

## Sorption Thermodynamics of Soursop Powders Obtained by Different Dehydration Technologies

Termodinámica de Sorción de Polvos de Guanabana Obtenidos por Diferentes Tecnologías de Deshidratación

Adela M. Ceballos Peñaloza<sup>1</sup>; Gloria Inés Giraldo Gómez<sup>2</sup>;  
Carlos Eduardo Orrego Alzate<sup>3</sup> and Javier Telis-Romero<sup>4</sup>

**Abstract.** The soursop (*Annona muricata* L.) is a perishable tropical fruit with high nutritional value. The aim of this work was to evaluate the sorption thermodynamics of soursop powders with maltodextrin (MD), obtained by different drying technologies, thus allowing understanding the mechanisms that govern this process. Adsorption isotherms of freeze dried (FD), spray drying (SD) and vacuum drying (VD) powders were determined at 20, 30, 40 and 50 °C by using the static gravimetric method. The results showed that the better fits the adsorption experimental data is the GAB model ( $R^2 > 0.9893$ ). The influence of the drying system in the model parameters was also shown. The monolayer moisture values between 5.28 and 9.30% (kg water/kg d.s) were within the reported range for dehydrated food.

**Key words:** Sorption isotherms, thermodynamic properties, isosteric heat of sorption, compensation theory.

**Resumen:** La guanábana (*Annona muricata* L.) es una fruta tropical perecedera y de gran valor nutricional. El objetivo de este trabajo fue evaluar la termodinámica de sorción de polvos guanábana con maltodextrina (MD) obtenidos por diferentes tecnologías de secado, lo que permite la comprensión de los mecanismos que regulan este proceso. Se determinaron las isothermas de adsorción por método gravimétrico estático a 20, 30, 40 y 50 °C, para polvos secados por liofilización (FD), aspersion (SD) y vacío (VD). Los resultados mostraron que el modelo de GAB se ajustó a los datos experimentales de adsorción ( $R^2 > 0.9893$ ). Se mostró la influencia del sistema de secado en los parámetros del modelo. Los valores de humedad de la monocapa, entre 5,28 y 9,30% (kg de agua/kg s.s), se encuentran dentro de los rangos reportados para alimentos deshidratados.

**Palabras clave:** Isothermas de sorción, propiedades termodinámicas, calor isostérico de sorción, teoría de

*Annona muricata* (L.) (family, Annonaceae) is a well-known tropical fruit tree, named "soursop", "guanábana" in Spanish speaking countries and "graviola" in Brazil. It is classified as sour fruit and a source of fiber, calcium, phosphorus and vitamin C (Chaparro *et al.*, 2004). It is considered as a nutraceutical and has a good functionality due to its polyphenol content and higher antioxidant capacity (Márquez, 2009). The soursop fruit is usually transformed into juice, pulp and concentrate. The largest producers are in the Caribbean, Central and South America (Colombia and Brazil), southeast China, Vietnam, Australia, New Zealand and Africa (IICA-PRODAR, 2006). Problems of crop seasonality and its high perishability make think that dehydration is a good alternative to add value and diversify soursop market.

The study of the thermodynamic sorption of water, allows knowing the behavior of the water inside and on the surface, its structure, properties, and the calculation of both energy and mass transfer requirements. For a biological system in equilibrium with its surroundings, it provides information related to the affinity sorbent-water, spontaneity of sorption processes and the concept of order and disorder into water, sorbent and the whole system (McMinn *et al.*, 2005). Likewise, it is important to understand the relationship between the thermodynamic states and how they are reached through time. The thermodynamic properties derived from the analysis of the adsorption isotherms, are interesting for a large number of applications in food science and technology, as shelf life prediction of dehydrated products, storage conditions selection and packaging

<sup>1</sup> Titular Professor. Universidad de Caldas - Facultad de Ingenierías - Departamento de Ingeniería. Calle 65 No 26-12. Manizales, Colombia. <adela.ceballos@ucaldas.edu.co>

<sup>2</sup> Associate Professor. Universidad Nacional de Colombia - Sede Manizales- Facultad de Ciencias Exactas Naturales. - Departamento de Física y Química. Manizales, Colombia. <gigiraldogo@unal.edu.co>

<sup>3</sup> Titular Professor. Universidad Nacional de Colombia - Sede Manizales- Facultad de Ciencias Exactas Naturales. - Departamento de Física y Química. Manizales, Colombia. <corregoa@unal.edu.co>

<sup>4</sup> Titular Professor. Universidad Estadual Paulista - Departamento de Ingeniería. San Jose de Rio Preto. Brazil. <javier@ibilce.unesp.br>

Received: January 29, 2013; accepted: August 04, 2013.

design to ensure good conditions for conservation (Chuzel, 1992). The sorption isotherms show the functional relationship between water activity and moisture content in equilibrium at a given temperature; changes with temperature and generally, for the same water activity, an increase in temperature causes a decrease in the water content of the product and thus a decrease in its hygroscopicity (Chuzel, 1992). Literature reports a large number of mathematical expressions for modeling the sorption isotherms, most of them reviewed by (Iglesias *et al.* (1976). The model of GAB (Guggenheim-Anderson-de Boer) is a semi-theoric three parameter model, considered as one of the best fits to the experimental data of food in a wide range of values (Giraldo *et al.*, 2011; McMinn and Magee, 2003; Rahman, 1995). The objective of this work was to evaluate the sorption thermodynamic soursop powders added with maltodextrin (MD), obtained by freeze dried (FD), spray drying (SD) and vacuum drying (VD), as well as the adjustment to the GAB model of the isotherms at four different temperatures. The determination of thermodynamic properties to understand the mechanisms governing the adsorption process of water in the soursop powder with MD was also studied.

## MATERIALS AND METHODS

**Experimental procedure.** Ripe soursop was purchased in a local market at Manizales-Colombia. Pulp was extracted and mixed with maltodextrin (MD) MOR-REX® 1920 with 20 dextrose equivalent (DE) until reached relation of 55% MD in dry basis (db). The operating conditions of the dryers were: Freeze drying (FD) Virtis (Genesis25, USA), an average freezing speed of 2.04 °C min<sup>-1</sup>, chamber pressure of 1.3 ± 0.3 mmHg, plate temperature between -10 °C and 80 °C, maximum product temperature 60 ± 5 °C. Spray drying (SD) Buchi -290 equipped with a nozzle was operated in co-current, with an inlet air temperature of 140 °C and a feed flow rate between 1 and 1.5 L h<sup>-1</sup>. Vacuum drying (VD) Marconi mark dryer (MA-030) at 26 mm Hg and 70 °C for 24 h. FD and VD samples were homogenized by grounding them into a mortar.

The adsorption isotherms were obtained using the static gravimetric method at 20, 30, 40, and 50 °C (Chuzel, 1992; Gabas *et al.*, 2007; Simal *et al.*, 2007) with saturated salt solutions of NaOH, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, NaNO<sub>2</sub>, NaCl, KCl and BaCl<sub>2</sub>, corresponding to a range of water activities of 0.059 to 0.9 (Fernández y Madriñán, 1992). Each solution

was transferred into separated jars. Triplicate samples of around 1 g of soursop powder previously dried in an oven at 40 °C were weighed into small plastic receptacles and placed on tripods in the jars, which were then tightly closed and placed in a temperature-controlled chamber. The required equilibration time was 4 to 5 weeks, based on the change in samples weight expressed on a dry basis, which did not exceeded 0.1% (0.001 g/g dry solids). The equilibrium moisture content was determined in a vacuum oven at 60 °C for 48 h (AOAC, 2001). To evaluate the influence of the drying method on the parameters of GAB, an ANOVA with 95% confidence level was made.

**Adsorption isotherms adjustment.** The experimental data of the adsorption isotherms for soursop powders with MD at four temperatures were adjusted to the GAB model, which has been extensively tested to describe isotherms of foods (Rahman, 1995) and fruit powders dried with MD as described by pineapple and loquat (Telis *et al.*, 2000; Gabas *et al.*, 2007), soursop (Ceballos *et al.*, 2009) and pineapple (Gabas *et al.*, 2009). The GAB model is shown in equation (1), (Rahman, 1995):

$$X = \frac{(C-1)K a_w X_m}{1 + (C-1)K a_w} + \frac{K a_w X_m}{1 - K a_w} \quad (1)$$

Where,  $X$  is moisture in equilibrium of the isotherms expressed as kg of water/kg d.s;  $a_w$  is water activity;  $C$ ,  $K$ , are dimensionless constants of the GAB model;  $X_m$  represents the monolayer moisture content.  $K$  indicates the difference in free enthalpy (standard chemical potential) between the sorbate molecules in the multilayer above the first layer and the pure liquid (Brunauers *et al.*, 1938; Telis-Romero *et al.*, 2005).  $C$  measures the difference between the chemical potentials of the sorbate in the upper layers of sorption and the monolayer (Al-Muhtaseb *et al.*, 2004). In order to adjust the GAB model, a nonlinear regression analysis was performed using ORIGIN software. The regression coefficient, the standard error associated with parameters and the mean relative deviation (% E), which evaluates the data adjusting degree to the model were estimated. Equation (2):

$$\%E = \frac{100}{N} \sum_{i=1}^n \frac{|m_{pi} - m_i|}{m_i} \quad (2)$$

Where,  $m_i$  is the moisture content at the observation  $i$ ;  $m_{pi}$  is predicted moisture content at that observation and  $N$  is number of experimental data. For values

%E<10, the fit is considered acceptable (McMinn and Magee, 2003; Al-Muhtaseb *et al.*, 2004; Simal *et al.*, 2007).

**Determination of thermodynamic properties.** The changes in the adsorption of water have effect on the Gibbs free energy. The calculation of  $\Delta G$  is defined by the Gibbs equation (3) as follows:

$$\Delta G = RT \ln a_w \quad (3)$$

Where  $a_w$  is water activity;  $T$  is temperature the isotherm in K;  $R$  is the universal gas constant.

Net isosteric heat of adsorption or differential enthalpy  $\Delta H_{diff}$  in  $J \text{ mol}^{-1}$ , is defined as the difference between total isosteric heat of water sorption  $H_v(T)$  and the heat of vaporization of pure water  $H_v^0(T)$ . Equation (4):

$$\left[ \Delta H_{diff} \right]_T = H_v(T) - H_v^0(T) \quad (4)$$

The differential enthalpy changes in the water-solid interface, at different stages of the adsorption process in food and agricultural products may be calculated from Clausius-Clapeyron equation (5) (Telis-Romero *et al.*, 2005):

$$\frac{\left[ \Delta H_{diff} \right]_T}{R} = \left[ \frac{d \ln(a_w)}{d(1/T)} \right]_x \quad (5)$$

Where  $\left[ \Delta H_{diff} \right]_T$  is a molar amount which depends on the isotherm temperature and represents the amount of energy over the heat of vaporization of water required for the water molecules to bind by a sorption process at a specific moisture level. In order to apply the isosteric method, it is assumed that the heat of vaporization of pure water and the heat of sorption do not vary with temperature, hence it is recommended to measure isotherms at more than two temperatures (McMinn *et al.*, 2004; Telis-Romero *et al.*, 2005; Lee and Lee, 2008).

With values obtained for enthalpy changes, the variation in the molar differential entropy  $\left[ \Delta S_{diff} \right]_T$  may be estimated using equation (6), (Gabas *et al.*, 2000; Fasina, 2006):

$$\left[ \Delta S_{diff} \right]_T = S_i - S_L = \frac{-\left[ \Delta H_{diff} \right]_T - RT \ln a_w}{T} \quad (6)$$

Where,  $S_i$  is differential molar entropy of water adsorbed on the solid;  $S_L$  is molar entropy of pure water in equilibrium with vapor.

**Enthalpy-entropy compensation theory.** Enthalpy-entropy compensation theory or the isokinetic theory explains the mechanisms that control the sorption of water vapor in the food and its spontaneity (Thys *et al.*, 2010). It establishes a linear relationship between differential entropy and enthalpy for a particular reaction generated by changes in the solute-solvent interactions. If the compensation theory is assumed to be valid for sorption, the isokinetic  $T_\beta$  temperature must be constant for all points, its value corresponds to the slope of the graph, (Rooney, 1998) and represents the temperature at which all the reactions temperature in the series proceed at the same rate (McMinn *et al.*, 2005). The result line is given by equation (7):

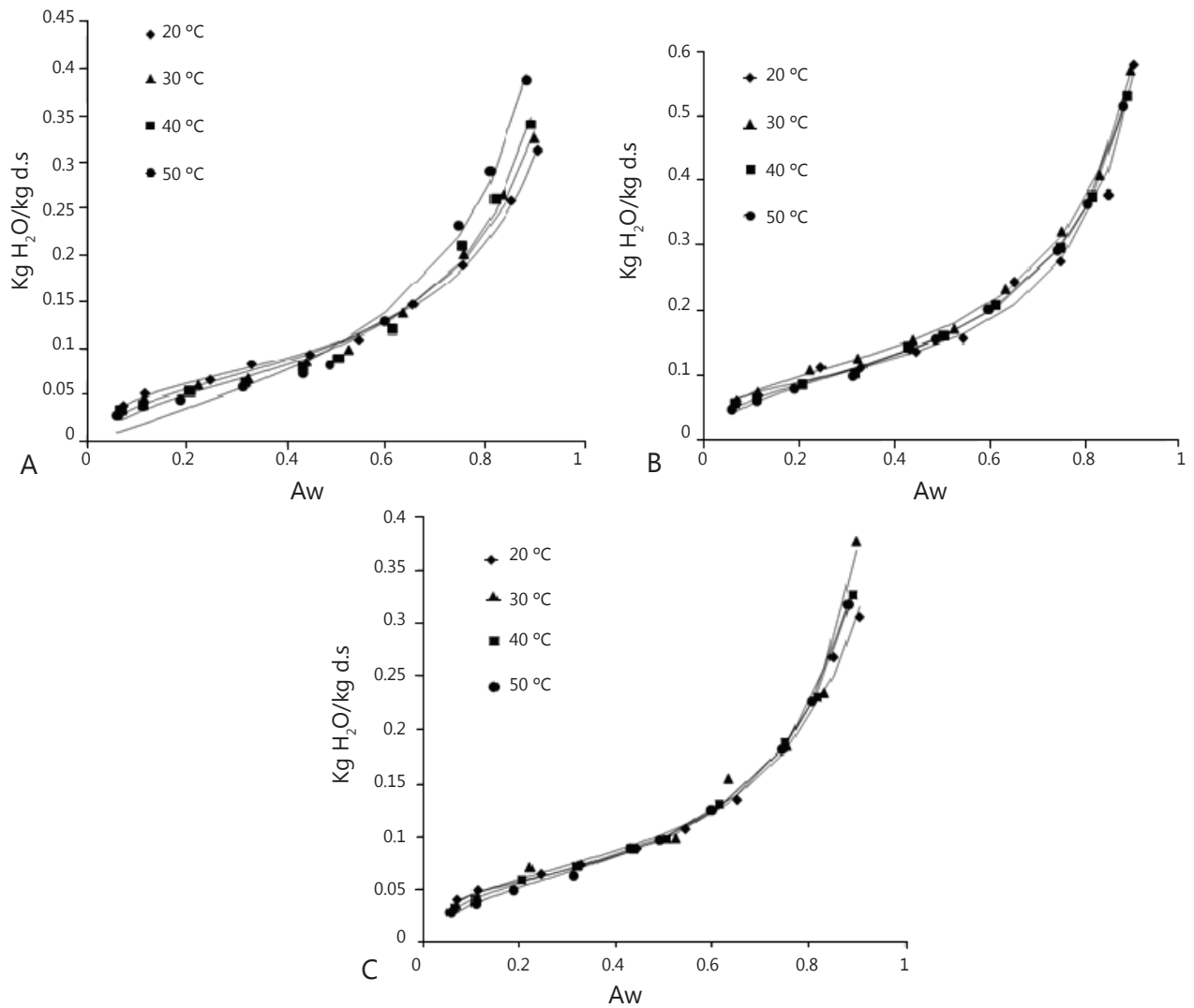
$$\left[ \Delta H_{diff} \right]_T = T_\beta (\Delta S_{diff}) - \Delta G_\beta \quad (7)$$

Where  $T_\beta$  is isokinetic temperature in K;  $\Delta G_\beta$  is Gibbs free energy in  $J \text{ mol}^{-1}$  at  $T_\beta$ . A negative sign indicates that the process of water adsorption is spontaneous and a positive sign a non-spontaneous process at  $T_\beta$  (Simal *et al.*, 2007).

## RESULTS AND DISCUSSION

**Adsorption isotherms.** Figure 1 (A-C) shows the equilibrium moisture content  $X$  dry basis (db) obtained experimentally for soursop powders with 55% MD (db), dried by FD, SD and VD at 4 temperatures, 20, 30, 40 and 50 °C, and the isotherms adjusted to GAB model. It can be noticed that for a same  $a_w$  at the 4 temperatures,  $X$  values for SD powder are larger than those of FD and VD; this suggests that the powders obtained by spray drying are more porous and thus more hygroscopic than the vacuum dried powders. The adsorption isotherms of soursop powder with MD, were affected by the type of dryer used (Ceballos *et al.*, 2009), this result was also observed by (Lee and Lee, 2007) showing differences in the pores formed in dried yeast powder using different dehydration technologies.

All the drying systems presented inversion points. For  $a_w$  values smaller than the inversion point, the behavior is similar to the described in literature (the higher the temperature, the lower moisture values) after the inversion point is reached, this ratio is changed (the higher the temperature, the higher moisture content).



**Figure 1.** Experimental equilibrium moisture for sourpop powders with MD at 4 temperatures obtained by: Freeze drying (FD and the isotherm adjusted to GAB model (A); spray drying (SD) and the isotherm adjusted to GAB model (B); vacuum drying (VD) and the isotherm adjusted to GAB model (C).

This result has been widely demonstrated in works with high-sugar foods such as peaches, raisins, currants, prunes and biscuits (Rahman, 1995). The inversion points of the isotherms between 20 and 50 °C are in  $a_w$  values between 0.53 to 0.50 for FD; 0.5 to 0.70 for SD and 0.3 to 0.35 for VD, respectively. This point is explained by an increase in sugar solubility caused by an increase in temperature. Inversion point values between 0.55 and 0.70 of  $a_w$  have been reported for products with high sugar content such as dried fruit (Tsami *et al.*, 1990; Telis-Romero *et al.*, 2005).

Table 1 shows the estimated parameters for GAB model adjusted to the experimental data for sourpop powders with MD at the experimental temperatures and statistical parameters.  $C$  value decreases with an increase of temperature for the 3 drying systems, indicating that at higher temperature, the binding energy of the first adsorbed layer decreases. For a temperature increase from 20 to 50 °C, there is a decrease in the  $C$  value for all the samples. Strong adsorbent-adsorbate interactions are exothermic, favored by lower temperatures, and are the cause of an increase in the  $C$  parameter with decrease in temperature (Diosady *et al.*, 1996; Gabas *et al.*, 2009).

**Table 1.** Estimated parameter for GAB model in soursop powders added with MD.

T (°C)	C	K	$X_m$ (Kg H <sub>2</sub> O /kg d.s.)	R <sup>2</sup>	E (%)
Freeze FD					
20	19.9598	0.8829	0.0637	0.998	3.223
30	12.8479	0.9050	0.0629	0.992	6.940
40	8.8972	0.9257	0.0618	0.989	2.941
50	2.3667	0.9096	0.0850	0.988	1.174
Spray SD					
20	38.6739	0.9444	0.0811	0.987	6.533
30	21.2918	0.9225	0.0972	0.984	2.375
40	15.4845	0.9292	0.0914	0.999	3.070
50	11.8622	0.9301	0.0930	0.999	3.208
Vacuum VD					
20	21.2418	0.8971	0.0595	0.993	4.283
30	30.6645	0.9529	0.0528	0.984	7.050
40	16.2651	0.9253	0.0574	0.999	1.862
50	11.6750	0.9298	0.0577	0.999	2.952

As well as, dependence on the drying type was also showed. Neither the  $K$  value nor  $X_m$  showed a clear dependence with temperature.  $X_m$  values were higher for SD powders (range from 0.0811 to 0.0972), followed by FD and VD (0.618 to 0.085 and 0.0528 to 0.0595), respectively. A similar result was reported by (Giraldo *et al.*, 2011) in blackberry powder with MD dried under the same conditions used in this work.

The  $C$  values obtained for soursop powders with MD dried by SD, VD and FD at 20 °C were 38.6739, 21.2418 and 19.9598, correspondingly. Similar tendency was observed in all the tested temperatures. These values are within the limits reported for acai powder dried with air (11.82) and by lyophilization (7.13) (Pavan *et al.*, 2012). Comparatively,  $C$  values for soursop powder with MD obtained by FD were lower than those reported for pineapple powder with MD and dried under the same conditions used in this work (22.852 and 12.798); and close to those reported for SD (18.097 and 6.030) and VD (25.384 and 11.093) at 20 and 50 °C, respectively (Gabas *et al.*, 2007), in blackberry powder with MD. In all of the cases,  $C$  value was much higher than 2. This constant is related to the net sorption heat and is used to classify the isotherms according to the Brunauer's classification (Brunauer *et al.*, 1938; Rahman, 1995); for  $C$  values higher than 2, isotherms are classified as type II (Martínez *et al.*, 1998). It can

be assumed that the monolayer adsorption heat is greater than the condensation heat, and it is constant for the monolayer occupation (Rahman, 1995). From isotherms analysis and the  $C$  values it can be inferred that soursop powder with MD isotherms are type II, this result agrees with the ones that were reported for fruit powders with MD as camu-camu (Silva *et al.*, 2006) and noni (Fabra *et al.*, 2011).

$K$  values between 0.8829 and 0.9529 were obtained, which are within the range of values reported in the literature for many foods (Rahman, 1995). Its variation did not present a clear dependence on temperature, but an ANOVA at 95% confidence, showed a significant difference among the drying systems. By comparing the results of this work (0.8829, 0.9444, 0.8971 at 20 °C and 0.9096, 0.9301 and 0.9298 at 50 °C for FD, SD and DV), with those of pineapple powder (0.901, 0.875 and 0.911 for FD, SD and VD at 20 °C, and 0.936, 0.956 and 0.920 at 50 °C, respectively; Gabas *et al.*, 2007), lyophilized acai juice (0.96 and hot-air drying at 25 °C of 0.92; Pavan *et al.*, 2012) and naranjilla powder (0.894 to 0.951; Gabas *et al.*, 2009), all are in the same range.

The  $X_m$  values (kg of water/kg d.s.) indicate the saturation moisture of the adsorption sites or the monolayer water content, and are dependent on the type of drying process. For the soursop powder with

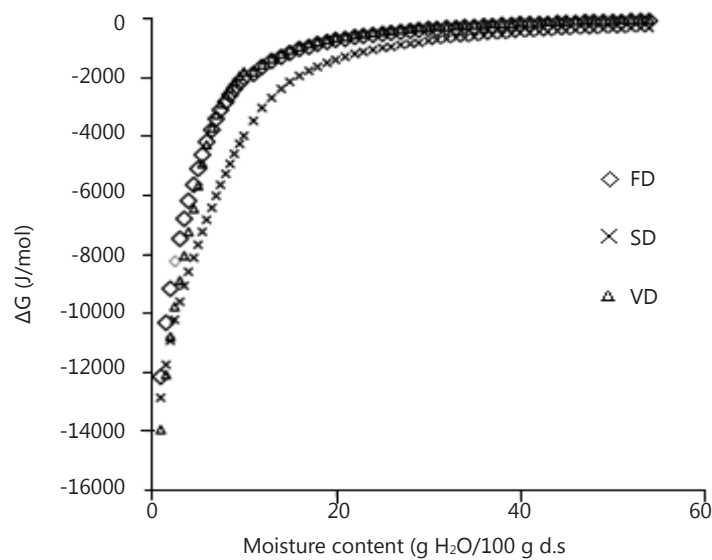


MD, values in the monolayer water were between 0.0528 and 0.0930 for the SD, 0.0637 and 0.0850 for FD, and 0.0528 and 0.0595 for VD. Although they do not show any definite trend with the temperature, the results were similar to those reported in different studies with fruit added with MD as pineapple pulp between 0.060 and 0.068 for FD; 0.093 and 0.115 for SD; 0.063 and 0.065 for VD (Gabas *et al.*, 2007), freeze-dried strawberry pulp (0.075) (Mosquera *et al.*, 2012), pineapple powder 0.049 and 0.074 (Gabas *et al.*, 2009). For noni free of MD is reported a value of 0.082 and at higher contents of MD the value went down to 0.034, indicating that the MD content decreases the equilibrium moisture (Fabra *et al.*, 2011); the work of (Lee

and Lee, 2008) indicates that  $X_m$  is affected by the drying system.

The  $R^2$  values for the adjustment of the curves were very close to unity and the  $\%E \leq 10\%$ , both confirm the good fit of the experimental data with the GAB model for the temperature range tested. This result agrees with the concept of numerous researches in food, which recommend the use of GAB model because of its good adjustment and the constants have a physical meaning.

**Thermodynamic properties.** In the Figure 2, changes in the Gibbs free energy are shown as a function



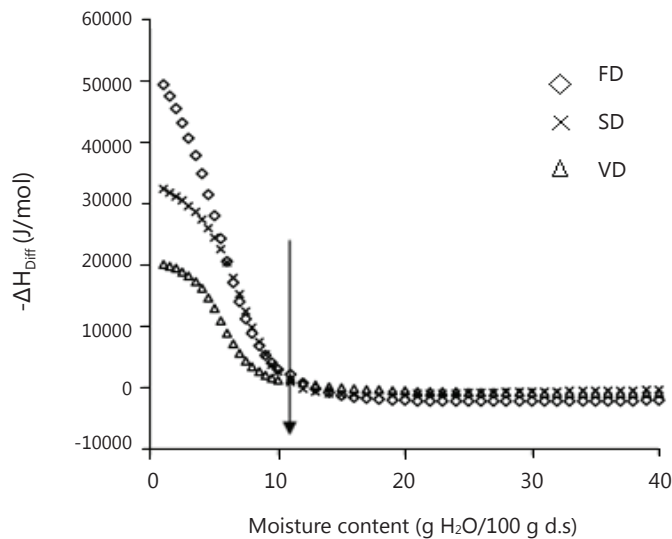
**Figure 2.** Gibbs free energy as a function of moisture content for soursop powder at 30 °C.

of moisture content on dry basis (%), during the adsorption of water by the soursop powders with MD obtained by different drying systems at 30 °C. For a 1% of moisture, powders obtained by VD had a  $\Delta G$  value of  $-13948 \text{ J mol}^{-1}$ ,  $-12857 \text{ J mol}^{-1}$  for SD and  $-12134 \text{ J mol}^{-1}$  for FD, indicating that were more hygroscopic at low moisture. However, the spray dried powders at humidities higher than 3.5% had lower  $\Delta G$  values, were the most hygroscopic over a wide range of humidities. The higher negative values of  $\Delta G$  are achieved for the same moisture, the more water molecules are easily trapped due to the greater forces of adsorption among the active points of the surface and the water molecules in the environment.

Figure 3 shows the relationship between the differential enthalpy  $\Delta H_{diff}$  or net heat of sorption

and the moisture content of the soursop powder, and its dependence on the three drying systems.

This property provides information about the energy changes that occur in food at a specific moisture level, produced by changes in the equilibrium moisture of the product. In the soursop powders with MD, differential enthalpy values decreases exponentially with increase in the humidity, tending to zero; this means that the heat of adsorption is equal to the heat of vaporization of water, and that this water begins to be more available for product degradation processes (Chuzel, 1992). The lowest values were presented for powders dried by VD and the highest for powders obtained by FD; these are the ones that require more energy to remove water from the monolayer. Net isosteric heat is zero when the heat of sorption value

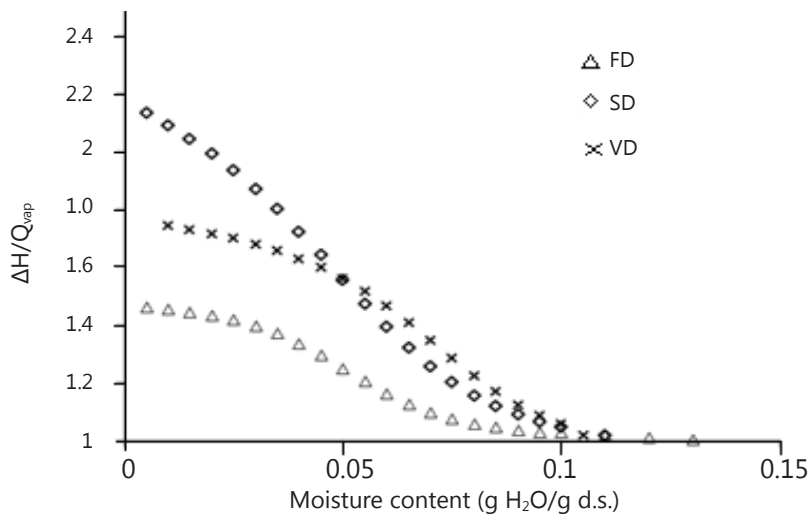


**Figure 3.** Influence of the drying system on the net isosteric heat of adsorption of water for soursop powder at 30 °C.

is the same as the heat of vaporization of water. The  $\Delta H_{diff}$  results showed that VD powders with moistures of 1% require 20 kJ/kmol, 32 kJ kmol<sup>-1</sup> for SD powders and 50 kJ kmol<sup>-1</sup> for FD powders, suggesting that all are affected by the changes in relative humidity, FD powders are the most sensitive to this change (Viganó *et al.*, 2012). These results are within the ranges reported for carrot 23 kJ kmol<sup>-1</sup> and tomato 52 kJ kmol<sup>-1</sup> (Nunes and Rotstein, 1991), and higher than the pineapple powders with MD obtained by VD 17.5 kJ kmol<sup>-1</sup>, FD 16.5 kJ kmol<sup>-1</sup> and SD 13.0 kJ kmol<sup>-1</sup> (Viganó *et al.*, 2012).

The point at which  $\Delta H_{diff}=0$  is identified with the start of the solubilization of the low molecular weight solutes. The three drying systems presented the solubility point at humidity of 14.7 g water/100 g d.s for VD, 12.8 for FD and 11.9 for SD. Despite having the same composition, each drying system produces powders with different structures, which has an influence in the solubility (Ceballos *et al.*, 2009).

Figure 4 represents the ratio of total sorption heat / heat of vaporization of water for the three drying systems at



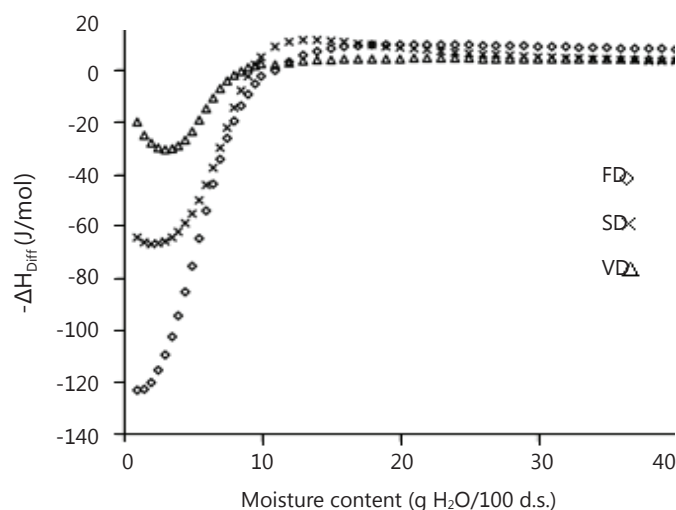
**Figure 4.** Relation total sorption heat/heat of vaporization of water for soursop powders with MD at different humidities.

different humidities. This value expresses the increase of energy needed to evaporate water from the product in relation to the evaporation of the same amount of water in the free state (Viganó *et al.*, 2012). The heat of evaporation of water was taken at the average temperature of experimental temperature range (35 °C) (McMinn and Magee, 2003).

It can be concluded from Figure 4 that drying soursop powder with MD until a final moisture content of 0.05 g of water/g d.s., requires approximately 215% more energy than if the same amount of free water were evaporated at the same temperature. Reaching the same moisture with spray and vacuum dryers requires

approximately 600% more energy. Until a equilibrium moisture of 0.1 kg water/kg d.s, the lyophilizer requires less energy than other dryers to reach the same moisture. These results allow predicting the energy costs for the different technological systems.

Differential entropy is calculated for each equilibrium moisture and each drying system with equation (6), results at 30 °C are shown in Figure 5. Experimental results indicate moisture dependence and negative value in the range of 0.5% to 10.0% of moisture content for SD powders; 0.5% to 8.5% for DV; 0.01% to 10.0% for FD, and at values greater than 10% of moisture, it depends only on moisture.



**Figure 5.** Drying system influence on the variation of the differential entropy in soursop powders with MD at 30 °C.

**Table 2.** Isokinetic temperature and Gibbs free energy for soursop powders.

Drying system	$T_{\beta}$ (K)	$\Delta G_{T_{\beta}}$ (J mol <sup>-1</sup> )	$R^2$
FD	356 ± 4	1482 ± 66	0.9996
SD	376 ± 8	4166 ± 188	0.9989
VD	501 ± 8	1364 ± 65	0.9893

The differential entropy is proportional to the number of available adsorption sites at a specific energy level, decreases for low moisture contents and increases rapidly when water is all over the surface (Al-Muhtaseb *et al.*, 2004). Entropic changes are associated with attraction or repulsion forces presented by the interface of water and sorbent; their quantification can contribute to the interpretation of dissolution and crystallization processes.

From fitting data of  $[\Delta H_{diff}]_{\tau}$  versus  $[\Delta S_{diff}]_{\tau}$  by linear regression, according to equation (7), the isokinetic temperature was calculated. Values of  $R^2$  greater than 0.9988 in all cases were obtained.

Table 2 shows the  $T_{\beta}$  and  $\Delta G_{T_{\beta}}$  values dependence of the drying system. The highest value of free energy to the isokinetic temperature was presented at the spray



dried powder, followed by lyophilized and vacuum drying powders; in every  $\Delta G_{T_{\beta}}$  case the values were positive, suggesting that the adsorption process at this temperature is non-spontaneous for soursop powder with MD at  $T_{\beta}$ . The  $\Delta G_{T_{\beta}}$  values and the sign are indicative of the affinity of the sorbent for water (McMinn *et al.*, 2005). This may explain the low solubility of the powders in water.

The results are consistent with the ranges reported for isokinetic temperatures of various materials such as potato and potato starches 376.6 K and 466.8 K, respectively, and a  $\Delta G$  between -1.525 and +0.107 kJ mol<sup>-1</sup> (McMinn *et al.*, 2005); mango 463 K (Telis-Romero *et al.*, 2005); loquat pulp between 458 and 475 K (Telis *et al.*, 2000); pineapple 342 K and 1.67 kJ mol<sup>-1</sup> of free energy (Simal *et al.*, 2007).

### CONCLUSIONS

The isotherms for soursop powder with MD, dehydrated using three different technologies, presented an influence of the drying system and a good fit with the GAB model ( $R^2 > 0.9893$ ). All isotherms showed a sigmoid shape type II and an inversion point for all drying systems. The negative  $\Delta G$  values suggest that adsorption process is spontaneous for the soursop powder with MD. The thermodynamic properties values of the soursop powders were influenced by the drying system, suggesting that differences in the structures caused by the drying technology used alter its porosity, and therefore influence their solubility, hygroscopicity and spontaneity of the adsorption processes.

### ACKNOWLEDGMENTS

This work was supported and funded by the Food Fruit Research Group at the Universidad Nacional de Colombia at Manizales and Food Research Group at UNESP-Sao Paulo.

### BIBLIOGRAPHY

Al-Muhtaseb, A., W. McMinn and T. Magee. 2004. Water sorption isotherms of starch powders. Part 2: Thermodynamic characteristics. *Journal of Food Engineering* 62(2): 135-142.

AOAC, 2001. Association of Official Analytical Chemist; Official Methods of Analysis, Washington D.C.

Brunauer, S., P.H. Emmett and E. Teller. 1938. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society* 60(2): 309-319.

Ceballos, A.M., G.I. Giraldo y C.E. Orrego. 2009. Evaluación de varios modelos de isothermas de adsorción de agua de un polvo de fruta deshidratada. *Vector* 4: 107-116.

Chaparro, M.C., A. Rojas, M. Peñuela, P. Gómez, V. Aristizabal y R. López. 2004. Caracterización de productos hortofrutícolas colombianos y establecimiento de las normas de calidad. CENICAFÉ-FNC-SENA, Chinchiná. 213 p.

Chuzel, G. 1992. Correlación entre actividad de agua y contenido de agua: equilibrio higroscópico e isothermas de sorción. *Actividad de agua en alimentos, procesamiento y conservación mediante su control*. Universidad del Valle, CIRAD, Cali, pp. 31-43.

Diosady, L.L., S.S. Rizvi, W. Cai and D.J. Jagdeo. 1996. Moisture sorption isotherms of canola meals, and applications to packaging. *Journal of Food Science* 61(1): 204-208.

Fabra, M.J., E. Márquez, D. Castro and A. Chiralt. 2011. Effect of maltodextrins in the water-content-water activity-glass transition relationships of noni (*Morinda citrifolia* L.) pulp powder. *Journal of Food Engineering* 103(1): 47-51.

Fasina, O.O. 2006. Thermodynamic properties of sweet potato. *Journal of Food Engineering* 75(2): 149-155.

Fernández, A.Q. y C.P. Madriñán. 1992. Principios y procedimientos experimentales para la obtención de curvas isothermas de sorción. *Actividad de agua en alimentos, procesamiento y conservación mediante su control*. Universidad del Valle y CIRAD, Cali, pp. 44-57.

Gabas, A.L., F.C. Menegalli and J. Telis-Romero. 2000. Water sorption enthalpy-entropy compensation based on isotherms of plum skind and pulp. *Journal of Food Science* 65(4): 680-684.

Gabas, A.L., J. Telis-Romero, G.I. Giraldo-Gómez y V. Telis. 2009. Propiedades termodinámicas de sorción de agua de la pulpa de lulo en polvo con encapsulantes. *Ciência e Tecnologia de Alimentos* 29(4): 911-918.

Gabas, A.L., V.R. Telis, P.J. Sobral and J. Telis-Romero. 2007. Effect of maltodextrin and arabic gum in water vapor

- sorption thermodynamic properties of vacuum dried pineapple pulp powder. *Journal of Food Engineering* 82(2): 246-252.
- Giraldo, G.I., C.E. Orrego-Alzate, L.M.Grajales, V. Telis, A.L. Gabas and J. Telis-Romero. 2011. Effect of drying methods on the thermodynamic properties of blackberry pulp powder. *Dyna* 78(168): 139-148.
- Iglesias, H.A., J. Chirife and P. Viollaz. 1976. Thermodynamics of water vapor sorption by sugar beet root. *International Journal of Food Science and Technology* 11(1): 91-101.
- IICA-PRODAR, 2006. Fichas técnicas. Productos frescos y procesados, frutas. En: [http://www.fao.org/inpho\\_archive/content/documents/vlibrary/ae620s/pfrescos/guanabana.htm](http://www.fao.org/inpho_archive/content/documents/vlibrary/ae620s/pfrescos/guanabana.htm); consulta: octubre 2009
- Lee, J.H. and M.J. Lee. 2008. Effect of drying method on the moisture sorption isotherms for *Inonotus obliquus* mushroom. *LWT - Food Science and Technology* 41(8): 1478-1484.
- Márquez, C.J. 2009. Caracterización fisiológica, físico-química, reológica, nutracéutica, estructural y sensorial de la guanábana (*Annona muricata* L. cv. Elita). Tesis de grado Doctorado en Ciencias. Facultad de Ciencias Agropecuarias. Universidad Nacional de Colombia. Medellín. 274 p.
- Martínez, N., A.M. Andrés, A. Chiralt y P. Fito. 1998. Termodinámica y cinética de sistemas alimento-entorno. Universidad Politécnica de Valencia, España. 372 p.
- McMinn, W., A. Al-Muhtaseb and T. Magee. 2004. Moisture sorption characteristics of starch gels. Part II: Thermodynamic properties. *Journal of Food Process Engineering* 27(3): 213-227.
- McMinn, W., A. Al-Muhtaseb and T. Magee. 2005. Enthalpy-entropy compensation in sorption phenomena of starch materials. *Food Research International* 38(5): 505-510.
- McMinn, W. and T. Magee. 2003. Thermodynamic properties of moisture sorption of potato. *Journal of Food Engineering* 60(2): 157-165.
- Mosquera, L.H., G. Moraga and N. Martínez-Navarrete. 2012. Critical water activity and critical water content of freeze-dried strawberry powder as affected by maltodextrin and arabic gum. *Food Research International* 47(2): 201-206.
- Nunes, R.V. and E. Rotstein. 1991. Thermodynamics of the water-foodstuff equilibrium. *Drying Technology* 9(1): 113-117.
- Pavan, M., S. Schmidt and H. Feng. 2012. Water sorption behavior and thermal analysis of freeze-dried, refractance window-dried and hot-air dried açai (*Euterpe oleracea* Martius) juice. *LWT - Food Science and Technology* 48(1): 75-81.
- Rahman, S. 1995. *Food properties handbook*. CRC Press, Inc, Florida, 500 pp.
- Rooney, J.J. 1998. Isokinetic temperature and the compensation effect in catalysis. *Journal of Molecular Catalysis A: Chemical* 133(3): 303-305.
- Silva, M.A., P.J. Sobral and T.G. Kieckbusch. 2006. State diagrams of freeze-dried camu-camu (*Myrcaria dubia* (HBK) Mc Vaugh) pulp with and without maltodextrina addition. *Journal of Food Engineering* 77(3): 426-432.
- Simal, S., A. Femenia, A. Castell-Palou and C. Roselló. 2007. Water desorption thermodynamic properties of pineapple *Journal of Food Engineering* 80(4): 1293-1301.
- Telis-Romero, J., M.N. Kohayakawa, Jr. V. Silveira, M.A. Pedro and A.L. Gabas. 2005. Enthalpy-Entropy compensation based on isotherms of mango. *Ciencia y Tecnología de Alimentos Campinas* 25(2): 297-303.
- Telis, V., A. Gabas, F. Menegalli and J. Telis-Romero. 2000. Water sorption thermodynamic properties applied to persimmon skin and pulp. *Thermochimica Acta* 343(1-2): 49-56.
- Thys, R., C. Zapata, L. Ferreira, A. Gomes and F. Cladera-Olivera. 2010. Adsorption isotherms of pinhão (*Araucaria angustifolia* seeds) starch and thermodynamic analysis. *Journal of Food Engineering* 100(3): 468-473.
- Tsami, E., Z.B. Maroulis, D. Marinou-Kouris and G.d. Saravacos. 1990. Heat of sorption of water in dried fruits. *International Journal of Food Science and Technology* 25(3): 350-359.
- Viganó, J., Azuara E., Telis V., Beristainb C., Jiménez M. and Telis-Romero J. 2012. Role of enthalpy and entropy in moisture sorption behavior of pineapple pulp powder produced by different drying methods. *Thermochimica Acta* 528: 63-71.