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

F. CLADERA-OLIVERA‡, C.P.Z. NOREÑA†, A.C. PETTERMANN‡ and L.D.F. MARCZAK‡

† Institute of Food Science and Technology, Federal University of Rio Grande do Sul, (ICTA-UFRGS), Porto Alegre, RS, Brazil.
florenceia.cladera@ufrgs.br, cazapatam@ufrgs.br, apettermann@hotmail.com
‡ Department of Chemical Engineering, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil. Il-gia@enq.ufrgs.br (Corresponding author)

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 known 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.

1. 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 ground. Cladera-Olivera et al. (2009) have reported the adsorption isotherms, for temperatures between 10 and 40°C, and applied 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 $\Delta h$ or $\Delta s$) 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 and cooked *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 in 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 fitting of isotherm models and is defined by:

$$\text{MRD} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{X_{pi} - X_{ei}}{X_{ei}} \right|$$

where $X_{pi}$ and $X_{ei}$ 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)

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

where $aw$ represents the water activity, $\Delta h$ the differential enthalpy of sorption (J mol$^{-1}$), $\Delta s$ 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 $\Delta H$ (J mol$^{-1}$) can be obtained from the following equation:

$$\Delta H = \Delta h + \Delta H_{wv}$$

where $\Delta H_{wv}$ is the latent heat of vaporization of free water (J mol$^{-1}$).

The differential enthalpy of sorption ($\Delta h$) 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 $-\Delta h/RT$; the differential entropy is obtained from the linear coefficient ($\Delta s/RT$) 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 $\Delta h$ and $\Delta s$ (Leffler and Grunwald, 1963; Telis et al., 2000; McMinn et al, 2005):

$$\Delta h = T_{\beta}\Delta s + \Delta G_{\beta}$$

where $T_{\beta}$ (K) is the isokinetic temperature and $\Delta G_{\beta}$ (J mol$^{-1}$) is the free energy at $T_{\beta}$ and these values were obtained by linear regression. From a thermodynamic viewpoint, the free energy change ($\Delta G$) 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 $T_{\beta}$ with the harmonic mean

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

Abbreviations: $X$, equilibrium moisture content (kg water kg$^{-1}$ dry solids); $aw$, water activity; $X_{aw}$, 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:

\[ T_m = \frac{n}{\sum (1/T)} \]  

where \( n \) is the total number of isotherms used.

The compensation theory only applies if \( T_\beta \neq T_m \). An approximate \((1-\alpha)100\%\) confidence interval for \( T_\beta \) may be calculated from the following equation (Bellido-Perez et al., 1996; Telis et al., 2000):

\[ T_\beta = T_m \pm t_{\alpha/2, \nu} \sqrt{\text{Var}(T_\beta)} \]  

where:

\[ T_\beta = \sum (\Delta h - \Delta S) / \sum (\Delta S - \Delta S) \]  

and

\[ \text{Var}(T_\beta) = \sum (\Delta h - \Delta S - T_\beta \Delta S)^2 / (m-2) \sum (\Delta S - \Delta S) \]  

where \( m \) is the number of \((\Delta h, \Delta S)\) data pairs, \( \bar{\Delta h} \) the average enthalpy, \( \bar{\Delta S} \) the average entropy and \( \bar{\Delta h}_\beta \) the average free energy.

III. RESULTS AND DISCUSSION

A. Proximate composition

Moisture represents 50.8 ± 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 ± 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 ± 0.1%; crude fibre, 1.6 ± 0.2%; lipid 1.11 ± 0.03% and ash 1.74 ± 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 < aw < 0.999 and it was not possible to obtain lower values of aw 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-
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*.

<table>
<thead>
<tr>
<th>Model</th>
<th>Constant</th>
<th>Temperature</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAB</td>
<td>$X_w$</td>
<td>0.0425</td>
<td>0.0435</td>
</tr>
<tr>
<td></td>
<td>$C$</td>
<td>0.0392</td>
<td>0.9455</td>
</tr>
<tr>
<td></td>
<td>$K$</td>
<td>0.968</td>
<td>0.983</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>10.22</td>
<td>7.50</td>
<td>7.69</td>
</tr>
<tr>
<td>Halsey</td>
<td>$A$</td>
<td>0.0004</td>
<td>0.0036</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>4.0253</td>
<td>2.5810</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>27.13</td>
<td>17.49</td>
<td><strong>5.24</strong></td>
</tr>
<tr>
<td>Peleg</td>
<td>$A$</td>
<td>0.1513</td>
<td>0.1209</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>0.2377</td>
<td>0.3729</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>Oswin</td>
<td>$A$</td>
<td>1.6800</td>
<td>1.0603</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>9.8900</td>
<td>7.3140</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>25.55</td>
<td>14.60</td>
<td><strong>6.45</strong></td>
</tr>
<tr>
<td>Chung-Pfost</td>
<td>$A$</td>
<td>-9.4835</td>
<td>-6.4574</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>1.1075</td>
<td>0.8542</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>7.88</td>
<td><strong>10.70</strong></td>
<td>15.15</td>
</tr>
<tr>
<td>Henderson</td>
<td>$A$</td>
<td>-2.4064</td>
<td>-2.5429</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>-0.5099</td>
<td>-0.6223</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>7.18</td>
<td><strong>5.90</strong></td>
<td><strong>5.33</strong></td>
</tr>
<tr>
<td>Chirife</td>
<td>$A$</td>
<td>0.0155</td>
<td>0.0207</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>-0.9242</td>
<td>-0.971</td>
</tr>
<tr>
<td>MRD (%)</td>
<td>7.38</td>
<td><strong>13.64</strong></td>
<td><strong>23.32</strong></td>
</tr>
</tbody>
</table>

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) obtained in previous works, for the sake 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. Isothermic 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 aw 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 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 \(\Delta h\) value is purely a mathematical result and has no physical meaning and it might be within the error of determination (Kaymak-Ertakin and Gedik, 2004).

The \(\Delta s\) 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, \(\Delta h\) and \(\Delta s\) did not vary with temperature (Aguerre et al., 1986, 2004). 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 aw > 0.12 higher values for raw pinhão were obtained.

### D. Enthalpy-entropy compensation theory

Figure 5 shows the differential enthalpy (\(\Delta h\)) versus differential entropy (\(\Delta s\)) 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 \(T_p\) and \(\Delta G_p\) (Eq. 4) were calculated from the data by means of linear regression. The isokinetic temperature (\(T_p\)) 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 sorption 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 ± 20K. 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 sorption 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 \(T_p\), confirming the suitability of the isokinetic theory.

According to Leffler (1955), if \(T_p > T_{hm}\) the process is enthalpy driven, while if \(T_p > T_{hm}\) 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 \(\Delta G\) 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 4. Differential entropy of desorption of cooked (●) pinhão and for raw pinhão (○) (Cladera-Olivera, 2008) as a function of equilibrium moisture content.](image-url)

![Figure 5. Differential enthalpy as a function of differential entropy for cooked pinhão.](image-url)
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 authors gratefully acknowledge the financial support of “Conselho Nacional de Desenvolvimento Científico e Tecnológico” (CNPq) and “Fundação de Apoio à Pesquisa do Rio Grande do Sul” (FAPERGS) from Brazil.

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