moisture content.

The analysis of this figure reveals that the differential enthalpy has a strong dependence on moisture content at low equilibrium moisture contents, since the energy required for sorption increases at low equilibrium moisture contents. Differential enthalpies are high at low moisture contents (<0.2 kg water kg^{-1} ds), decrease sharply as the moisture content increases and become almost constant at 0.3 kg water kg^{-1} ds for raw and cooked *pinhão*. Process of cooking result in a an increase in differential enthalpy at very low moisture content, probably due to the starch gelatinization and consequently higher energy requirement to remove water. However, a decrease in differential enthalpy for higher moisture content was obtained for cooked *pinhão* and a lower energy requirement to remove water comparing with raw *pinhão*. It should be noted that a negative Δh value is purely a mathematical result and has no physical meaning and it might be within the error of determination (Kaymak-Ertekin and Gedik, 2004).

The Δs values for sorption at given moisture content were also calculated by linear regression using Eq. (2). It was assumed that, at a specific moisture content, Δh and Δs did not vary with temperature (Aguerre *et al.*, 1986). These results are shown in Fig. 4, which presents the differential entropy as a function of the moisture content together with results previously reported for raw *pinhão* (Cladera-Olivera *et al.*, 2008).

This figure indicates that the differential entropy also displays a strong dependence on moisture content at low equilibrium moisture contents and increases sharply at moisture content below 0.2 kg water kg^{-1} ds. Differences between raw and cooked *pinhão* for differential entropies were similar to that differential enthalpies. Values for differential entropy also were higher for cooked *pinhão*, at very low moisture content indicating that there are a higher number of available sorption sites at a specific energy level. However, for $a_w > 0.12$ higher values for raw *pinhão* were obtained.

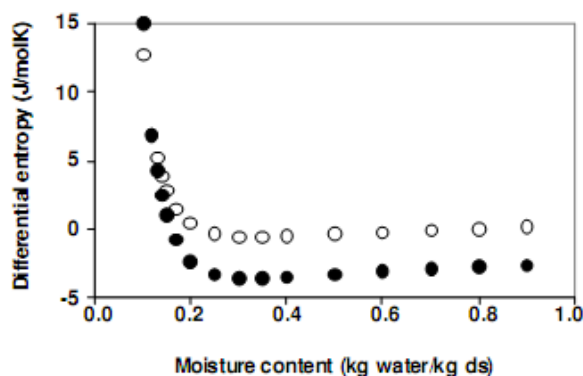


Figure 4. Differential entropy of desorption of cooked (●) *pinhão* and for raw *pinhão* (○) (Cladera-Olivera, 2008) as a function of equilibrium moisture content.

D. Enthalpy-entropy compensation theory

Figure 5 shows the differential enthalpy (Δh) versus differential entropy (Δs) for cooked *pinhão*. As can be noted, a linear relation between these variables was obtained (with a coefficient determination $r^2 = 0.993$), indicating that compensation exists. Similar results were obtained for raw *pinhão* (Cladera-Olivera *et al.*, 2008), *pinhão* flour (Cladera-Olivera *et al.*, 2009) and *pinhão* starch (Thys *et al.*, 2010). The parameters T_β and ΔG_β (Eq. 4) were calculated from the data by means of linear regression. The isokinetic temperature (T_β) is the temperature at which all sorption reactions will take place at the same rate. A value of 401 ± 17 K (within a 95% confidence interval) for desorption of cooked *pinhão* was found. For desorption isotherms of raw *pinhão* we have previously reported a value of 422 ± 18 K and for *pinhão* flour 407 ± 20 K. For starch materials, McMinn *et al.* (2005) found values between 366.8 and 466.8 K. For quinoa grains, Tolaba *et al.* (2004) found a value of 361.0 K, for garlic, Madamba *et al.* (1996) found a value of 348 ± 9 K, for oatmeal biscuit and oat flakes, McMinn *et al.* (2007) found values of 430.9 ± 1.88 and 443.4 ± 0.91 , respectively. Values between 458 and 475 K were obtained for desorption and desorption of persimmon skin and pulp (Telis *et al.*, 2000). The harmonic mean temperature (Eq.5) was calculated and a value of 300 K was found. This value is significantly different from T_β , confirming the suitability of the isokinetic theory.

According to Leffler (1955), if $T_\beta > T_{hm}$ the process is enthalpy driven, while if $T_\beta < T_{hm}$ the process is entropy controlled. As the former condition is satisfied in this study, desorption mechanism can be considered to be enthalpy-driven. Same results were obtained for raw *pinhão*, flour and starch (Cladera-Olivera *et al.*, 2008; 2009; Thys *et al.*, 2010). McMinn *et al.* (2005), Aguerre *et al.* (1986) and Beristain *et al.* (1996) also reported an enthalpy-controlled mechanism in the sorption of starch materials.

The value of ΔG obtained (524 J mol^{-1}) suggests that desorption process is non-spontaneous ($\Delta G > 0$). For desorption isotherms of raw *pinhão* we have previously reported a smaller value (192 J mol^{-1}). This can be explained by starch gelatinization and higher affinity for water than raw *pinhão*. For desorption of starch materi-

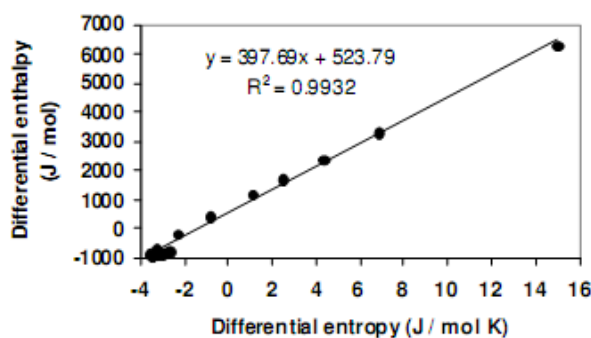


Figure 5. Differential enthalpy as a function of differential entropy for cooked *pinhão*.

als McMinn *et al.* (2005) found values between -1525 and 69 J mol^{-1} , for oatmeal biscuit and oat flakes McMinn *et al.* (2007) found values of 280 and 325 J mol^{-1} , respectively.

IV. CONCLUSIONS

In this work we present the desorption isotherms of cooked *pinhão*, a seed widely consumed in both Southern and Southeastern Brazil due to their high nutritious value. The results showed that temperature has little effect on the desorption behavior. As expected, the equilibrium moisture content decreased as water activity decreased at constant temperature. Within the temperature range studied, 15 to 40°C , and water activity range of 0.425 to 0.999 , the Chirife model was found to best represent the experimental data.

The differential enthalpy of desorption was calculated and found to decrease as the moisture content increased; and it was also found that this variable became almost constant as moisture content of $0.3 \text{ kg water kg}^{-1}$ ds was approached; the differential entropy behaved similarly. Plots of differential enthalpy versus differential entropy satisfied the enthalpy-entropy compensation theory (isokinetic theory). Results suggested that desorption processes in cooked *pinhão* are enthalpy-controlled (isokinetic temperature $>$ harmonic mean temperature) and not spontaneous ($\Delta G > 0$) as describe previously for raw *pinhão*.

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