Engenharia Agrícola

ISSN: 1809-4430 (on-line)

www.engenhariaagricola.org.br

Scientific Paper
Doi: http://dx.doi.org/10.1590/1809-4430-Eng.Agric.v42n2e20200141/2022

THERMODYNAMIC PROPERTIES OF THE WATER ADSORPTION PROCESS IN BARU FLOURS

Thiago A. Arruda-Silva[1*], Niédja M. C. Alves[2], Nahyara B. C. Galle[1], Silmara B. dos Santos[2], Evelise Andreatta[2]

[1*]Corresponding author: Federal University of Mato Grosso (UFMT), Postgraduate Program in Agricultural Engineering (PGEAgri)/ Rondonópolis - MT, Brazil. E-mail: thiagoaurelio_roo@hotmail.com | ORCID: https://orcid.org/0000-0001-8280-7454

KEYWORDS

Dipteryx alata Vogel, GAB model, differential enthalpy, differential entropy, isokinetic theory.

ABSTRACT

Baru almonds and their byproducts have gained popularity in the population diet because of their high nutritional values. Despite this, there is limited information on how to store their flours properly, particularly their whole and partially defatted flours. Thus, this study aimed to use the Guggenheim–Anderson–de Boer (GAB) model to determine the thermodynamic properties of enthalpy, entropy, and Gibbs's free energy variation, as well as the spreading pressure, all of which are inherent to the moisture adsorption process in baru flours. The oil content, ash content, moisture content, pH, and wettability of the baru flour samples were characterized. The adsorption isotherms were determined using the static gravimetric method at temperatures of 298.15, 303.15, and 308.15 K and adjusted to the GAB model. The differential enthalpy variation was positive and decreased as the moisture content in the flours increased, whereas the differential entropy variation exhibited an opposite trend. The isokinetic theory was validated, as the process was driven by entropy. The spreading pressure increased as water activity increased.

INTRODUCTION

Baru (*Dipteryx alata* Vogel) is a plant that grows in the Brazilian Savannah (Cerrado). It is arboreal and produces fruits that are 5 cm long. Each fruit has a single ellipsoid-shaped seed with high protein and lipid contents, making it very popular in the national market. Almonds are consumed roasted and are used in traditional Brazilian sweets, cakes, and liqueurs. They also have a high potential for oil extraction, which produces partially defatted flour as a byproduct (Resende & Franca, 2019).

Baru flours are a viable alternative for celiacs because of the possibility of substituting wheat flour in many recipes. Furthermore, their use has increased in the Brazilian diet, as they have been incorporated into school meal menus and have increased the income sources of agroextractive producers. Many studies have been conducted in recent years to evaluate the nutritional and sensory properties of baru products, particularly their flour (Pineli et al., 2015a; Pineli et al., 2015b; Siqueira et al., 2012; Guimarães et al., 2010; Cruz et al., 2011).

Although we have data on baru flour, there is limited information on its storage, processing, and drying, all of which are essential in the production chain of any product. Moisture adsorption isotherms and the thermodynamic properties of adsorbed water are important sources of information for postharvest technologies (Červenka et al., 2015).

Numerous mathematical models have been proposed in the literature to represent moisture adsorption curves or isotherms (Rodríguez-Bernal et al., 2015). Among these models, the model proposed by Guggenheim–Anderson–de Boer (GAB) has explained the hygroscopic behavior of many products (Ahmed et al., 2018; Alamri et al., 2018; Červenka et al., 2015; Rodríguez-Bernal et al., 2015; Yogendrarajah et al., 2015; Abebe & Ronda, 2015).

The thermodynamic properties of adsorbed water have been determined using the equilibrium water contents estimated by these models. These properties include differential enthalpy and entropy, Gibbs free energy variation (ΔG), and spreading pressure. These properties are

[1] Federal University of Mato Grosso (UFMT), Postgraduate Program in Agricultural Engineering (PGEAgri)/ Rondonópolis - MT, Brazil.
[2] Federal University of Mato Grosso (UFMT), Institute of Agricultural and Technological Sciences (ICAT)/ Rondonópolis - MT, Brazil.

Area Editor: Gizele Ingrid Gadotti
Received in: 9-1-2020
Accepted in: 8-27-2021

crucial for understanding food microstructure, drying processes, and physical phenomena on the food surface in order to determine the amount of energy required for removing water from foods and to recommend more suitable packaging for storage (Mahanti & Chakraborty, 2019; Paul & Das, 2019; Moussaoui et al., 2019; Santos & Martins, 2016).

Thus, based on the above, this study aimed to investigate the thermodynamic properties of moisture adsorption in whole baru flour (WBF) and partially defatted baru flour (PDBF). Furthermore, the GAB model was used to analyze the use of the estimated hygroscopic equilibrium moisture data in determining the enthalpy and differential entropy, enthalpy–entropy compensation theory, ΔG, and spreading pressure.

MATERIAL AND METHODS

Raw Material

Almonds were acquired from a native vegetation fragment of the Cerrado and processed in the Agricultural Products Postharvest Laboratory of the Federal University of Mato Grosso, Campus de Rondonópolis. During the processing, the almond integument was removed by heating for 2 min at 100°C and by friction between the grains. Afterward, it was crushed in a domestic blender at a speed of 19,000 rpm. The resulting material was manually homogenized in a domestic sieve (200 mm mesh) to produce the WBF.

Partial oil extraction was used to prepare PDBF. The oil was extracted chemically in an oil and grease extractor by immersion. For this experiment, 50 g of WBF was measured and immersed in hexane at 373.15 K for 1 h and 30 min.

Thereafter, the oil content, ash content, pH, wettability, and moisture content of the obtained flours were determined using the methodology established by Adolfo Lutz Institute (IAL, 2008), with four replications. The results were subjected to analysis of variance with a completely randomized design, as well as Tukey’s test at 5% significance, using the R software (R Core Team, 2019).

Moisture Adsorption Isotherms

The static gravimetric method was used to determine the WBF and PDBF moisture adsorption isotherms were determined at temperatures of 298.15, 303.15, and 308.15 K, with water activity ranging from 0.070 to 0.975. Hygroscopic equilibrium moisture (M_e) experimental data were adjusted to the GAB (Equation 1) models using the SigmaPlot 14.0 software, and the determination coefficient (R^2), relative mean error (P) (Equation 2), and estimated mean error (SE) (Equation 3) were considered satisfactory.

$$M_e = \frac{(X_m \cdot c \cdot k \cdot a_w)}{(1 - k \cdot a_w) \cdot (1 - k \cdot a_w + c \cdot k \cdot a_w)}, \tag{1}$$

Where:

a_w represents the water activity, dimensionless;

c and k are the adjustment parameters, dimensionless, and

X_m represents the moisture in the molecular monolayer, g g^{-1} dry basis.

$$P = \frac{100}{n} \sum_{i=1}^{n} \left(\frac{Me_{exp} - Me_{theo}}{Me_{exp}} \right), \tag{2}$$

$$SE = \sqrt{\frac{\sum_{i=1}^{n} (Me_{exp} - Me_{theo})^2}{GLR}}, \tag{3}$$

Where:

Me_{exp} is the experimental equilibrium moisture, % d.b.;

Me_{theo} is the predicted equilibrium moisture, % d.b.;

GLR is the degree of freedom of the model residue, and

n is the number of observed data.

Thermodynamic Properties

Differential enthalpy variation (ΔH) was determined using the derivative of the Clausius–Clapeyron equation (Equation 4) that was established by Rizvi (2005). A pure water system was in the calculations, with constant water content and constant vaporization heat of pure water and ΔH.

$$\frac{\partial \ln (a_w)}{\partial T} = \frac{\Delta H}{RT^2}, \tag{4}$$

Where:

T is the temperature, K;

ΔH is the differential enthalpy variation, J mol^{-1}, and

R is the universal gas constant, 8,314 J mol^{-1} K^{-1}.

Equation 5 is the integral solution of [eq. (4)], considering that the differential enthalpy is independent of the temperature:

$$\ln (a_w) = -\frac{\Delta H}{R}\frac{1}{T} + C, \tag{5}$$

where: C is a model constant. Although it is assumed that ΔH does not vary with temperature, the use of this equation necessitates the measurement of adsorption isotherms at more than two temperatures (Santos & Martins, 2016).

Thus, we used the obtained mathematical expressions to determine the a_w values by adjusting the moisture adsorption isotherms of WBF and PDBF to the GAB model. An ln (a_w) versus 1/T graph was constructed using the water activity values and the evaluated temperatures, and linear regression models were adjusted. The angular coefficient, which is equivalent to ΔH/R, was used to determine the enthalpy variation in the corresponding water activity since the universal gas constant is known. Thus, the ΔH versus M_e curve was constructed using the relationship between a_w and M_e.

Differential entropy (ΔS, J mol^{-1} K^{-1}) and enthalpy are linked by the Gibbs–Helmholtz equation (Equation 6) (Rivzi, 2005):

$$\Delta G = \Delta H - T\Delta S, \tag{6}$$

Where:

ΔG is the Gibbs free energy variation (J mol^{-1}), which can also be measured using the following equation:

$$\Delta G = - RT \ln (a_w). \tag{7}$$

The linear model can be written as follows by applying [eq. (7)] to [eq. (6)] and reordering its terms:

$$\ln(a_w) = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R}. \quad (8)$$

It can be seen from eqs (5) and (8) that the constant C is equal to $\Delta S/R$. Thus, the differential entropy is equivalent to the linear coefficient of the line equation in the $\ln(a_w)$ versus 1/T graph.

The data obtained from the enthalpy and differential entropy were fitted with a better equation to represent their change as a function of equilibrium moisture, taking R^2 and SE into account.

According to Santos & Martins (2016), the enthalpy–entropy compensation theory, or isokinetic theory, suggests a linear relationship between these properties (Equation 9), wherein the isokinetic temperature (T_B) and ΔG can be calculated (Fakhfakh et al., 2018) using a 95% security level for R^2.

$$\Delta H = \Delta G + T_B\,\Delta S. \quad (9)$$

Krug et al. (1976) confirmed the validity of the enthalpy–entropy compensation theory by comparing T_B to the harmonic mean of the studied temperatures (Equation 10).

$$T_{hm} = \frac{n}{\sum_{i=1}^{n}\frac{1}{T}}, \quad (10)$$

Where:

T_{hm} is the harmonic mean temperature, K;

n is the number of temperatures used in the study.

If T_B differs from T_{hm}, the compensation theory is validated for the process (Lago & Noreña, 2015). If $T_B > T_{hm}$, the process is driven by enthalpy; otherwise, if $T_B < T_{hm}$, adsorption is controlled by entropy (Símon et al., 2016).

The spreading pressure (φ, J m^{-2}) was calculated using [eq. (11)]:

$$\varphi = \frac{K_B \cdot T}{A_m}\int_0^{a_w}\frac{\theta}{a_w}\,\partial a_w, \quad (11)$$

Where:

K_B is the Stefan–Boltzmann constant, 1.38×10^{-23} J K^{-1};

A_m is the surface area of the water molecule, 1.06×10^{-19} m^2, and

θ is the ratio between the water and moisture contents in the molecular monolayer.

The expression below (Equation 12) was obtained by substituting the GAB model in a_w in [eq. (11)] and solving it, and it was used to determine the spreading pressure (φ) for WBF and PDBF.

$$\varphi = \frac{K_B \cdot T}{A_m} \cdot \ln\left[\frac{1 + c \cdot k \cdot a_w - k \cdot a_w}{1 - k \cdot a_w}\right], \quad (12)$$

Where:

C and k are the parameters estimated by the GAB model for each temperature condition and flour type.

RESULTS AND DISCUSSION

Flour Characterization

Seeds, grains, and almonds can have a wide range of properties based on the seasons and the climatic conditions to which the mother plants are exposed. Nevertheless, the ash content, oil content, pH, and moisture values are consistent with those available in the literature (Pineli et al., 2015a; Siqueira et al., 2015; Cruz et al., 2011), as shown in Table 1, which lists the characterization results of the analyzed properties of the respective flours.

TABLE 1. Values for the WBF and PDBF characterization properties.

Properties	WBF	PDBF
Ash content (%, w. b.)	3.04 ± 0.14 b	3.96 ± 0.02 a
Oil content (% d. b.)	45.60 ± 0.83 a	30.16 ± 0.23 b
Wettability (g s^{-1})	0.362 ± 0.074 a	0.021 ± 0.003 b
pH	6.53 ± 0.05 a	6.40 ± 0.02 b
Moisture (% d. b.)	4.09 ± 0.22 a	3.19 ± 0.25 b

Means followed by the same letters on the lines are not statistically different from each other based on Tukey's test at a 5% significance level.

According to the statistical analysis, all the analyzed properties of the WBF and PDBF differed significantly. The PDBF had a higher ash content than the WBF because of a decrease in the oil content, which increased the components that make up the ash content, such as proteins and minerals. The 0.9% variation in water levels can be explained by the different processes that the flours were subjected to. In terms of pH, the PDBF was slightly more acidic. Thus, the WBF had a higher wettability than the PDBF. There is still no information about this property for baru flours; however, the relatively high degree obtained for the integral can be explained by the relatively small amount of interaction sites with water in its content, which shortens the time it takes for complete wetting to be achieved and increases the magnitude of the variable.

Moisture Adsorption Isotherms

Figure 1 shows the curves that were adjusted from the hygroscopic equilibrium moisture experimental data found for WBF and PDBF at the temperatures evaluated in this study using the GAB model.

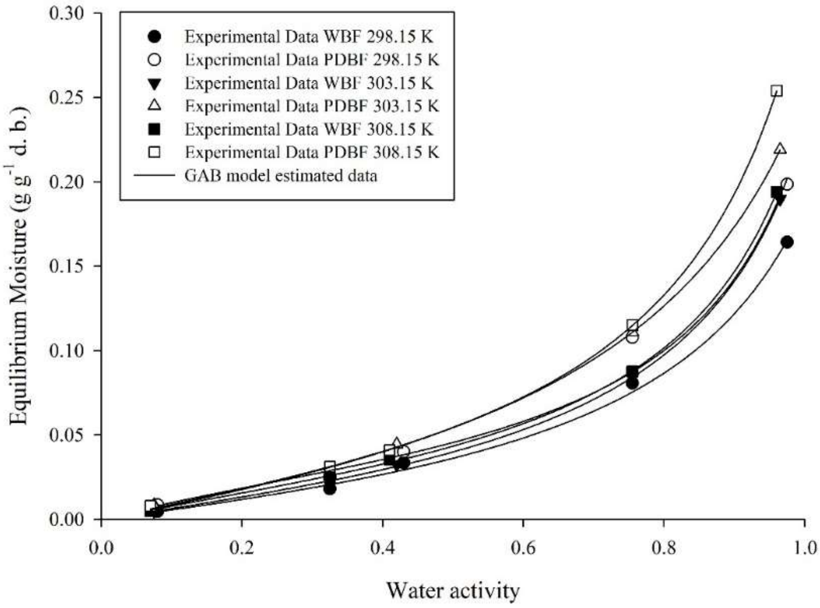

FIGURE 1. Moisture adsorption isotherms of the WBF and PDBF adjusted to the GAB model at different temperatures.

WBF had an equilibrium humidity range of 0.0047–0.1939 g g^{-1} on a dry basis, while PDBF had an equilibrium humidity range of 0.0079–0.2540 g g^{-1} on a dry basis. The hygroscopic equilibrium water content increased as the water activity of the products (WBF and PDBF) increased. It can also be observed that PDBF had a higher equilibrium humidity than WBF for the same water and temperature activity, which is explained by its lower oil content. Since fatty acids are hydrophobic substances, WBF is expected to interact less with water by balancing with the environment at a lower M_e than PDBF. Despite their differences, both isotherms can be classified as Type III or Flory–Huggins isotherms (Sing et al., 1985). This type of isotherms is characterized by low M_e values of up to 0.70 aw because the binding energy of the first adsorption layer is less than the energy between the water molecules (Al-Muhtaseb et al., 2002). This characteristic is common in hydrophobic foods such as flour. Pear seeds (Hassini et al., 2015), black peppercorns (Yogendrarajah et al., 2015), palmyra palm jaggery granules (Jagannadha et al., 2017), and dehydrated yacon bagasse (Lago & Noreña, 2015) are examples of products that exhibit this isotherm behavior.

The GAB model was well adjusted, with adequate R^2, SE, and P values. Table 2 shows the statistical criteria and the adjustment parameters.

TABLE 2. GAB model adjustment parameters based on the WBF and PDBF hygroscopic equilibrium data.

Temperature (K)	Parameters of the GAB model for WBF					
	X_m	C	K	R^2 (%)	SE	P (%)
298.15	0.0404	1.6815	0.8096	99.86	0.0028	1.6392
303.15	0.0401	1.8789	0.8412	99.99	0.0010	2.3010
308.15	0.0385	2.4713	0.8521	99.81	0.0039	9.0557
Temperature (K)	Parameters of the GAB model for PDBF					
	X_m	C	K	R^2 (%)	SE	P (%)
298.15	0.0358	3.6215	0.8571	99.98	0.0021	9.6785
303.15	0.0660	1.5906	0.7780	99.95	0.0027	7.6884
308.15	0.0540	1.9158	0.8444	99.79	0.0036	4.8236

The PDBF had a higher water content in the first layer than the WBF at the same temperature conditions. The C constant values were higher than the k constant values at all temperatures and for both flours. This fact may indicate that the energy required for single-layer adsorption is higher than that required for multilayer adsorption (Yogendrarajah et al., 2015).

The GAB model has been frequently used to describe the sorption phenomenon of various products in the literature, as well as different types of isotherms, and it is known for its high adjustability and versatility. The GAB model has been used to estimate the equilibrium moisture content of products such as yerba mate (Červenka et al., 2015), black peppercorns (Yogendrarajah et al., 2015), coffee fruits, green and pulped coffee (Goneli et al., 2013), prickly pear seeds (Hassini et al., 2015), potato flakes and sweet potato (Lago et al., 2013), wheat flour (Syamaladevi et al., 2016), and cassava bagasse (Polachini et al., 2016).

Thermodynamic Properties

Differential Enthalpy

Equation 4 was used to calculate the differential enthalpy of adsorption for WBF and PDBF, which is also known as liquid isosteric heat, using the equilibrium humidity estimated by the GAB model. Figure 2 shows ΔH as a function of the water content in the flours.

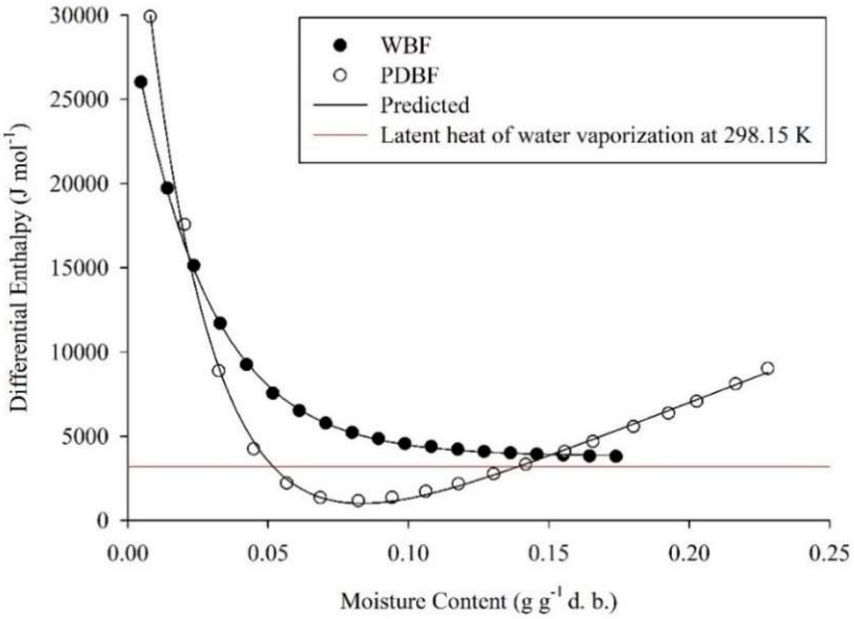

FIGURE 2. Differential enthalpy for the baru flours as a function of water content.

The differential enthalpy values for both flours were high with low water contents. This phenomenon could be explained by the saturation of active binding sites, which decreases the binding forces of water with the hydrophilic constituents of the product. Based on this finding, it can also be related to the fact that low water contents require more energy for their removal. Thus, differential enthalpy is an important factor to consider when managing drying processes. Positive ΔH values were also observed, indicating that water molecule adsorption in the flours was an endothermic process.

The WBF behaved as expected, remaining above the usual latent heat of water vaporization in agricultural products (Lago & Noreña, 2015, Goneli et al., 2013, Solomon & Zewdu, 2016). However, the PDBF produced an unexpected curve, with values below the latent heat of water vaporization and a rapid increase. This feature has been reported in recent studies, such as the study on swamp lily rhizomes (Ascheri et al., 2009), but further studies are required to verify the effect of lipid substances on this property. The effect of graded oil contents (measured by the Soxhlet test) on this property is another option.

Generally, the behavior of the differential enthalpy curve is a specific property for each product, with the assumption of the additional sigmoid, polynomial, or exponential aspects. Herein, exponential equations are proposed to predict the variation of the net isosteric heat of adsorption for WBF (Equation 13), which had R^2 and SE values of 99.98% and 0.0984, respectively, and for PDBF (Equation 14), which had R^2 and SE values of 99.87% and 0.2784, respectively.

$$\Delta H = [26{,}559.80 \cdot \exp(-36.96 \cdot M_e)] + 3{,}819.54, \quad (13)$$

$$\Delta H = [49{,}598.39 \cdot \exp(-41.45 \cdot M_e)] + (64{,}627.31 \cdot M_e) - 5{,}941.53. \quad (14)$$

Differential Entropy

The differential entropy for baru flour was calculated using [eq. (8)]. Figure 3 shows the ΔS as a function of the equilibrium moisture contents of WBF and PDBF.

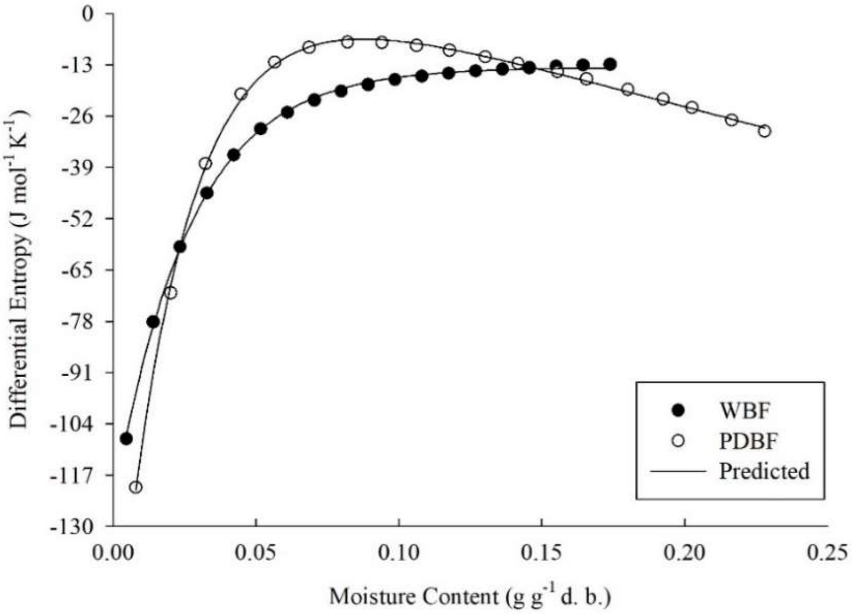

FIGURE 3. Differential entropy of the baru flours as a function of water content.

Both flours had negative ΔS values, and the higher the water content, the higher the differential entropy values. Iglesias et al. (1976) explained this behavior as being indicative of the existence of chemical adsorption or structural changes in the material. The restriction of the mobility of water molecules is another factor that supports the negative differential entropy values. In the thermodynamic system, entropy is related to the arrangement of water molecules, that is, their degree of order or disorder. As moisture content increases and sorption sites fill, multiple layers emerge, each with its own spatial arrangement that allows water molecules to move around freely (Benado & Rizvi, 1985). Some products, such as ground roasted coffee (Collazos-Escobar et al., 2019), manioc flour (Ayala-Aponte, 2016), powdered starch (Al-Muhtaseb et al, 2004), quince pulp, seeds, pulp loquat (Moreira et al., 2004), and mushroom powder (Pascual-Pineda et al, 2020), have been identified to exhibit this type of entropy behavior.

The WBF exhibited similar behavior to these products in that it stabilized near the zero scales for M_e. However, the PDBF tended to increase in entropy until an approximate humidity of 0.085 g g^{-1} (dry basis) and then decreased in ΔS values. Similar trends have been found in products such as jatropha seeds (Santos & Martins, 2016), millet grain flours (Sharma et al., 2017), and chia seeds (Velázques-Gutiérrez et al., 2015). The exponential models were fitted to the ΔS data. The R^2 and SE values obtained from [eq. (15)] for WBF were 99.96% and 0.5780, respectively, while those obtained from [eq. (16)] for PDBF were 99.92% and 0.8310, respectively.

$$\Delta S = [-111.6975 \cdot \exp(37.9082 \cdot M_e)] - 13.6366, \qquad (15)$$

$$\Delta S = [-180.4990 \cdot \exp(42.5063 \cdot M_e)] + (-192.5477 \cdot M_e) - 14.9254. \qquad (16)$$

Enthalpy–Entropy Compensation Theory

Figures 4a and 4b show the relationship between enthalpy and differential entropy using the enthalpy–entropy compensation theory.

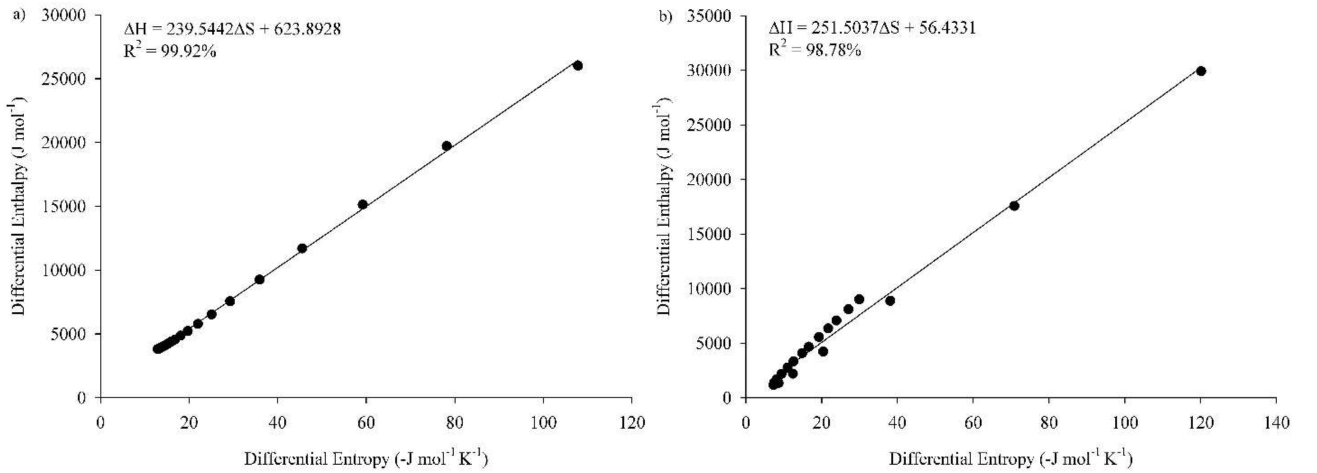

FIGURE 4. Relationship between differential enthalpy and differential entropy for the moisture adsorption process for (a) WBF and (b) PDBF.

The angular coefficient is equivalent to the isokinetic temperature in the equation of the lines observed in the ΔH versus ΔS graph, and the linear coefficient is equivalent to Gibbs free energy. Both flours had R^2 values above 95%, which was within the established safety limit. WBF had a T_B of 239.54 K, while PDBF had a T_B of 251.50 K. According to Equation 10, the harmonic mean of the studied temperatures was 303.10 K. The isokinetic theory could be applied to both WBF and PDBF since T_B differed from T_{hm}. Since the T_B for both flours was smaller than the T_{hm}, the adsorption process for baru flours is controlled by entropy. According to Velázques-Gutiérrez et al. (2015), the entropy adsorption process for chia seeds is justified by the fact that adoption occurs predominantly in micropores.

The enthalpy–entropy compensation theory is an important tool for investigating the sorption phenomenon. It can be used to evaluate the molecular interaction and the spatial organization of molecules (Velázques-Gutiérrez et al., 2015). This theory is studied using the ΔH versus ΔS graph. Generally, research on the compensation theory in sorption phenomena in food and agricultural products has discovered a linear relationship between enthalpy and entropy, which was also observed for the baru flours in this study (Velázques-Gutiérrez et al., 2015).

The ΔG is used as an indicator of product affinity for water, as well as an indicator of whether or not a water adsorption process is spontaneous, allowing for the quantification of useful or available energy in the process (Santos & Martins, 2016, Cladera-Oliveira et al., 2011). Negative ΔG values indicate that the process is spontaneous, while positive ΔG values indicate that it is not spontaneous. WBF and PDBF had ΔG values of 623.89 and 56.43 J mol^{-1}, respectively, implying that their adsorption processes did not occur spontaneously. Additionally, the adsorption process for stevia powder (Hidar et al., 2018), mate (Červenka et al., 2015), and jatropha flour (Cladera-Oliveira et al., 2011) is not spontaneous. The sharp decrease in the ΔG values of WBF and PDBF may be related to the decrease in oil content, making it possible to assume that the adsorption process for baru flour tends to be spontaneous at low lipid levels.

Spreading Pressure

Figure 5 shows the spreading pressure variation (φ) for WBF and PDBF.

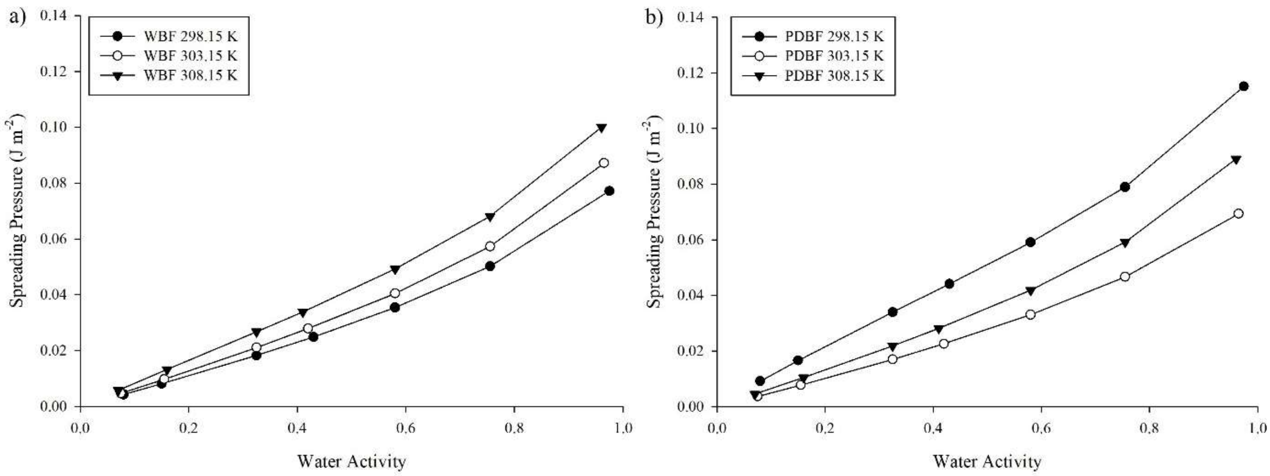

FIGURE 5. Spreading pressure as a function of water activity for (a) WBF and (b) PDBF.

Figure 5 shows the spreading pressure variation (φ) for WBF and PDBF. WBF had the highest φ values at relatively high temperatures and high water activities, whereas PDBF had the highest φ values at relatively high a_w contents and low temperatures.

Spreading pressure is a thermodynamic parameter that provides excess free energy on the adsorbent surface. It is used to estimate the increase in surface tension at available sorption sites as water molecules are adsorbed. This property can be used to determine the hydrostatic pressure required to avoid volume increase as relative humidity increases (Fasina et al., 1999; Willems, 2014).

Based on the spreading pressure data, it can be inferred that high magnitudes of φ indicate a high affinity of the water molecules with the adsorption sites of the adsorbent material in terms of a product's hygroscopicity (Torres et al., 2012). The hydrophobicity of lipid materials can be validated by comparing the two investigated flours. Therefore, the PDBF (with lower oil content) had higher spreading pressure values than the WBF (with higher oil content) at relatively low temperatures. In contrast to the results obtained for dehydrated yacon bagasse (a product with high carbohydrate content and a low oil content) (Lago & Noreña, 2015), the present results show that WBF and PDBF reached relatively high spreading pressure values.

CONCLUSIONS

Considering the statistical criteria used, the hygroscopic equilibrium moisture values calculated by the GAB model provided a satisfactory safety level in the determination of the thermodynamic properties of WBF and PDBF.

The differential enthalpy for WBF decreased as equilibrium humidity increased, whereas that for PDBF was lower than the latent heat of water vaporization. WBF and PDBF had negative differential entropy variations, which increased as humidity increased. The exponential models were well adjusted to the differential enthalpy and differential entropy data for WBF and PDBF.

The enthalpy–entropy compensation theory was validated linearly, indicating that the moisture adsorption process was controlled by entropy. WBF had a relatively high ΔG.

The spreading pressure for the WBF and PDBF tended to increase with water activity, but PDBF had higher values.

REFERENCES

Abebe W, Ronda F (2015) Flowability, moisture sorption and thermal properties of tef *[Eragrostis tef* (Zucc.) Trotter] grain flours. Journal of Cereal Science 63:14-20. DOI: https://doi.org/10.1016/j.jcs.2015.02.003

Ahmed MW, Aziz MG, Islam MN (2018) Modeling of moisture adsorption isotherm of selected commercial flours of Bangladesh. The Agriculturists 16:35-42. DOI: https://doi.org/10.3329/agric.v16i02.40341

Alamri MS, Mohamed AA, Hussain S, Ibraheem MA, Qasem AAA (2018) Determination of moisture sorption isotherm of crosslinked millet flour and oxirane using GAB and BET. Journal of Chemistry ID 2369762. DOI: https://doi.org/10.1155/2018/2369762

Al-Muhtaseb AH, McMinn WAM, Magee TRA (2004) Water sorption isotherms of starch powders. Part 2: thermodynamic characteristics. Journal of Food Engineering 62:135-142. DOI: https://doi.org/10.1016/S0260-8774(03)00202-4

Al-Muhtaseb AH, McMinn WAM, Magee TRA (2002) Moisture sorption isotherm characteristics of food products: a review. Food and Bioproducts Processing 80:118-128. DOI: https://doi.org/10.1205/09603080252938753

Ascheri DPR, Moura WS, Ascheri, JLR, Junior EAF (2009) Propriedades termodinâmicas de água do amido de rizomas do lírio-do-brejo (*Hedychium coronarium*). Ciência e Tecnologia de Alimentos 29:454-462. DOI: http://dx.doi.org/10.1590/S0101-20612009000200036

Ayala-Aponte AA (2016) Thermodynamic properties of moisture sorption in cassava flour. Dyna 83:139-145. DOI: http://dx.doi.org/10.15446/dyna.v83n197.51543

Benado AL, Rizvi SSH (1985) Thermodynamic properties of water on rice as calculated from reversible and irreversible isotherms. Journal of Food Science 50:101-105. DOI: https://doi.org/10.1111/j.1365-2621.1985.tb13286.x

Cladera-Oliveira F, Marczak LDF, Noreña CPZ, Pettermann AC (2011) Modeling water adsorption isotherms of pinhão (*Araucaria angustifolia* seeds) flour and thermodynamic analysis of the adsorption process. Journal of Food Process Engineering 34:826-843. DOI: https://doi.org/10.1111/j.1745-4530.2009.00437.x

Červenka L, Hloušková, L, Žabčíková S (2015) Moistre adsorption isotherms and thermodynamic properties of green and roasted Yerba mate (*Ilex paraguariensis*). Food Biosciense 12:122-127. DOI: https://doi.org/10.1016/j.fbio.2015.10.001

Collazos-Escobar GA, Gutiérrez-Guzmán N, Váquiro-Herrera HA (2019) Modeling dynamic adsorption isotherms and thermodynamic properties of specialty ground roasted-coffee. Coffee Science 14:93-103. DOI: http://dx.doi.org/10.25186/cs.v14i1

Cruz KS, Silva MA, Freitas O, Neves VA (2011) Partial characterization of proteins from baru (*Dipteryx alata* Vog) seeds. Journal of the Science of Food and Agriculture 91:2006-2012. DOI: https://doi.org/10.1002/jsfa.4410

Fakhfakh R, Mihoubi D, Kechaou N (2018) Moisture sorption isotherms and thermodynamic properties of bovine leather. Heat Mass Transfer 54:1163-1176. DOI: https://doi.org/10.1007/s00231-017-2223-0

Fasina OO, Ajibola OO, Tyler RT (1999) Thermodynamics of moisture sorption in winged bean seed and gari. Journal of Food Process Engineering 22:405-418. DOI: https://doi.org/10.1111/j.1745-4530.1999.tb00496.x

Goneli ALD, Corrêa PC, Oliveira GHH, Afonso Júnior PC (2013). Water sorption properties of coffee fruits, pulped and green coffee. Food Science and Technology 50:386-391. DOI: https://doi.org/10.1016/j.lwt.2012.09.006

Guimarães RCA, Favaro SP, Viana ACA, Braga Neto JA, Neves VA, Honer MR (2010) Study of the proteins in the defatted flour and protein concentrate of baru nuts (*Dipteryx alata* Vog). Ciência e Tecnologia de Alimentos 32:464-470. DOI: http://dx.doi.org/10.1590/S0101-20612012005000065

Hassini L, Bettaieb E, Desmorieux H, Torres SS, Toil A (2015) Desorption isotherms and thermodynamic properties of prickly pear seeds. Industrial Crops and Procucts 67:457-465. DOI: https://doi.org/10.1016/j.indcrop.2015.01.078

Hidar N, Ouhammou M, Idlimam A, Jaouad A, Bouchdoug M, Lamharrar A, Kouhila M, Mahrouz M (2018). Investigation of water adsorption and thermodynamic properties of stevia powder. Journal of Food Measurement and Characterization 12:2615-2625. DOI: https://doi.org/10.1016/j.indcrop.2015.01.078

IAL - Instituto Adolfo Lutz (2008) Métodos físico-químicos para análise de alimentos. São Paulo, IAL. 1020p.

Iglesias HA, Chirife J, Viollaz P (1976) Thermodynamics of water vapour sorption by sugar beet root. Journal of Food Technology 11:91-101. DOI: https://doi.org/10.1111/j.1365-2621.1976.tb00705.x

Jagannadha Rao PVK, Das M, Das SK (2017) Effect of anti-caking agents on moisture sorption isotherms of palmyra-palm jaggery granules. International Journal of Processing Post Harvest Technology 8:113-122. DOI: http://doi.org/10.15740/HAS/IJPPHT/8.2/113-122

Krug RR, Hunter WG, Grieger RA (1976) Enthalpy–entropy compensation. 1. Some fundamental statistical problems associated with the analysis of Van't Hoff and Arrhenius data. The Journal of Physical Chemistry 80:2335-2341 DOI: https://doi.org/10.1021/j100562a006

Lago CC, Noreña CPZ (2015) Thermodynamic analysis of sorption isotherms of dehydrated yacon (*Smallanthus sonchifolius*) bagasse. Food Bioscience 12:26-33. DOI: https://doi.org/10.1016/j.fbio.2015.07.001

Lago CC, Liendo-Cárdenas M, Noreña, CPZ (2013) Thermodynamic sorption properties of potato and sweet potato flakes. Food and Bioproducts Processing 91:389-395. DOI: https://doi.org/10.1016/j.fbp.2013.02.005

Mahanti NM, Chakraborty SK (2019) Thermodynamic properties of ready-to-puff pressure parboiled preconditioned brow rice. Journal of Food Measurement and Characterization 13:1469-1478. DOI: https://doi.org/10.1007/s11694-019-00062-2

Moreira R, Chenlo F, Torres MD, Vallejo N (2004) Thermodynamic analysis of experimental sorption isotherms of loquat and quince fruits. Journal of Food Engineering 88:514-521. DOI: https://doi.org/10.1016/j.jfoodeng.2008.03.011

Moussaoui H, Bahammou Y, Idlimam A, Lamharrar A, Abdenouri N (2019) Investigation of hygroscopic equilibrium and modeling sorption isotherms of the argan products: a comparative study of leaves, pulps, and fruits. Foods and Bioproducts Processing 114:12-22. DOI: https://doi.org/10.1016/j.fbp.2018.11.002

Pascual-Pineda LA, Hernández-Marañon A, Castillo-Morales M, Uzárraga-Salazar R, Rascón-Diaz MP, Flores-Andrade E (2020) Effect of wáter activiy on the stability of freeze-dried oyster mushroom (*Pleurotus ostreatus*) powder. Drying Technology 39(8). DOI: https://doi.org/10.1080/07373937.2020.1739064

Paul ID, Das M (2019) Moisture sorption isotherm and thermodynamic properties of Jamun (*Syzygium cumini* L.) Powder made from Jamun pulp and seed. International Journal of Food Studies 8:111-126. DOI: https://doi.org/10.7455/ijfs/8.1.2019.a10

Pineli LLO, Carvalho MV, Aguiar LA, Oliveira GT, Celestino SMC, Botelho RBA, Chiarello MD (2015 a) Use of baru (Brazilian almond) waste from physical extraction of oil to produce flour and cookies. Food Science and Technology 60:50-55. DOI: https://doi.org/10.1016/j.lwt.2014.09.035

Pineli LLO, Aguiar LA, Oliveira GT, Botelho RBA, Ibiapina MDFP, Lima HC, Costa AM (2015 b) Use of baru (Brazilian almond) waste from physical extraction of oil to produce gluten free cakes. Plants Foods for Human Nutrition 70:50-55. DOI: http://dx.doi.org/10.1007/s11130-014-0460-7

Polachini TC, Betiol LFL, Lopes-Filho JF, Telis-Romero J (2016) Water adsorption isotherms and thermodynamic properties of cassava bagasse. Thermochimica Acta 632:79-85. DOI: https://doi.org/10.1016/j.tca.2016.03.032

R Core Team (2019) R: a language and environment for statistical computing. Vienna, R Foundation for statistical Computing. Available: https://www.R-project.org/.

Resende LM, Franca AS (2019) Flours based on exotic fruits and their processing residues - features and potential applications to health and disease prevention. In: Preedy VR, Watson RR, Patel VB. Flour and breads and their fortification in health and disease prevention. London, Academic Press, p387-401. DOI: https://doi.org/10.1016/B978-0-12-814639-2.00030-7

Rizvi SSH (2005) Thermodynamics properties of foods in dehydration. In: Rao MA, Rizvi SSH, Datta AK. New York, CRC Press, p239-326.

Rodríguez-Bernal JM, Flores-Andrade E, Lizarazo-Morales C, Bonilla E, Pascual-Pineda LA, Gutierréz-López G, Quintanilla-Carvajal MX (2015) Moisture adsorption isotherms of the borojó fruit (*Borojoa patinoi*. Cuatrecasas) and gum Arabic powders. Food and Bioproducts Processing 94:187-198. DOI: https://doi.org/10.1016/j.fbp.2015.03.004

Santos SB, Martins MA (2016) Equilibrium moisture and thermodynamic properties on desorption process of Jatropha seeds. Journal of Chemical Engineering and Process Technology 7:e1000318. DOI: https://doi.org/10.4172/2157-7048.1000318

Sharma N, Goyal SK, Alam T, Fatma S, Niranjan K (2017) Effect of germination on the functional and moisture sorption properties of high-pressure-processed foxtail millet grain flour. Food and Bioprocess Technology 11:209-222. DOI: https://doi.org/10.1007/s11947-017-2007-z

Símon C, Esteban LG, Palacios P, Fernández FF, García-Iruela A (2016) Thermodynamic properties of the water sorption isotherms of wood of limba (*Terminalia superba* Engl. & Diels), obeche (*Triplochiton scleroxylon* K. Schum.), radiata pine (*Pinus radiata* D. Don) and chestnut (*Castanea sativa* Mill.). Industrial Crops and Products 94:122-131. DOI: https://doi.org/10.1016/j.indcrop.2016.08.008

Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquérol J, Siemieniewska T (1985) Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). Pure and Applied Chemistry 57:603-619.

Siqueira EMA, Marin AMF, Cunha MSB, Fustinoni AM, Sant'ana LP, Arruda SF (2012) Consumption of baru seeds [*Dipteryx alata* Vog.], a Brazilian savanna nut, prevents iron-induced oxidative stress in rats. Food Research International 45:427-433 DOI: https://doi.org/10.1016/j.foodres.2011.11.005

Siqueira APS, Pacheco MTB, Naves MMV (2015) Nutritional quality and bioactive compounds of partially deffated baru almond flour. Food Science and Technology 35:127-132. DOI: http://dx.doi.org/10.1590/1678-457X.6532

Solomon WK, Zewdu AD (2016) Thermodynamic properties of moisture adsorption in tef (*Eragrostis tef*) seed. Engineering in Agriculture. Environment and Food 9:339-345. DOI: http://dx.doi.org/10.1016/j.eaef.2016.05.001

Syamaladevi RM, Tadapaneni RK, Xu J, Villa-Rojas R, Tang J, Carter B, Sablani S, Marks B (2016) Water activity change at elevated temperatures and thermal resistance of *Salmonella* in all purpose wheat flour and peanut butter. Food Research International 81:163-170. DOI: https://doi.org/10.1016/j.foodres.2016.01.008

Torres MD, Moreira R, Chenlo F, Vázquez MJ (2012) Water adsorption isoterms of carboxymethyl cellulose, guar, locust bean, tragacanth and xanthan gums. Carbohydrate Polymers 89(2):592-598. DOI: https://doi.org/10.1016/j.carbpol.2012.03.055

Velázques-Gutiérrez SK, Figueira AC, Rodríguez-Huezo ME, Román-Guerrero A, Carrillo-Navas H, Pérez-Alonso C (2015) Sorption isotherms, thermodynamic properties and glass transition temperature of mucilage extracted from chia seeds (*Salvia hispanica* L.) Carbohydrate Polymers 121:411-419. DOI: https://doi.org/10.1016/j.carbpol.2014.11.068

Willems W (2014) Hydrostatic pressure and temperature dependence of wood moisture sorption isotherms. Wood Science and Technology 48:483-498. DOI: http://doi.org/10.1007/s00226-014-0616-5

Yogendrarajah P, Samapundo S, Devlieghere F, Saeger S, Meulenaer B (2015) Moisture sorption isotherms and thermodynamic properties of whole black peppercorns (*Piper nigrum* L.). Food Science and Technology, 64, 177-188. DOI: https://doi.org/10.1016/j.lwt.2015.05.045