

EFFECT OF DRYING METHODS ON THE THERMODYNAMIC PROPERTIES OF BLACKBERRY PULP POWDER

EFFECTO DEL MÉTODO DE SECADO EN LAS PROPIEDADES TERMODINÁMICAS DE PULPA DE MORA EN POLVO

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ABSTRACT: Three different types of maltodextrin encapsulated dehydrated blackberry fruit powders were obtained using vibrofluidized bed drying (VF), spray drying (SD), vacuum drying (VD), and freeze drying (FD). Moisture equilibrium data of blackberry pulp powders with 18% maltodextrin were determined at 20, 30, 40, and 50°C using the static gravimetric method for the water activity range of 0.06–0.90. Experimental equilibrium moisture content data versus water activity were fit to the Guggenheim–Anderson–de Boer (GAB) model. Agreement was found between experimental and calculated values. The isosteric heat of sorption of water was determined using the Clausius–Clapeyron equation from the equilibrium data; isosteric heats of sorption were found to increase with increasing temperature and could be adjusted by an exponential relationship. For freeze dried, vibrofluidized, and vacuum dried pulp powder samples, the isosteric heats of sorption were lower (more negative) than those calculated for spray dried samples. The enthalpy-entropy compensation theory was applied to sorption isotherms and plots of ΔH versus ΔS provided the isokinetic temperatures, indicating an enthalpy-controlled sorption process.

KEYWORDS: Fruit pulp, drying methods, water activity, isotherms, thermodynamic properties

RESUMEN: Se obtuvieron cuatro clases de polvos deshidratados de mora encapsulados con maltodextrina utilizando secado por vibrofluidización (VF), por aspersión (SD) vacío (VD) y liofilización (FD). Se determinaron los datos de humedad de equilibrio de los polvos de pulpa de mora con 18% de maltodextrina a temperaturas de 20, 30, 40 y 50°C usando el método estático gravimétrico para el intervalo de actividad de agua entre 0.06–0.90. Los valores experimentales del contenido de humedad de equilibrio en función de la actividad de agua fueron ajustados con el modelo de Guggenheim–Anderson–de Boer (GAB) hallándose una buena concordancia entre los valores experimentales y los calculados. El calor isostérico de sorción, calculado utilizando la ecuación de Clausius–Clapeyron a partir de los datos de equilibrio, se incrementó con el aumento de la temperatura y fue ajustado con una relación exponencial. Para muestras de polvos liofilizados, vibrofluidizados y a vacío, el calor de sorción fue menor (más negativo) que los calculados para muestras secas en el secador por aspersión. La teoría de la compensación entalpía-entropía fue aplicada a las isotermas de sorción y de las gráficas de ΔH contra ΔS se obtuvieron las temperaturas isocinéticas, indicando un proceso de sorción controlado por la entalpía.

PALABRAS CLAVE: Pulpa de mora, métodos de secado, actividad de agua, isotermas, propiedades termodinámicas

NOMENCLATURE

a_w	Water activity
C, K	Constants of (1)
q_0	Isosteric heat of sorption of the first water molecular layer
Q_{st}	Isosteric heat of sorption (KJ/mol)
q_{st}	Net isosteric heat of sorption (KJ/mol)
R	Universal gas constant (8.314 J/mol K)
T	Absolute temperature (K)
T_B	Isokinetic temperature
X_0	Initial moisture content
X_{eq}	Equilibrium moisture content
X_m	Monolayer moisture content (drybasis)
ΔG	Free energy (KJ/mol)
ΔH	Enthalpy change ((KJ/mol)
ΔS	Entropy change (KJ/mol K)
λ	Pure water heat of vaporization (KJ/mol)

1. INTRODUCTION

Almost 90% of international blackberry production is transformed into processed products: nectars and juices, frozen pulps, concentrates, jams and jellies, and dehydrated powders [1]. Dried fruit juice produces a stable, easy-to-handle form of the juice that reconstitutes rapidly into a good quality product, and is seen mainly as a convenience food, having long storage lives at ordinary temperatures [2-4].

Dehydration of fruit juices is a difficult operation, mainly because of the undesirable changes in the quality of the dehydrated product. The high temperatures and long drying times required to remove the water from the sugar containing fruit material in conventional air-drying may cause serious damage to the flavor, color, and nutrients of the product [5]. To reduce these undesirable changes, techniques such as spray drying, freeze drying, vacuum drying, and vibrofluidization are employed. Maltodextrin has been used as additive to decrease the stickiness of the resulting food powders [6].

For food, sorption isotherms give information about the sorption mechanism and interactions between the food components and water, and they are useful for the design of drying processes and identifying their energy requirements. Moisture sorption isotherms describe the

relationship between the equilibrium moisture content and water activity [7-9]. Numerous mathematical models that describe the sorption behavior of water in foods are available in the literature. Several of these models are based on theories of sorption mechanisms; others are purely empirical or semi-empirical [9-11]. The criterion used to select the most appropriate model is the adjustment grade for the experimental data and the physical meaning of the model [4].

The isosteric heat of sorption is a differential molar quantity derived from the temperature dependence of the isotherm, which represents the energy or intermolecular bonding between water molecules and absorbing surfaces at a particular hydration level. Usually, the moisture content at which the heat of absorption is similar to that of vaporization for pure water is considered to be an indicator of the free water content. The net isosteric heat of sorption can be used to estimate the energy requirements of drying. Conventionally, during the sorption process, the net isosteric heat is a positive quantity when heat is evolved and it becomes negative when heat is absorbed [12,13].

The aim of this work was to analyze the effects of different drying methods such as spray drying, vacuum drying, freeze drying and drying in a vibrofluidized bed on the sorption isothermal data for blackberry pulp powders, in order to calculate the constants of the sorption isotherm GAB model for each powder and to determine the isosteric heats of sorption from the experimental data.

2. MATERIAL AND METHODS

2.1 Raw material

Blackberry (Mora de Castilla: *Rubus glaucus Benth*) [soluble solid content of 6 – 9 °Brix, moisture content of 91 – 94% (wet basis)] was obtained at the local market (São José do Rio Preto, SP, Brazil) and stored at 7 °C prior to use. The blackberry was prepared in a pilot plant finisher and sieved through a 1.6 mm-mesh.

The dextrose equivalent (DE) is a measure of the reducing power of starch derived polysaccharides/ oligosaccharides compared to d-glucose on a dry weight basis [14]. Commercial maltodextrins of different dextrose equivalent values (DE 2-20) possess different

physicochemical properties including solubility and viscosity. An aqueous solution with 50% solids (mass basis) was prepared by dispersing commercial maltodextrin MOR-REX[®] 1920 (Corn Products Brazil) in distilled water at 40 °C using a mechanical stirrer. This solution was added to the blackberry pulp so that the mass ratio between the maltodextrin solution and pulp was 18% maltodextrin (MD) on dry basis (i.e., 18 g of maltodextrin/100 g total solids). According to technical specifications provided by the manufacturer, maltodextrin MOR-REX[®] 1920 presents 17.0 £ DE £ 19.9. Blackberry pulp with MD was used for the different drying methods.

2.2 Drying methods

2.2.1 Vibrofluidized bed

The drying chamber of the vibrofluidized bed consisted of a vertical glass cylinder 165 mm in diameter and 704 mm high. The chamber was suspended by a spindle and connected to a direct current motor that drove an eccentric wheel that imparted vertical sinusoidal vibrations to the drying chamber. The frequency and amplitude of vibration could be set from 15 to 40 Hz and from 1 to 3 mm, respectively. The air temperature used was 70 °C, and the air velocity was 3.8 m/s. The inert particles were supported by a grid having 9.4% free cross-sectional area, which was made from 2.5 mm holes punched in a 2 mm stainless steel sheet, forming a 60° rotated triangular staggered array configuration. The paste material to be dried was fed continuously to the drying chamber at constant rate with a peristaltic pump and dispersed by a central single stream nozzle 5 mm in diameter. The dry powder separated from inert particles by attrition was carried out of the drying chamber along with the exhausted air and collected in a cyclone.

2.2.2 Spray Dryer

Powder was obtained by spray dryer (model SD 5.0, Labmaq do Brazil Ltda). The spray dryer operates concurrently and has a spray nozzle with an orifice of 2 mm in diameter. The inlet and outlet air temperatures for all samples investigated were about 140 °C and 102 °C, respectively. The liquid feed to the dryer was between 1 and 1.5 L/h. The flow of the drying air was about 12 m³/h. The experiments were performed at constant process conditions. The dry powder was

separated from inert particles by attrition, removed from the drying chamber along with the exhausted air, and collected in a cyclone.

The obtained material was placed into plastic bags and stored in a desiccator containing silica gel until utilization.

2.2.3 Freeze dryer

The sample blackberry pulp was put in three stainless steel trays and frozen before drying in a freezer (Liotop, FV500) at -40 °C. The freeze dryer used was developed by Liobras/Brazil (L101). Freeze drying tests were performed for 48 hours with the vacuum chamber total pressure and temperature equal to 67 Pa and -45 °C, respectively.

The freeze dryer is composed of a cylindrical transparent acrylic drying chamber of 35 cm covered with a **stainless steel** top and eight silicone faucets to fit round-bottom glass bottles (vacuum relief system). The bottles were connected to the faucets using a silica adapter and a stainless steel pipe. The drying chamber has a shelf inside that supports four **stainless steel** trays. The samples can be placed on the trays or in the glass bottles. The vacuum is produced using a vacuum pump that is connected to the freeze dryer through a hose. The temperature and pressure are displayed on a front panel. The dried product was removed and ground in a hammer mill.

2.2.4 Vacuum chamber dryer

The fruit pulp samples were dried on a stainless steel tray inserted into a vacuum chamber (Marconi, MA 030) at 60 °C for 48 h. The dried product was ground in a hammer mill.

2.3 Sorption isotherms

Equilibrium moisture content of pulp at several water activities were determined by the static gravimetric method [7-8], at 20, 30, 40, and 50 °C. Ten saturated salt solutions were prepared corresponding to a range of water activities of 0.06 to 0.90. Each solution was transferred into separated jars in such an amount so as to occupy a space of about 1.5 cm deep at the bottom of the jar. Triplicate samples of around 1 g of blackberry

powder were weighed in 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 – 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 [15].

2.4 Mathematical development

The GAB (Guggenheim-Anderson-de Boer) equation was used to fit blackberry pulp powder sorption isotherm data. This model has three parameters that have physical meaning, and it has been found to adequately represent water activity experimental data in the range of practical interest for most foods, i.e., 0.10 ≤ a_w ≤ 0.90 [8, 16]. It is given by (1) [4, 17]:

$$X = \frac{(C-1)Ka_w X_m}{1+(C-1)ka_w} + \frac{ka_w X_m}{1-ka_w} \quad (1)$$

with C and K , the constants related to the temperature effect, being expressed by (2) and (3):

$$C = C_G \exp\left(\frac{\Delta H_C}{RT}\right) \quad (2)$$

$$K = K_G \exp\left(\frac{\Delta H_K}{RT}\right) \quad (3)$$

where ΔH_c and ΔH_k are functions of the heat of sorption of water: $\Delta H_c = H_m - H_n$ and $\Delta H_k = \lambda - H_n$.

The parameters were estimated by fitting the mathematical model to experimental data using a nonlinear regression. The adequacy of the fitted function was evaluated by the determination coefficient (R^2) and the mean relative percentage deviation (P) which is defined by (4):

$$P = \frac{100}{n} \sum_{i=1}^n \frac{|m_{pi} - m_i|}{m_i} \quad (4)$$

where m_i is the experimental value, m_{pi} is the predicted value, and n , the number of experimental data. It is believed that a P value lesser than 10% indicates that the approach to the model is good [18-19].

The effect of the temperature and the drying method on the parameters of GAB was determined by analysis of variance (ANOVA) with a 5% significance level (p value <0.05 were significant differences).

The net isosteric heat of sorption or enthalpy of sorption (q_{st}) is defined as the difference between the total heat of sorption (Q_{st}) and the heat from the vaporization of water. It can be determined from the (5), which is derived from the Clausius-Clapeyron equation [20]:

$$\left. \frac{\partial \ln(a_w)}{\partial (1/T)} \right|_X = \frac{Q_{st} - \lambda}{R} = \frac{-q_{st}}{R} \quad (5)$$

The isosteric heat of sorption is a differential molar quantity derived from the isotherm temperature dependence and its application requires the measurement of sorption isotherms at two or more temperatures [21]. An empirical exponential relationship between the isosteric heat of sorption and moisture content, as proposed by Tsami et al. [22], can be fitted to these quantities, according to (6):

$$q_s = q_0 \exp\left[-\frac{Xeq}{X_0}\right] \quad (6)$$

The change in molar differential entropy of sorption can be calculated from the Gibbs-Helmholtz equation as used by Telis et al. [17]:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (7)$$

where the free energy is calculated as

$$\Delta G = -RT \ln a_w \quad (8)$$

The effect of a change in water sorption on free energy is usually accompanied by changes on both the enthalpy and the entropy. Substituting (8) with (7) and rearranging results in (9):

$$\ln a_w = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (9)$$

The isosteric heat of sorption or enthalpy of sorption and entropy can then be calculated from (9) by plotting $\ln a_w$ versus $1/T$ for certain values of the material moisture content and then determining the slope $(-DH/R)$ and the linear coefficient $(\Delta S/R)$. Several researchers have used the above procedure for the determination of q_{st} [23] and calculated the heat of the sorption of water for dried fruits [24]; for some vegetables [25]; for garlic [21]; for potatoes and for the skin and pulp of persimmon [17]. A plot of ΔH versus ΔS from values of (9) can be evaluated for each set of sorption data. These values can be correlated according to (10):

$$\Delta H = T_B(\Delta S) + \Delta G_B \tag{10}$$

The isokinetic temperature has an important physical meaning as it represents the temperature at which all reactions in the series proceed at the same rate. Since there is a high degree of linear correlation between enthalpy and entropy, the compensation theory was assumed to be valid for sorption. Krug et al. [26] and Madamba et al. [25] recommend a test for the compensation theory that involves comparing the isokinetic temperature with the harmonic mean temperature T_{hm} that is defined by (11) as:

$$T_{hm} = \frac{n}{\sum_{i=1}^n (1/T)} \tag{11}$$

An approximate (1 - α) 100% confidence interval for T_B may be calculated from (12):

$$T_B = T_B \pm t_{m-2, \alpha/2} \sqrt{Var(T_B)} \tag{12}$$

where:

$$T_B = \frac{\sum (\Delta H - \overline{\Delta H})(\Delta S - \overline{\Delta S})}{(\Delta S - \overline{\Delta S})^2} \tag{13}$$

$$Var(T_B) = \frac{\sum (\Delta H - \overline{\Delta H} - T_B \Delta S)^2}{(m - 2) \sum (\Delta S - \overline{\Delta S})^2} \tag{14}$$

m is the number of $(DH, \Delta S)$ data pairs, $(\overline{\Delta H})$ is the average enthalpy, and $\overline{\Delta S}$ is the average entropy.

3. RESULTS AND DISCUSSION

3.1 Adsorption isotherms

Experimental results for the equilibrium moisture content of blackberry at each water activity (a_w) for the different temperatures are given in Table 1. Moisture content at each water activity represents the mean value of three replications, where a maximum standard deviation relative of 6% was observed. Figure 1 shows the experimental sorption isotherms for blackberry powder obtained by different drying methods at 20 °C with the respective fittings of GAB.

Through analysis of this figure, it can be seen that all the curves exhibit type II behavior according to Brunauer’s classification [27], which is typical of fruits rich in sugars [11, 16, 28-30], and similar behavior was observed at the other temperatures.

Table 1. Experimental equilibrium moisture contents (dry basis) for blackberry powders

Temp. (°C)	a_w	x_{eq} SD	x_{eq} FD	x_{eq} VD	x_{eq} VF
20	0.070	0.031	0.028	0.027	0.031
	0.113	0.041	0.037	0.035	0.041
	0.246	0.065	0.059	0.058	0.066
	0.331	0.078	0.071	0.070	0.080
	0.446	0.099	0.089	0.087	0.101
	0.547	0.121	0.111	0.111	0.124
	0.655	0.164	0.143	0.157	0.164
	0.754	0.214	0.190	0.189	0.219
	0.853	0.326	0.282	0.295	0.315
	0.907	0.443	0.377	0.408	0.433
30	0.069	0.026	0.023	0.0243	0.027
	0.112	0.037	0.031	0.033	0.037
	0.223	0.057	0.052	0.053	0.057
	0.324	0.073	0.064	0.068	0.067
	0.439	0.094	0.085	0.086	0.093
	0.526	0.115	0.104	0.110	0.119
	0.635	0.159	0.133	0.140	0.154
	0.756	0.226	0.195	0.200	0.215
	0.835	0.286	0.269	0.270	0.294
	0.900	0.442	0.385	0.385	0.422

Temp. (°C)	a_w	X_{eq} SD	X_{eq} FD	X_{eq} VD	X_{eq} VF
40	0.066	0.023	0.019	0.020	0.022
	0.111	0.034	0.028	0.031	0.034
	0.206	0.053	0.045	0.047	0.051
	0.319	0.072	0.062	0.063	0.067
	0.432	0.094	0.084	0.083	0.091
	0.506	0.111	0.097	0.098	0.108
	0.615	0.144	0.126	0.128	0.140
	0.753	0.225	0.194	0.200	0.213
	0.820	0.273	0.253	0.248	0.277
0.893	0.418	0.372	0.353	0.406	
50	0.059	0.018	0.016	0.015	0.016
	0.110	0.030	0.025	0.024	0.026
	0.189	0.045	0.038	0.034	0.044
	0.314	0.066	0.055	0.057	0.063
	0.432	0.089	0.080	0.076	0.086
	0.489	0.103	0.091	0.085	0.092
	0.599	0.135	0.119	0.116	0.131
	0.746	0.204	0.188	0.184	0.207
	0.809	0.258	0.241	0.242	0.266
0.884	0.376	0.363	0.377	0.397	

For the constant a_w , an increase in temperature causes a decrease in the amount of adsorbed water. An exception to this rule is shown by certain sugars and other low-molecular-weight food constituents, which become more hygroscopic at higher temperatures because they dissolve in water [4, 23, 31]. The blackberry results were in agreement with the above statement for water activity below 0.5, while the effects of higher temperatures on the equilibrium moisture content are not clear.

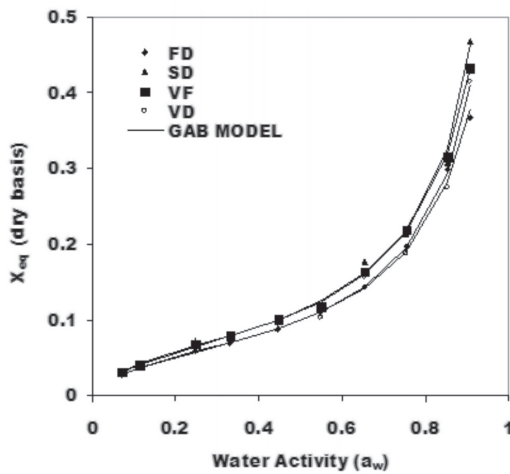


Figure 1. Adsorption curve for the blackberry power at 20 °C obtained by vacuum drying (VD), freeze drying (FD), spray drying (SD), and vibro-fluidization (VF).

3.2 Fitting the GAB model to experimental data

The GAB model was selected because it has been considered the best-fit model for many food materials over a wide range of water activity, in addition to giving information on the moisture content of the monolayer. The results obtained in this work are within the limit values of the constants C and K suggested by Lewicki [32] based on mathematical analysis of the model. To guarantee a relatively good description of the sigmoidal isotherms and to fulfill the requirements of the BET model, as well as assuring that the calculated monolayer moisture content (X_m) is within $\pm 15.5\%$ from the true monolayer capacity, Lewicki [32] stated that the constants should be in the ranges $0.24 \leq K \leq 1$ and $5.67 \leq C \leq \infty$.

The value of the monolayer moisture content (X_m) indicates the amount of water that is strongly adsorbed to specific sites at the food surface, and this is a value that must be reached in order to assure food stability. Below this value, rates of deteriorative reactions are minimal [19]. Table 2 shows the values of GAB parameters of blackberry powder obtained from the four drying methods at different temperatures. It is observed that X_m values are in the range of 5.8 to 6.97. The higher values are obtained for SD and VF, while VD and FD give smaller values. The analysis of these values shows they are independent of temperature. Some authors have obtained similar results for different foods in which it is observed that the monolayer moisture content is constant and independent of temperature [4, 28, 33], whereas other authors have observed that X_m depends on the temperature [8, 30].

Table 2. Values of GAB parameter of blackberry powers obtained by four drying methods

Temp. (°C)	Const.	SD	FD	VD	VF
20	X_m	0.0657	0.0585	0.0580	0.0657
	C	10.86	11.51	10.97	11.26
	K	0.941	0.938	1.010	0.937
	R^2	0.993	0.996	0.994	0.999
	$P\%$	0.97	0.56	0.19	0.08
30	X_m	0.0697	0.0570	0.0597	0.0610
	C	8.18	8.69	8.72	9.23
	K	0.935	0.948	0.945	0.946
	R^2	0.999	0.995	0.999	0.999
	$P\%$	2.23	1.56	0.17	1.02
40	X_m	0.0673	0.0575	0.0592	0.0649
	C	7.07	6.91	7.15	7.15
	K	0.944	0.955	0.946	0.945
	R^2	0.994	0.999	0.995	0.992
	$P\%$	0.28	0.93	1.09	0.04
50	X_m	0.0662	0.0575	0.0580	0.0638
	C	5.87	5.56	5.42	5.30
	K	0.935	0.958	0.955	0.956
	R^2	0.992	0.999	0.997	0.993
	$P\%$	0.54	0.02	0.13	0.04

An ANOVA with a 5% significance level used to evaluate the influence of drying method and temperature on GAB parameters showed that X_m is not influenced by temperature, but that it is affected by the drying method. Tsami et al. [34] pointed out that the observed differences in moisture sorption capacity can be explained by the differences in bulk porosity and the pore size of the dried material.

The values of C are within the reported limits for fruits [8]. Strong adsorbent–adsorbate interactions, which are exothermic, are favored at lower temperatures, causing an increase in C with decreasing temperature [4, 11, 30, 35]. This is in accordance with (2) that describes the temperature dependence of C , which means that higher temperatures diminish the union energy of the first absorbed layer. This work exhibited behavior in agreement with the literature, increasing temperature from 20 to 50 °C produced a steady decrease in C . For all samples of dried blackberries, the parameter C decreased from 11.508 – 10.859 at 20 °C, to 5.869 – 5.229 at 50 °C.

The value of K provides a measure of the interactions between the molecules in the multilayers with the adsorbent, and it tends to fall between the energy value of the molecules in the monolayer and that of liquid water. If K is equal to 1, the multilayers have properties of liquid water, and the sorption behavior can be modeled by the BET equation [4, 36-37]. For all samples, K was between 1.010 and 0.937, and these values are in agreement with those obtained by Telis et al. [17] for persimmon, Gabas et al [4] for pineapple pulp powder, and Garcia-Pérez et al. [33] for lemon peel. For all samples, the parameter K showed little change with temperature increase or drying method, and an ANOVA with 5% significance level confirms its independence of temperature and drying method.

3.3 Sorption thermodynamic properties

The GAB-obtained parameters were used to estimate the water activities for certain moisture contents at different temperatures, and the net isosteric heats of sorption were determined by applying (5). The moisture content dependence of net isosteric heat sorption of water (q_{st}) for dried blackberry pulp powder obtained via vacuum drying, freeze drying, spray drying, and vibro-fluidization are shown in Figure 2. For nearly

the entire range of moisture contents, the values of q_{st} for freeze dried, vibro-fluidized and vacuum dried samples were lower (more negative) than for spray dried samples, indicating a higher degree of water binding for these methods compared to spray drying. All moisture contents of the blackberry spray dried samples had positive values. It is important to note that, for moisture content less than 0.3 kg/kg (dry basis), the negative increase in the net isosteric heat of sorption should be considered in the simulation of energy requirements of the drying process.

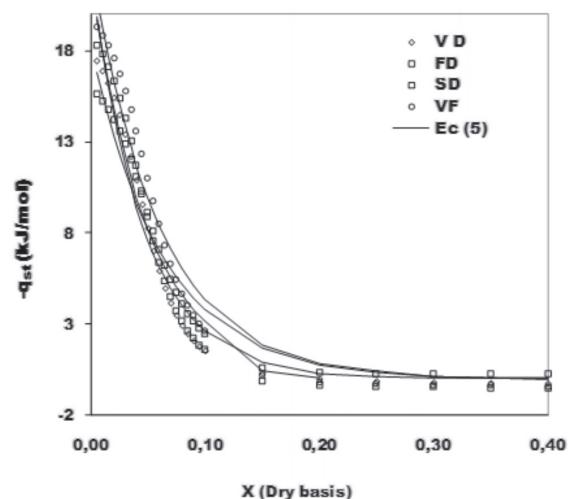


Figure 2. Net isosteric heat of sorption for the four drying methods.

The blackberry results given in Figure 2 clearly show an increase in isosteric heats with decreasing moisture content. The elevated net heats of sorption of water at low moisture content are an indication of strong water–food interactions in the fruit. As the moisture content increases, the available sites for sorption of water reduced, resulting in lower values of q_{st} [17]. This is in agreement with the work of Mazza and LeMaguer [38] for yellow globe onion, Saravacos et al. [5] for sultana raisins, Telis et al. [17] for persimmon, and Telis-Romero et al. [31] for mangoes. According to Wang and Brennan [39], the decrease in the isosteric heat with higher amounts of sorbed water can be quantitatively explained by considering that initially sorption occurs on the most active available sites, giving rise to high interaction energy. As these sites become occupied, sorption occurs on the less active ones, resulting in lower heats of sorption. For very low moisture contents, the values q_{st} (kJ/mol) are highly

negative, which means that sorption is a compulsive reaction. According to Tsami [23], the more negative the value of q_{st} , the higher the degree of binding of water on the food surface will be.

Experimental values of q_{st} were fitted using (6), and the constants q_0 and X_0 , as well as values for the determination coefficient (R^2), are shown in Table 3. In general, the R^2 values were satisfactory. The calculated values of q_0 were similar for all samples. These results are in agreement with works obtained for fruits and vegetables [4, 24, 31].

Table 3. Estimated parameters of adjusted data to (6) for blackberry powders

	q_0 (KJ/mol)	X_0 (% dry basis)	R^2
SD	18.2	6.4	0.97
FD	21.7	5.2	0.96
VD	22.6	4.7	0.97
VF	22.6	6.1	0.97

The values of ΔH and ΔS were obtained from the straight lines calculated by (9) at different blackberry moisture contents. Figure 3 shows that changes in water sorption affect both enthalpy and entropy. If the law of compensation is applied to the moisture range studied, the results correlate with (10).

The isokinetic temperature (T_B) was calculated by linear regression for all data sets with a 95% confidence interval. The harmonic mean temperature (T_{hm}) was calculated from (11). According to Krug et al. [40], a linear chemical compensation pattern exists only if $T_B \neq T_{hm}$. The isokinetic temperature for the sorption of blackberry is shown in Table 4 with the R^2 value. The harmonic mean temperature was calculated as $T_{hm} = 307.6$ K; this value is significantly different from all values of T_B described above, and it confirms the suitability of the isokinetic theory for blackberry water sorption. According to Leffler [41], if $T_B < T_{hm}$, the process is enthalpy driven, while for the opposite condition ($T_B > T_{hm}$), the process is considered to be entropy-controlled.

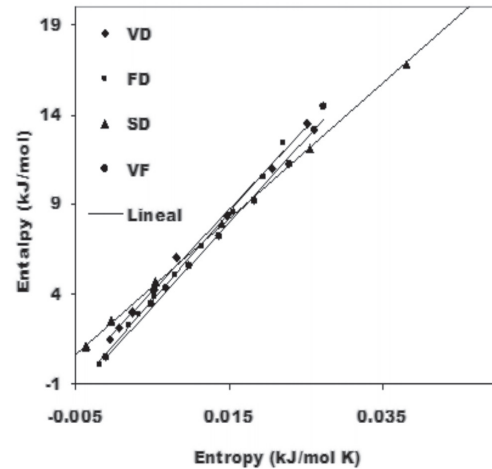


Figure 3. Enthalpy-entropy relationship for water sorption of blackberry (10).

Table 4. Isokinetic temperatures for blackberry dried by spray, freeze, vacuum drying, and vibro-fluidization

	T_B (K)	R^2
SD	507.1 ± 7	0.993
FD	457.6 ± 6	0.996
VD	477.1 ± 6	0.995
VF	446.7 ± 6	0.997

4. CONCLUSIONS

The equilibrium moisture content increased with decreasing temperature at constant water activity. The GAB isotherm model was found to be adequate for describing the experimental data obtained from blackberry pulp powders that had been dried by various techniques: spray drying, freeze drying, vacuum drying and vibro-fluidization. At the same water activity, all samples showed lower equilibrium moisture contents and were less affected by changes in temperature. The net isosteric heats of the sorption of pulp powders that had been freeze dried, vibro-fluidized, and vacuum dried were lower (more negative) than the values for spray dried samples. These values were calculated using the Clausius-Clapeyron equation. An empirical exponential relationship was used to describe the heat of sorption dependence on the material moisture content. The enthalpy-entropy compensation and the isokinetic theory were successfully applied to the water sorption of blackberry pulp, suggesting that this process occurs by enthalpy-controlled mechanisms.

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REFERENCES

- [1] CABRAL, R.A.F., ORREGO, C.E., GABAS, A.L. AND TELIS-ROMERO, J. Rheological and thermophysical properties of blackberry juice, *Ciência e Tecnologia de Alimentos* 27(3), 589-596, 2007.
- [2] AGUILERA, J.M. AND STANLEY, D.W. Microstructural principles of food processing and engineering (2nd ed.). Aspen Publishers, New York, 1999.
- [3] Krokida, M.K. AND MARINOS-KOURIS, D. Rehydration kinetics of dehydrated products. *J. Food Engineering*, 57, 1-7, 2003.
- [4] GABAS, A.L., TELIS, V.R.N., SOBRAL, P. AND TELIS-ROMERO, J. Effect of maltodextrin and arabic gum in water vapor sorption thermodynamic properties of vacuum dried pineapple pulp powder. *J. Food Engineering*, 82, 246-252, 2007.
- [5] SARAVACOS, G.D., TSIOURVAS, D.A. AND TSAMI, E. Effect of temperature on the water adsorption isotherms of sultana raisins. *J. Food Science*, 51(2), 381-383, 1986.
- [6] ADHIKARI, B., HOWES, T., BHANDARI, B.R., TROUNG, V. Effect of addition of maltodextrin on drying kinetics and stickiness of sugar and acid-rich foods during convective drying experiments and modelling. *J. of Food Engineering*, 62 (1), 53-68, 2004.
- [7] ROCKLAND, L.B. AND BEUCHAT, L.R. Water activity: theory and applications to food. Marcel Dekker, New York, 1987.
- [8] RAHMAN, S. Food properties handbook. CRC Press, New York, 1995.
- [9] KAYMAK-ERTEKIN, F. AND SULTANOGLU, M. Moisture sorption isotherm characteristic of peppers. *J. Food Engineering*, 47, 225-231, 2001.
- [10] HOSSAIN, M.D., BALA, B.K., HOSSAIN, M.A. AND MONDOL, M.R.A. Sorption isotherms and heat of sorption of pineapple, *J. Food Engineering*, 48, 103-107, 2001.
- [11] GOULA, A.M.G., KARAPANTSIOS, T.D., ACHILIAS, D.S. AND ADAMOPOULOS, K.G. Water sorption isotherms and glass transition temperature of spray dried tomato pulp, *J. Food Engineering*, 85, 73-83, 2008.
- [12] DUCKWORTH, R.B., The properties of water around the surfaces of food colloids. *Proceedings of the Institute of Food Science and Technology*, 5, 50-62, 1972
- [13] CLEMENTE, G., BON, J., BENEDITO, J, AND MULET, A. Desorption isotherms and isosteric heat of desorption of previously frozen raw pork meat. *Meat Science*. 82(4). 413-418, 2009.
- [14] WANG, Y.-J. AND L. WANG, Structures and properties of commercial maltodextrins from corn, potato and rice starches. *Starch*. 52, 296-304, 2000
- [15] AOAC. Official Methods of Analysis, 15 ed. Washington DC, Association of Official Agricultural Chemists, 1990.
- [16] TIMMERMANN, E., CHIRIFE, I. AND IGLESIAS, H. Water sorption isotherms of foods and foodstuffs: BET or GAB parameters, *J. Food Engineering* 48, 19-31, 2001.
- [17] TELIS, V.R.N., GABAS, A.L., MENEGALLI, F.C. AND TELIS-ROMERO, J. Water sorption thermodynamic properties applied to persimmon skin and pulp, *Thermochemica Acta*, 343, 49-56, 2000.
- [18] LOMAURO, C.J., A.S. BAKSHI, AND T.P. LABUZA, Evaluation of food moisture sorption isotherm equations. Part I. Fruit, vegetable and meat products. *Lebensmittel-Wissenschaft und Technology*, 18: 111-117, 1985
- [19] CHOUDHURYA, D., J.K. SAHUB, AND G.D. SHARMAA, Moisture sorption isotherms, heat of sorption and properties of sorbed water of raw bamboo (*Dendrocalamus longispatus*) shoots. *Industrial crops and product*, 33: . 211-216, 2011
- [20] WALSTRA, P. Physical chemistry of foods. Marcel Dekker, New York, 2003.
- [21] MCLAUGHLIN, C.P. AND MAGEE, T.R.A. The determination of sorption isotherm and the isosteric heats of sorption for potatoes, *J. Food Engineering*, 35, 2175-2191, 1998.
- [22] TSAMI, E., MAROULIS, Z.B., MARINOS-KOURIS, D. AND SARAVACOS, G.D. Heat of sorption of water in dried fruits, *Int. J. Food Science and Technology*, 25, 350-359, 1990.

- [23] TSAMI, E. Net isosteric heat of sorption in dried fruits, *J. Food Engineering* 14, 327-335, 1991.
- [24] KIRANOUDIS, C.T., MAROULIS, Z.B., TSAMI, E. AND MARINOS-KOURIS, D. Equilibrium moisture content and heat of desorption of some vegetables, *J. Food Engineering*, 20, 55-74, 1993.
- [25] MADAMBA, P.S., DRISCOLL, R.H. AND BUCKLE, K.A. Enthalpy-entropy compensation models for sorption and browning of garlic, *J. Food Engineering*, 28, 109-119, 1996.
- [26] KRUG, R.R., HUNTER, W.G. AND GRIEGER, R.A. Enthalpy-entropy compensation. 1- Some fundamental statistical problems associated with the analysis of van't Hoff and Arrhenius data. *J. Physical Chemistry*, 80, 2335-2341, 1976.
- [27] RIZVI, S.S.H. In M.A. Rao & S.S.H. Rizvi (Eds.), *Engineering properties of foods*. Academic Press, New York, 1995.
- [28] KAYMAK-ERTEKIN, F. AND GEDIK, A. Sorption isotherms and isosteric heat of sorption for grapes, apricots, apples and potatoes, *Lebensmittel-Wissenschaft und-Technologie*, 37, 429-438, 2004.
- [29] BASU, S., SHIVHARE, U.S. AND MUJUMDAR, A.S. Models for sorption isotherms for foods: a review. *Drying Technology*, 24, 917-930, 2006.
- [30] SIMAL, S., FEMENIA, A., CASTELL-PALOU, A. AND ROSSELLO, C. Water desorption thermodynamic properties of pineapple, *J. Food Engineering*, 80, 1293-1301, 2007.
- [31] TELIS-ROMERO, J., KOHAYAKAWA, M.N., SILVEIRA, V., Jr. and Pedro, M.A.M. Enthalpy-entropy compensation based on isotherms of mango, *Ciência e Tecnologia de Alimentos*, 25(2), 293-303, 2005.
- [32] LEWICKI, P. The applicability of the GAB model to food water sorption isotherms. *Int. J. Food Science and Technology*, 32, 553-557, 1997.
- [33] GARCÍA-PÉREZ, J.V., CÁRCEL, J.V., CLEMENTE, G. AND MULET, A. Water sorption isotherms for lemon peel at different temperatures and isosteric heats, *Lebensmittel-Wissenschaft und-Technologie*, 41, 18-25, 2008.
- [34] TSAMI, E., KROKIDA, M.K. AND DROUZAS, A.E. Effect of drying method on sorption characteristics of model fruit powders, *J. Food Engineering*, 39, 381-392, 1999.
- [35] DIOSADY, L.L., RIZVI, S.S.H., CAI, W. AND JAGDEO, D.J. Moisture sorption isotherms of canola meals and applications to packaging, *J. Food Science*, 61(1), 204-208, 1996.
- [36] SOBRAL, P.J.A., LEBERT, A. AND BIMBENET, J.J. Isothermes de désorption de la pomme de terre entre 40 et 70°C, *Science des Aliments*, 19(6), 711-720, 1999.
- [37] PÉREZ-ALONSO, C., BERISTAIN, C.I., LOBATO-CALLEROS, C., RODRIGUEZ-HUEZO, M.E. AND VERNON-CARTER, E.J. Thermodynamic analysis of the sorption isotherms of pure and blended carbohydrate polymers, *J. Food Engineering*, 77(4), 753-760, 2006.
- [38] MAZZA, G. AND LEMAGUER, M. Water sorption properties of yellow globe onion (*Allium cepa* L.), *Can. Inst. Food Science and Technology J.*, 11, 189-193, 1978.
- [39] WANG, N. AND BRENNAN, J.G. Moisture sorption isotherm characteristics of potatoes at four temperatures, *J. Food Engineering*, 14(4), 269-287, 1991.
- [40] KRUG, R.R., HUNTER, W.G. AND GRIEGER, R.A. Enthalpy-entropy compensation. 2-Separation of the chemical from the statistical effect, *Physical Chemistry*, 80, 2341-2351, 1976.
- [41] LEFFLER, J.E. The Enthalpy-entropy relationship and its implications for organic chemistry, *Organic Chemistry*, 20, 1202-1231, 1955.