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# Physicochemical, thermal and sorption properties of nutritionally differentiated flours and starches

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ABSTRACT

The aims of this work were to analyze physicochemical and thermal properties of ahipa and cassava flours and starches and to determine their water sorption isotherms and thermodynamic properties. Both flours are naturally gluten-free products, obtained by relatively simple procedures (grating or slicing). Ahipa flour gelatinized at lower temperature than cassava, indicating a better aptitude for cooking. Gelatinization temperatures of flours were higher than those of their starches. Water holding capacity of ahipa flours was significantly higher than those of cassava, leading the slicing process the highest values. Sorption isotherms were determined at 10, 20 and 30 °C. Experimental data were satisfactorily fitted using different mathematical models. Thermodynamic parameters associated with water adsorption process were calculated from GAB model, as well as the monolayer water content. All samples could be considered as products with an acceptable stability.



## 1. Introduction

Many of the developing countries' economies are greatly reliant on root and tuber (R&T) crops as a source of food, nutrients, and profits. Cassava, one of the most important calories supply in the tropics, is relevant in the agriculture of areas where resources are scarce. Cassava can be considered a traditional R&T crop. On the other hand, the neotropical genus *Pachyrhizus* DC. (Yam beans) is one of the few legume genera with edible tuberous roots. *Pachyrhizus* species could be developed as a new source of non-traditional flour and starch. This genus is native to Southern and Central America and the main cultivated species are: *Pachyrhizus tuberosus*, the "Amazonian yam bean", grown in Bolivia, Peru, Ecuador, and Brazil; *Pachyrhizus erosus*, the "jacatupe" or "Mexican yam bean", found in Central America and the Caribbean, and *Pachyrhizus ahipa*, the "Andean yam bean" or "ahipa" from the Andes of Bolivia and Northern Argentina (Forsyth et al., 2002). Interest in *Pachyrhizus* species use have arose as it is demonstrated by several studies on the subject (Doporto et al., 2011; Leonel et al., 2005; López et al., 2010). Nevertheless, references about ahipa roots industrialization are rather scarce.

In order to develop gluten-free breads for celiac patients, a number of alternative flour types to wheat such as corn, cassava, rice, soybean and chickpea flour have been used (Demirkesen et al., 2010). In the same way that cassava, ahipa flour can be considered a nutritionally differentiated product since it is a naturally gluten-free flour (with prolamins content below 0.1 mg/100 g, according to currently available detection methods).

Water sorption of foodstuffs is a major subject in different areas of food science and engineering. Sorption isotherms of food products provide helpful information for the design, modeling and optimization of many operations and technological processes (i.e. drying, aeration). Likewise, the study of water sorption phenomenon allows predicting the stability and quality during packaging and storage of food products. According to Vishwakarma et al. (2011), the adsorption of moisture by foods is a process wherein water molecules progressively and reversibly combine with the food solids via chemical sorption, physical adsorption, and multilayer condensation. Moisture content at which vapor pressure of water present in food equals that of the surroundings is referred to as equilibrium moisture content (EMC). Moisture sorption isotherm gives the relationship between EMC and the corresponding water activity at constant temperature.

On the other hand, thermodynamic approach relates to the understanding of water equilibrium with its surroundings at certain relative humidity and temperature, water which is unavailable for solvation of solutes and water remaining unfrozen below the normal freezing point. Some thermodynamic functions used in analyzing sorption behavior of biological systems include total heat of sorption, differential heat of sorption, differential entropy, enthalpy–entropy compensation, integral enthalpy and integral

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entropy (Al-Muhtaseb et al., 2002; Aviara and Ajibola, 2002; Fasina, 2006; Thys et al., 2010). They are needed in the analyses of energy requirements in the dehydration process and to predict kinetic parameters of the sorption phenomena. Besides, they are useful in predictive drying models, in calculating energy consumption during drying/wetting of agricultural materials, in the design of drying equipment and in describing any heat and mass transfer related process.

The objectives of the present work were: (a) to analyze certain physicochemical (e.g. color, water holding capacity) and thermal properties of the flours and starches obtained from ahipa and cassava roots and (b) to determine their water sorption isotherms and thermodynamic properties, in order to establish the best conditions of storage for these products.

## 2. Materials and methods

### 2.1. Plant material

Ahipa (*Pachyrhizus ahipa* (Wedd.) Parodi) and cassava (*Manihot esculenta* Crantz) plants were grown at the Instituto Nacional de Tecnología Agropecuaria (INTA) Montecarlo farm (Misiones, Argentina; 26°33′40.15″ Latitude South and 54°40′20.06″ Longitude West). Ahipa and cassava roots were received at the CIDCA laboratory and processed immediately. Roots were selected, discarding wounded or unhealthy ones, and then they were thoroughly washed with tap water until removal of any soil rest. A sanitation step was included consisting in an immersion in NaClO solution (250 ppm of chlorine, 10 min). Then, roots were dried at room temperature.

### 2.2. Flour obtaining procedures

The detailed ahipa flour (AF) obtaining procedures from manually peeled roots were previously described (Doporto et al., 2011). The ahipa flour used in the present study was obtained by slicing (AFS) or by grating plus pressing (AFG). Likewise, cassava flour samples were obtained by slicing (CFS) or grating (CFG), from washed, sanitized and peeled roots, following a procedure similar to that applied in ahipa samples. Processed ahipa and cassava roots (sliced or grated) were dried at 50 °C until constant weight was reached and then they were grinded.

### 2.3. Starch extraction

The starch extraction began with the washing and disinfection of ahipa and cassava roots as previously described. Then, the roots were peeled and processed in a rotatory disc grater. The paste of grated roots was placed in water (2 L water/kg roots) and stored at 4 °C during 24 h. The mixture was filtered through a muslin cloth and the starch aqueous suspension (starch slurry) was collected in a beaker. The suspension was poured off at 4 °C. The residue left on the muslin cloth (ahipa or cassava pulp) was resubmitted to extraction, being triturated again with a domestic mixer. This filtration and extraction process was repeated at least five times until the supernatant became transparent after filtration. The successive starch slurries obtained were kept undisturbed at 4 °C for 24 h to allow solid sedimentation. This settled insoluble material, constituted mainly by starch, was recovered. Ahipa and cassava starches were carefully removed from the beaker, transferred onto acrylic plates, dried at 40 °C in a hot-air oven, and milled.

### 2.4. Determinations

#### 2.4.1. Color measurements

Color of ahipa and cassava flours and starches was measured using a Chroma Meter CR-400 (Konica Minolta Sensing Inc., Japan) and expressed in terms of lightness ($L^*$), red–green coordinate ($a^*$ value), and blue–yellow coordinate ($b^*$). The functions hue angle [$h° = \tan^{-1}\ ^{(b*/a*)}$] and Chroma [$C^* = (a^{*2} + b^{*2})^{1/2}$] were calculated.

#### 2.4.2. Scanning electron microscopy

Morphology of ahipa and cassava flour (particles smaller than 230 μm) and starch were analyzed by scanning electron microscopy (SEM), with a JEOL 35 CF electron microscope (Japan) (López et al., 2010). The images were obtained with a software program designed to acquire images digitally (IDX), with a resolution of 1024 × 800 pixels. AnalySis Pro 3.0 software program was used for the processing and analysis of the images.

#### 2.4.3. Thermal properties

Thermal properties of the flours and starches were determined by DSC according to Doporto et al. (2011), using a Q100 differential scanning calorimeter controlled by a TA 5000 module (TA Instruments, New Castle, Delaware, USA) with a quench-cooling accessory, under a $N_2$ atmosphere (20 mL min$^{-1}$). Approximately 7 mg of ahipa and cassava flour plus 15 μL of distilled water or 20% w/w aqueous starch suspensions were weighed in aluminum pans and closed hermetically; an empty pan was used as reference. The scanning rate was 10 °C/min. Heating range covered 10–120 °C for all samples.

#### 2.4.4. Water holding capacity (WHC)

WHC was measured according to Szymońska et al. (2003). Ahipa and cassava flour and starch samples (1 g) were placed in centrifuge tubes and 10 mL distilled water were added. After homogenization and stabilization for 15 min, suspensions were centrifuged (850×g; 15 min). Supernatants were discarded and the gels were weighed. WHC was calculated as follows:

$$\mathrm{WHC}\ (\%) = [(F - C)/(C - G)] \times 100$$

where, $F$ is the weight of the tube containing the wet sample after it decanted (g); $C$ is the weight of the tube containing the dried sample (g) and $G$ is the weight of the centrifuge tube (g).

#### 2.4.5. Water sorption isotherms

Water adsorption isotherms were determined using the static gravimetric method standardized by "The European Cooperative Project COST 90" (Spiess and Wolf, 1983). Ahipa and cassava flour and starch samples were placed in previously weighed aluminum containers and kept in a desiccator containing anhydrous $CaCl_2$ for 7 days to completely dehydrate the samples and to ensure the subsequent adsorption process. Then, the samples were weighed and placed in sealed containers with saturated solutions of different salts giving rise to a water activity range from 0.11 to 0.91 (Thys et al., 2010). Samples were stored at 10, 20 and 30 °C and weighed daily until the equilibrium was reached.

After this period, the final moisture content of samples was determined by drying in an oven at 105 °C until constant weight was reached (gravimetric method). Sorption isotherms of ahipa and cassava flours and starches were determined at least in triplicate. Experimental data were mathematically modeled with the following sorption isotherm models: BET (Brunauer–Emmett–Teller), GAB (Guggenheim–Anderson–de Boer), Halsey, Peleg, Oswin, Henderson, Chrife and Smith (Thys et al., 2010). For BET model, only $a_w$ values <0.5 were taken into account for the regression. The values of the parameters of each model and their goodness of fit were estimated by the correlation coefficient ($r^2$).

*2.4.6. Thermodynamic properties*

The differential enthalpy ($\Delta h$) and entropy ($\Delta S$) of sorption was determined according to Cladera-Olivera et al. (2009) from moisture sorption data. The values of ln ($a_w$) were plotted versus $1/T$ for certain moisture content and then $\Delta h$ was determined from the slope of the curve (which corresponded to $-\Delta h/R$) meanwhile $\Delta S$ was obtained from the linear coefficient ($\Delta S/R$) of the straight. $R$ corresponds to the universal gases constant and $T$ to the absolute temperature.

From the enthalpy–entropy compensation theory that proposes a linear relationship between $\Delta h$ and $\Delta S$, the isokinetic temperature (K) and the free energy ($\Delta G$, J mol$^{-1}$) were calculated (Al-Muhtaseb et al., 2002; Cladera-Olivera et al., 2008; Fasina, 2006). The isokinetic temperature represents the temperature at which all reactions in series proceed at the same rate. From the thermodynamic point of view, $\Delta G$ can be used as an indicative of the sorbent affinity for water, providing a criterion as to whether water sorption is a spontaneous or non-spontaneous process.

*2.5. Statistical analysis*

All determinations were carried out at least by duplicate. For the statistical analysis of the results the program Systat® Software (Version 10.0) was used. Analysis of variance (ANOVA) and comparison of means by the Fisher's least significant difference (LSD) test were conducted, at a significance level $p = 0.05$. For mathematical modeling of sorption isotherm data, the nonlinear regression module of SYSTAT 10.0 (SYSTAT, Inc., Evanston, IL, USA) was used.

## 3. Results and discussion

Fig. 1 shows SEM micrographs of ahipa and cassava flours obtained by slicing (Fig. 1a and c, respectively) as well as ahipa (Fig. 1b) and cassava starches (Fig. 1d) images. Regarding the flour obtaining procedure, no differences were observed in SEM micrographs. Ahipa and cassava flours were characterized by the presence of starch granules as well as irregular, deformed, truncated particles with low sphericity, which could be mainly associated to protein aggregates and fiber components. Besides, these irregular particles were more abundant in ahipa than in cassava flour.

With regard to morphology, all the starch granules exhibited round and polygonal shapes, presenting those of ahipa more irregular limits (Fig. 1b). Besides, SEM micrographs indicated that granules were not damaged during the starch extraction procedure, since smooth surfaces without cracks were observed. Ahipa starch granules exhibited straight monomodal size distribution which varied between 2 and 20 μm, with a mean value of 8.85 ± 3.69 μm (Fig. 1b); Forsyth and coworkers (2002) reported a granule size value close to that obtained in the present work. For cassava starch granules a bimodal distribution was obtained with two distinct populations of granules centred at about 3 and 10 μm (Fig. 1d). Siroth and coworkers (1999) have stressed that the size distribution of cassava starch granules depends on the crop phase at harvest time. Likewise, granule shape, size and surface are simple physical characteristics which have an impact on starch functionality.

*3.1. Color measurement*

Results of color analyses are shown in Table 1. The $L^*$ values did not differ significantly for both ahipa flour samples. Conversely, CFG had significantly higher $L^*$ values than CFS. The obtaining procedure had slight ($p < 0.05$) incidence on hue values both in ahipa and cassava flour samples. AFS had significantly higher Chroma values than AFG, so the color of AFS was more saturated, with a minor contribution of the grey tint. There was no significant difference between the Chroma values of CFG and CFS.

Both cassava flour types had significantly higher values of $L^*$ and hue than ahipa flour samples. $L^*$ coordinate of ahipa flour samples were similar to those reported in the literature for maize, nixtamalized maize and taro flours ($L^*$ equal to 84.7, 85.3 and 81.2, respectively) (Rodríguez-Miranda et al., 2011). Cassava flours exhibited significantly higher $L^*$ values (Table 1) than ahipa and the above mentioned flours. Lower $L^*$ and Chroma values measured in ahipa flour might be related to enzymatic and chemical browning reactions caused by relatively high sugar and protein contents (Doporto et al., 2011) and the thermal processing that promotes these lowering-quality phenomena.

Referring to the color of the extracted starches, a high degree of whiteness was observed (Table 1), especially for cassava starch; Boudries and coworkers (2009) have pointed out that $L^*$ values

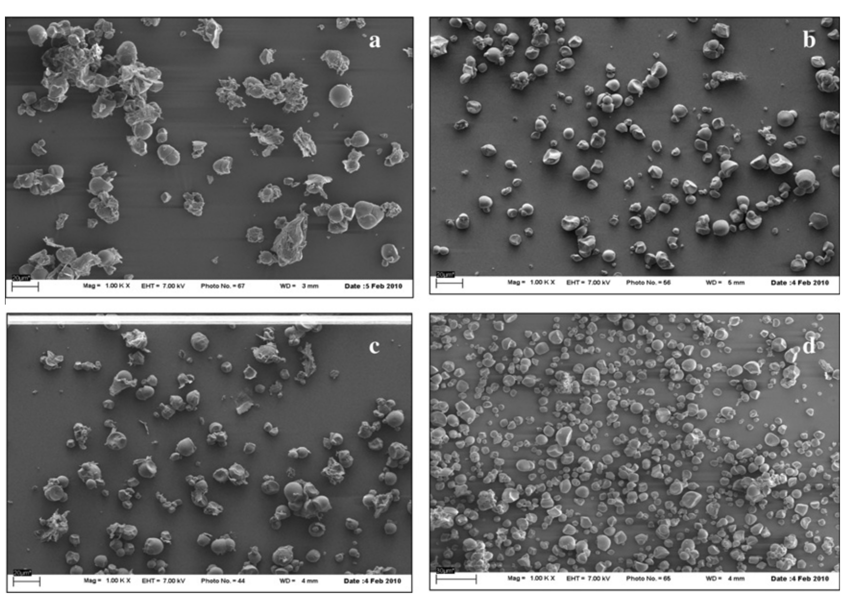


**Fig. 1.** Scanning electronic microscopy (SEM) images of (a) ahipa flour obtained by slicing, (b) ahipa starch, (c) cassava flour obtained by slicing and (d) cassava starch.

**Table 1**
$L^*$, hue (h°) and Chroma values of ahipa and cassava flours and starches.

| Sample | $L^*$ | hue (h°) | Chroma ($C^*$) |
|---|---|---|---|
| AFG | 85.4 ± 2.0$^a$ | 84.7 ± 0.2$^a$ | 11.3 ± 0.5$^a$ |
| AFS | 84.1 ± 1.1$^a$ | 85.4 ± 0.4$^b$ | 15.1 ± 1.0$^b$ |
| CFG | 92.9 ± 0.8$^c$ | 92.3 ± 0.3$^d$ | 10.9 ± 0.5$^a$ |
| CFS | 90.9 ± 0.9$^b$ | 91.3 ± 0.3$^c$ | 11.9 ± 0.5$^a$ |
| Ahipa starch | 93.5 ± 0.7$^c$ | 85.8 ± 0.5$^b$ | 4.4 ± 0.2$^c$ |
| Cassava starch | 96.2 ± 0.7$^d$ | 91.9 ± 0.4$^{cd}$ | 4.9 ± 0.2$^d$ |

AFG: ahipa flour obtained by grating plus pressing; AFS: ahipa flour obtained by slicing; CFG: cassava flour obtained by grating; CFS: cassava flour obtained by slicing; Reported values correspond to the media ± standard deviation. Different letters as superscripts within a column indicate significant differences at a significance level $p$ = 0.05.

higher than 90 give a satisfactory whiteness for the starch purity. Pérez Sira and Lares Amaiz (2004) isolated starch from white and pigmented sorghum using a treatment of steeping, with high ($L^*$ = 91.3) and low $L^*$ values ($L^*$ = 78.4) respectively.

The hue and Chroma values of ahipa and cassava starches (Table 1) were slightly higher than those reported for piñon (*Araucaria araucana*) seed starch by Henríquez and coworkers (2008) (hue = 80.05 ± 0.43; Chroma = 4.03 ± 0.13).

### 3.2. Thermal properties

Thermograms corresponding to ahipa and cassava flours showed a single thermal event associated with the gelatinization of starch. Concerning thermal properties, it was observed that ahipa flours gelatinized at lower temperature than those of cassava, regardless of the obtaining procedure (Table 2). This difference indicates better aptitude for cooking. It was further noted that flours obtained from slices presented gelatinization temperatures higher than those obtained by the grating process, being the difference significant ($p < 0.05$) for ahipa flour (Table 2).

In general, the gelatinization temperatures of ahipa and cassava flours were higher than those of their starches. This trend was also reported by Jane et al. (1992) for flours and starches of different botanical origin. Both ahipa and cassava flours showed similar differences in gelatinization temperatures respect to the corresponding starches. The mentioned difference was greater for the flours obtained by slicing than the ones processed by grating (≈6 and 4 °C, respectively).

The values of $T_0$, $T_{gp}$ and $\Delta H$ found for cassava flour were consistent with those reported by Charoenkul and coworkers (2011), particularly for cassava varieties that were classified by these authors as belonging to "mealy and firm group", according to the type of texture of cooked roots.

### 3.3. Water holding capacity (WHC)

Ahipa flour WHC (191 ± 0.8% and 132 ± 0.6% for AFS and AFG, respectively) was significantly higher than the values found for both cassava flour samples (CFS: 110 ± 2.1%; CFG: 101 ± 2.8%) (Fig. 2). This observation could be due to the higher protein content in ahipa flour that may effectively contribute to increasing water holding capacity. The obtaining procedure significantly affected the WHC of ahipa and cassava flours: products coming from a slicing processing had significantly ($p < 0.05$) higher WHC than the products obtained by grating. On the other hand, ahipa starch showed significantly lower WHC than cassava starch.

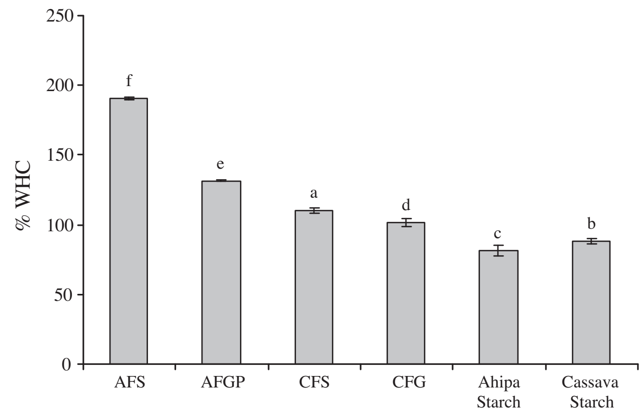


**Fig. 2.** Water holding capacity (%) of ahipa and cassava flour and starch. AFS: ahipa flour obtained by slicing; AFG: ahipa flour obtained by grating plus pressing; CFS: cassava flour obtained by slicing; CFG: cassava flour obtained by grating. Different letters between bars indicate statistically significant differences ($p < 0.05$).

Results showed that WHC of both ahipa and cassava flours and starches were relatively low when compared to other food ingredients or additives, such as dietary fibers from oat bran (2.10 g of water/g of dry matter), rice bran (4.89 g of water/g of dry matter), soy flour (4.79–6.75 g of water/g of dry matter) and wheat bran (5.03 g of water/g of dry matter) (Abdul-Hamid and Luan, 2000; Chen, 1988; Heywood et al., 2002). Likewise, WHC values of ahipa and cassava samples were far below those reported by Aziz and coworkers (2011) for native banana pseudo-stem flour and boiled tender core of banana pseudo-stem flour (10.66 and 18.28 g of water/g of dry matter, respectively).

### 3.4. Water sorption isotherms

Fig. 3 shows the experimental values of equilibrium moisture content as a function of water activity ($a_w$) at 10, 20 and 30 °C for ahipa and cassava flours and starches. The standard deviations for the equilibrium moisture content of each experimental point were lower than 0.001 and they are not shown in the figure for greater clarity.

Regardless the flour obtaining procedure, adsorption isotherms presented a sigmoid shape and corresponded to Type II isotherms according to BET classification. Similar results were described for potato flour (McMinn and Magee, 2003), for the flour obtained

**Table 2**
Thermal parameters of ahipa and cassava flours and starches.

| Sample | | | Onset temperature, $T_o$ (°C) | Peak temperature, $T_p$ (°C) | Enthalpy, $\Delta H$ (J/g dry basis) |
|---|---|---|---|---|---|
| Starch | Ahipa | | 64.3 ± 0.2$^a$ | 67.2 ± 0.1$^a$ | 9.5 ± 0.6$^{ac}$ |
| | Cassava | | 51.7 ± 0.8$^b$ | 69.9 ± 0.0$^b$ | 9.7 ± 0.4$^{ac}$ |
| Flour | Ahipa | AFG | 64.3 ± 1.2$^a$ | 71.2 ± 0.8$^c$ | 9.4 ± 0.5$^a$ |
| | | AFS | 68.5 ± 0.8$^c$ | 73.1 ± 0.9$^d$ | 8.6 ± 0.2$^b$ |
| | Cassava | CFG | 67.1 ± 0.2$^d$ | 74.0 ± 0.6$^d$ | 10.8 ± 0.7$^c$ |
| | | CFS | 70.1 ± 0.8$^c$ | 75.7 ± 0.9$^e$ | 10.5 ± 0.9$^{ac}$ |

AFG: ahipa flour obtained by grating plus pressing; AFS: ahipa flour obtained by slicing; CFG: cassava flour obtained by grating; CFS: cassava flour obtained by slicing; Reported values correspond to the media ± standard deviation. Different letters as superscripts within a column indicate significant differences at a significance level $p$ = 0.05.

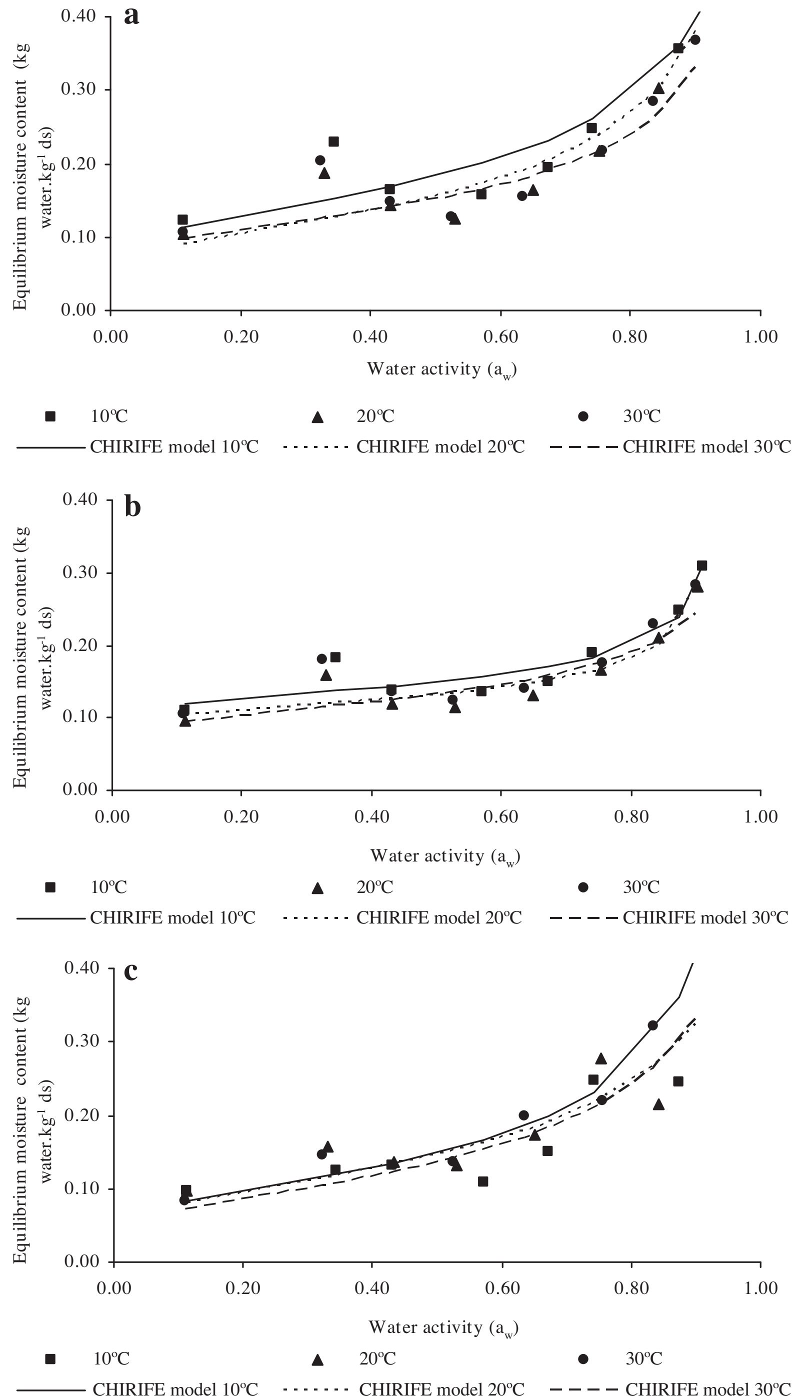


**Fig. 3.** Experimental data of equilibrium moisture content (dry basis) as a function of $a_w$ at 10, 20 and 30 °C and their corresponding fitting to the Chirife model for (a) ahipa flour obtained by slicing (AFS); (b) ahipa flour obtained by grating plus pressing (AFG); (c) cassava flour obtained by slicing (CFS); (d) cassava flour obtained by grating (CFG); (e) ahipa starch; (f) cassava starch.

from seeds of *Araucaria angustifolia* (Thys et al., 2010) and for starches of different botanical origin (Al-Muhtaseb et al., 2004).

The shapes of the curves and the experimental data agree with the response of most biological materials, particularly for powdered food (Fasina, 2006) indicating that at constant water activity, the amount of water that flours and starches can hold decreases with increasing temperature. This may probably occur because water molecules at low temperatures have a lower kinetic energy, which is not enough to overcome the corresponding adsorption energy (Polatoğlu et al., 2011). At the same time, water molecules interact with the hydrophilic components of the product, such as carbohydrates and proteins. This interaction occurs through hydrogen bonds, causing an exothermic reaction, which is not favoured with increasing temperature. For products such as corn flour, which is high in carbohydrates and proteins with polar groups, Gálvez and coworkers (2006) have mentioned the availability of a high number of active sorption centres.

The mathematical model that best fitted the experimental data for ahipa and cassava flour was that proposed by Chirife, while GAB was more adequate to fit data corresponding to both starch

**Table 3**
Fitting parameters for the GAB model applied to sorption data of ahipa and cassava flours and starches.

| Temperature (°C) | GAB parameters | Ahipa | | | Cassava | | |
|---|---|---|---|---|---|---|---|
| | | AFS | AFG | Starch | CFS | CFG | Starch |
| 10 | $X_m$ | 0.088 | 0.092 | 0.118 | 0.084 | 0.095 | 0.116 |
| | $K$ | 0.887 | 0.738 | 0.610 | 0.767 | 0.647 | 0.712 |
| | $C$ | 9.37 | 13.8 | 1.10 | 2.71 | 2.73 | 26.2 |
| | $R^2$ | 0.982 | 0.977 | 0.987 | 0.974 | 0.970 | 0.993 |
| 20 | $X_m$ | 0.072 | 0.078 | 0.096 | 0.082 | 0.082 | 0.088 |
| | $K$ | 0.917 | 0.770 | 0.612 | 0.862 | 0.840 | 0.792 |
| | $C$ | 2.73 | 11.1 | 4.54 | 1.81 | 2.38 | 14.2 |
| | $R^2$ | 0.977 | 0.975 | 0.991 | 0.966 | 0.967 | 0.997 |
| 30 | $X_m$ | 0.066 | 0.063 | 0.088 | 0.079 | 0.068 | 0.072 |
| | $K$ | 0.936 | 0.899 | 0.618 | 0.897 | 0.908 | 0.797 |
| | $C$ | 6.34 | 9.78 | 1.37 | 0.754 | 0.253 | 10.3 |
| | $R^2$ | 0.979 | 0.969 | 0.995 | 0.959 | 0.985 | 0.990 |

$X_m$, monolayer equilibrium moisture content (g water/g dry solid); $K$ and $C$ (values $\times 10^{14}$) are the fitting parameters of the GAB equations and $R^2$ the correlation coefficient. AFG: ahipa flour obtained by grating plus pressing; AFS: ahipa flour obtained by slicing; CFG: cassava flour obtained by grating; CFS: cassava flour obtained by slicing.

samples (Fig. 3). Besides, a cross-over at $a_w$ near 0.7 was observed for flour samples and ahipa starch kept at 20 and 30 °C (Fig. 3). Similar results were informed by Perdomo and coworkers (2009), who stressed that this fact could be attributed to the enhancement in the molecular mobility of the most active sites, since at this high $a_w$ values, water could be squeezed out mainly of the starch crystals. This is a common effect observed in high-carbohydrate foods such as banana, sugar beet root, raisins and barley malt, among others (Barreiro et al., 2003; Perdomo et al., 2009).

On the other hand, BET and GAB models are the most used in food science because their parameters have physical meaning, as the heat of sorption and the monolayer moisture content ($X_m$), which is indicative of product stability. The two parameters-BET equation only describe adequately experimental data below $a_w = 0.5$ while the three parameters-GAB model, considered one of the most appropriate to describe the sorption isotherms of food products, is applied throughout the whole $a_w$ range. Table 3 presents the parameters and correlation coefficients obtained by fitting the experimental data with the GAB model for ahipa and cassava flours and starches.

The estimated values of water content of the monolayer ($X_m$) were, in general, lower for the flours obtained by slicing (Table 3). Likewise, regardless the obtaining procedures, the $X_m$ values of both flours were indicative of an acceptable stability for these products. Labuza (1984) have stressed that the maximum monolayer moisture content for foods corresponds to 10% (dry basis), because when this value is exceeded, the stability of the product is compromised. Although there are no references concerning ahipa flour, $X_m$ values found were higher than those for piñon flour, which ranged between 0.05 and 0.07 g water/g dry solids (Clader-a-Olivera et al., 2009). A similar trend was observed in the case of starches. The $X_m$ values of cassava starch were lower than those reported by Perdomo and coworkers (2009), which were 0.0954 g water/g dry solids at 20 °C. There are no reports concerning ahipa starch isotherms data.

On the other hand, Table 3 also shows the $X_m$ trend to decrease with increasing temperature for ahipa flours and starch. This phenomenon could be attributed to the reduced availability of active sites for water adsorption, taking into account that the starch content (one of the major hydrophilic components) in ahipa flour is lower than that of cassava flour (Charoenkul et al., 2011; Doporto et al., 2011).

From GAB model, thermodynamic parameters can be estimated. Fig. 4 shows the variation of isosteric heat (differential enthalpy) and differential entropy as a function of moisture content for ahipa flour obtained by slicing (AFS) and the correlation between them. This correlation allows Gibbs free energy change ($\Delta G$) estimation as well as the isokinetic temperature at which all sorption reactions will take place at the same rate. $\Delta G$ is a measure of the work done by the system to accomplish an adsorption or desorption pro-

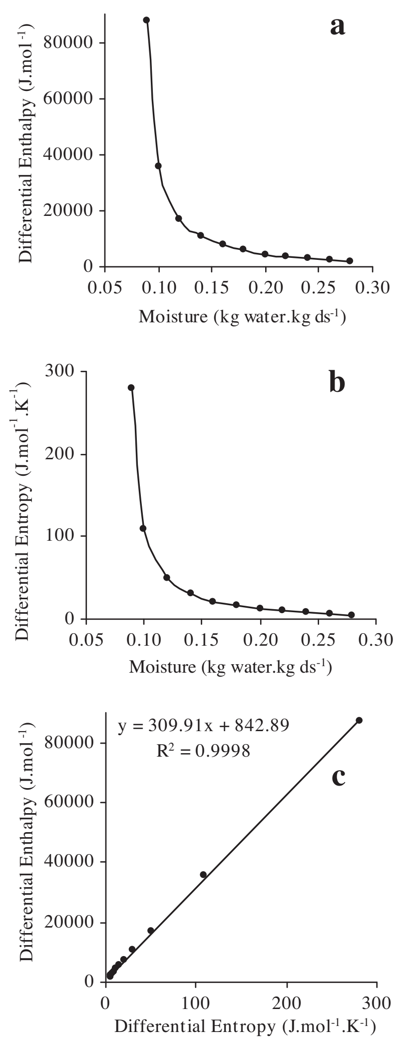


**Fig. 4.** (a) Differential enthalpy and (b) Differential entropy as a function of moisture content of ahipa flour obtained by the slicing procedure. (c) Differential enthalpy versus differential entropy as well as the compensation equation for the same flour (AFS: ahipa flour obtained by slicing).

**Table 4**
Thermodynamic parameters calculated for ahipa and cassava flours and starches.

| Parameters | Ahipa | | | Cassava | | |
|---|---|---|---|---|---|---|
| | AFS | AFG | Starch | CFS | CFG | Starch |
| Isokinetic temperature (K) | 309.9 | 305.6 | 300.0 | 389.0 | 310.3 | 309.0 |
| Free energy change $\Delta G$ (J mol$^{-1}$) | 842.8 | 1009.0 | 558.8 | 2977.0 | 1504.0 | 323.7 |

AFG: ahipa flour obtained by grating plus pressing; AFS: ahipa flour obtained by slicing; CFG: cassava flour obtained by grating; CFS: cassava flour obtained by slicing.

cess. $\Delta G$ can be used as indicator of the state of adsorbed water by solid particles, which determines the physical, chemical and microbial stability of biological materials during storage (Aviara and Ajibola, 2002).

Fig. 4a and b show that both differential enthalpy and entropy exponentially decreased with the increase in moisture content, with a strong dependence at low moisture contents. This behavior could be attributed to the location of the bound water and the degree to which the water–solid interaction is greater than the interaction of the water molecules (Fasina, 2006; McMinn and Magee, 2003; Thys et al., 2010). Thus, at low moisture contents the energy required to desorbing water molecules will be higher since they are strongly bounded to the available sites of the solid matrix.

Fig. 4c shows that differential enthalpy varied linearly with differential entropy (with a regression coefficient higher than 0.999 in all cases), indicating that the compensation theory is applicable in the studied systems. The obtained values are summarized in Table 4 for the flours and starches tested. In general, the isokinetic temperature as well as the $\Delta G$ calculated for cassava samples were higher than those of ahipa ones. With regard to the flour of both tuberous roots, the obtaining procedure affected the thermodynamic parameters, being those of the flours obtained by slicing higher than those coming from the grating process (Table 4). Besides, both starches exhibited lower $\Delta G$ and isokinetic temperature values than their corresponding flours. A similar trend was observed by Thys et al. (2010) for the isokinetic temperature of pinhão starch (428 K), and by Cladera-Olivera et al. (2009) for its corresponding flour (398 K). Likewise, in the case of sweet potato, Fasina (2006) has stressed that the enthalpy–entropy compensation theory was satisfied with an isokinetic temperature of 407.9 K. The obtained isokinetic temperature values were within the range of those of quinoa grains (361 K) (Tolaba et al., 2004), garlic (348 K) (Madamba et al., 1996), oatmeal biscuit and oat flakes (430.9 and 443.4 respectively) (McMinn et al., 2007), and sucuk (323.4 K) (Polatoğlu et al., 2011).

Cladera-Olivera and coworkers (2009) have pointed out that water adsorption of pinhão flour was a non-spontaneous process with a $\Delta G$ value of 339 J mol$^{-1}$, which is lower than those found for ahipa and cassava flours in the present work. Besides, considering other starch-based products, McMinn and coworkers (2007) reported $\Delta G$ values of 280 and 325 J mol$^{-1}$ for oatmeal biscuits and oat flakes respectively.

## 4. Conclusions

Ahipa and cassava flours show the distinctive characteristic of being naturally gluten-free products. Both flours can be obtained by relatively simple procedures such as the alternatives assayed in the present work, conserving a good level of integrity of the starch granules. Both flours differed in terms of luminosity and basic tint, being higher the values reported for cassava flour. Ahipa and cassava starches showed a high degree of whiteness. Regardless of the obtaining procedure, ahipa gelatinized at lower temperature than cassava flour, indicating a better aptitude for cooking. In general, the gelatinization temperatures of ahipa and cassava flours were higher than those of their starches. Water holding capacity of ahipa flour (AFS and AFG) was significantly higher than the values found for cassava flour samples (CFS and CFG). In order to achieve higher WHC values, the slicing processing method should be recommended.

In food systems, water is an active component that controls biochemical reactions, determines texture properties and the overall physical and biological behavior. Within the tested temperature range, ahipa and cassava flours and starches could be considered as products with an acceptable stability, although the analyses of hygienic-sanitary quality are required. Sorption isotherms could be satisfactorily modeled using different mathematical models. The best fit of the experimental data was obtained with Chirife model for flours and GAB model for starches. The latest allowed estimating the water content of the monolayer. From GAB fittings at the studied temperatures, the thermodynamic parameters associated with water adsorption process were calculated. In all cases the enthalpy–entropy compensation theory was verified and the isokinetic temperature and the associated Gibbs free energy were obtained, indicating a non-spontaneous process.

The flours and starches from these tuberous roots could be incorporated as ingredients in gluten-free foods. Future research would be focused on studying the effects of these ingredients on the organoleptic, sensorial and technologic properties of processed foods, as well as the interaction between water molecules and flours and starches systems.

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