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Moisture sorption isotherms of sunflower seeds: Thermodynamic analysis

Isotermas de sorção de água de sementes de girassol: Análise termodinâmica

Renata Cássia Campos[1*], Paulo César Correa[1], Iasmine Ramos Zaidan[2],
Úrsula Ramos Zaidan[1], Rildo Araújo Leite[3]

[1]Universidade Federal de Viçosa/UFV, Viçosa, MG, Brasil
[2]Universidade Federal do Espírito Santo/UFES, Alegre, ES, Brasil
[3]Instituto Federal do Norte de Minas Gerais/IFNMG, Arinos, MG, Brasil
*Corresponding author: camposrc16@gmail.com

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ABSTRACT

The study of the thermodynamic properties provides the knowledge of the sorbent affinity by the water and the spontaneity of the sorption process, important to design drying equipment and to predict hygroscopic behavior during storage. This work aimed to determine and evaluate isotherms of hygroscopic equilibrium and thermodynamic properties for different equilibrium conditions (water contents and temperatures) in sunflower seeds, using the indirect static method. Sunflower seeds with initial water content of 0.164 (decimal, dry basis - d.b.) were used. Fifteen mathematical models were tested for hygroscopic equilibrium modeling, and the Smith model presented the best fit. It was verified that the thermodynamic properties were influenced by the water content, the integral isosteric desorption heat increased with the decrease of the equilibrium water content, ranging from 1.787 to 2.670 kJ kg^{-1} to 0.198 to 0.0518 (decimal, d.b.), respectively, the desorption process of the sunflower seeds was controlled by the enthalpy and the Gibbs free energy, which varied from 3.6363 to 200.1730 kJ kg^{-1}, was positive for the temperatures studied, with increase to during the desorption process, proving to be a non-spontaneous process.

Index terms: Hygroscopic equilibrium; isosteric heat; enthalpy; entropy; Gibbs free energy.

RESUMO

O estudo das propriedades termodinâmicas proporciona o conhecimento da afinidade do sorvente pela água e da espontaneidade do processo de sorção, sendo importante para projetar equipamentos de secagem e predizer o comportamento higroscópico durante o armazenamento. Este trabalho visou a determinar e avaliar isotermas de equilíbrio higroscópico e propriedades termodinâmicas, para diferentes condições de equilíbrio (teores de água e temperaturas) em sementes de girassol, utilizando-se o método estático indireto. Foram utilizadas sementes de girassol com teor inicial de água de 0,164 (decimal, base seca - b.s). Foram testados quinze modelos matemáticos para modelagem de equilíbrio higroscópico, sendo que o modelo de Smith foi o que apresentou melhor ajuste. Verificou-se que as propriedades termodinâmicas foram influenciadas pelo teor de água, o calor isostérico integral de dessorção aumentou com o decréscimo do teor de água de equilíbrio, variando de 1,787 a 2,670 kJ kg^{-1} para 0,198 a 0,0518 (decimal, b.s.), respectivamente, o processo de dessorção das sementes de girassol foi controlado pela entalpia e a energia livre de Gibbs, que variou de 3,6363 a 200,1730 kJ kg^{-1}, foi positiva para as temperaturas estudadas, com aumento ao longo do processo de dessorção, demonstrando ser um processo não espontâneo.

Termos para indexação: Equilíbrio higroscópico; calor isostérico; entalpia; entropia; energia livre de Gibbs.

INTRODUCTION

The sunflower (*Helianthus annuus* L.) is an annual dicotyledonous that has high oil productivity, therefore, due to this characteristic is a plant with great potential for biodiesel production. In addition to presenting a positive scenario for the production of biofuel, the sunflower can be used for various functionalities such as ornamentation, grains in natura and/or bran (feed) for animal feed, forage and silage, replacing almonds like confectioner's sunflower (Lustri et al., 2017). The seeds have an oil yield between 48 and 52%. The oil has high content of unsaturated fatty acids, linoleic (63.71%), oleic (24.43%), palmitic (6.80%), stearic (2.96%) and linolenic (0.49%) (Grunvald et al., 2014; Lustri et al., 2017).

In order to minimize losses from mechanical damage and / or bird attack, sunflower seeds are harvested with a high water content. However, this high water content favors microbial development, loss of vegetative potential, increases respiratory rate, promoting heating, loss of quality and quantity of raw material and facilitates the development of free fatty acids facilitating the deterioration of seeds during storage. Oil seeds in general are vulnerable to the consequences of deterioration in the storage process because they have a high lipid content (Abreu et al., 2013).

A cereal or grain has a hygroscopic nature, so it can gain or lose water, depending on the humidity in the space where it is or the vapor pressure generated by the water content itself, phenomena known as water adsorption and desorption. The absorption of water by the seeds seriously compromises their storage potential, not only in terms of physical properties and modifications of the type discussed above, but especially in view of the possibility of biological activation, proliferation of microorganisms (fungi and bacteria), changes in stability biochemistry and changes in seed germination potential (Correa et al., 2014).

It is important to know the thermodynamic properties in drying processes and in the storage of agricultural products, to design drying equipment, to study the properties of the adsorbed water, to calculate the energy required in this process and to evaluate the microstructure of the food and the study of the physical phenomena that occur on the food surface. When studying the thermodynamic properties of a product, it is sought to solve problems related to stability issues and optimization of the conditions of industrial processes (Correa et al., 2017; Oliveira et al., 2013).

One such property is equilibrium moisture, which is the moisture content of a hygroscopic material after being exposed to an environment under controlled temperature and relative humidity conditions, for an extended period of time. In this way, by knowing the equilibrium moisture of the grains, it is possible to obtain conclusions regarding the potential stability of these products, from the conditions in which they are stored (Correa et al., 2014, 2017). Other thermodynamic properties that are used in the analysis of sorption behavior in biological systems are isosteric sorption, entropy and differential enthalpy heat and compensation theory, which are calculated from sorption isotherms (Bala, 2017).

The dependence of the equilibrium water content of a given product with relative humidity and equilibrium temperature can be expressed by mathematical equations, which are called sorption isotherms or hygroscopic equilibrium curves (Correa et al., 2014). The sorption isotherms that can be obtained by means of mathematical models and the other thermodynamic properties, have been studied by several researchers (Baptestini et al., 2017; Barbosa et al., 2016; Corrêa et al., 2017; da Silva et al., 2015; de Oliveira et al., 2017).

Considering the importance of the knowledge of the thermodynamic properties of sunflower seeds, it was proposed, in the present work, to determine the isotherms of hygroscopic equilibrium and to evaluate the other thermodynamic properties, for different levels of equilibrium water.

MATERIAL AND METHODS

The present work was developed in the Laboratory of Physical Properties and Quality of Agricultural Products belonging to the National Storage Training Center (CENTERINAR), located in the campus of the Federal University of Viçosa (UFV), Viçosa - Minas Gerais (MG).

Sunflower seeds, processed in bark, were obtained from the local market (Viçosa, Minas Gerais). The seeds had an initial water content of approximately 0.164 (decimal, d.b.). To obtain the hygroscopic equilibrium in different situations, 5 samples, 15g each, were placed in desiccators. Each desiccator had a saturated solution of the following products: lithium chloride, potassium acetate, magnesium chloride, magnesium carbonate, magnesium nitrate, sodium, potassium thiocyanate and zinc sulfate. They were kept in climatic chamber at different temperatures: 10, 25, 40, 55 °C. Relative humidities were established between 11% and 94%.

During desorption, the seed sample units were weighed periodically in order to monitor weight loss. When the weight did not vary within the 2% limit, between three consecutive weighings, the hygroscopic equilibrium was considered to have been reached, and the moisture content of the seeds was determined by the oven method at 105 ± 3 °C for 24 hours (Zenebon et al., 2008).

To the observed data of the hygroscopic equilibrium obtained for each condition of temperature and relative humidity, we adjusted the mathematical models commonly used for the description of sorption phenomena in agricultural products (Table 1).

Statistical analysis

The adjustment of the mathematical models was performed by non-linear regression using the Gauss-Newton method, applying Statistica 8.0® software. In the selection of the best model to predict the equilibrium water content of sunflower seeds, the following were considered: the magnitude of the coefficient of determination (R^2), the relative mean error (MRE), the standard deviation of the estimate waste (SDE). The MRE and SDE values for each mathematical model were calculated by Equations 1 and 2, respectively:

Table 1: Mathematical models for the representation of hygroscopic equilibrium curves.

Models	Equation	
Copace	$Xe = \exp[(a - b.T) + c.Aw]$	(1)
Sigma-copace	$Xe = \exp\{a - b.T + [c.\exp(Aw)]\}$	(2)
Sigma-copace II	$Xe = 1/(a.T.b + Aw.c)$	(3)
Copace 3	$Xe = \exp(a + b/T + c.Aw^3)$	(4)
Henderson modificado	$Xe = \{\log(1 - Aw)/[-a(T + b)]\}^{1/c}$	(5)
Chung-Pfoste	$Xe = a - b.\ln[(c - T).\ln(Aw)]$	(6)
COP	$Xe = \exp(a - b.T + c.Aw)$	(7)
Frend	$Xe = a.(Aw^{1/b})$	(8)
Oswin modificado	$Xe = (a + b.T).[Aw/(1 - Aw)]^{1/c}$	(9)
Scop	$Xe = \exp[a - b.T + c.\exp(Aw)]$	(10)
Smith	$Xe = a - b.T - c.\log(1 - Aw)$	(11)
Halsey	$Xe = \{\exp(a - b.T)/[-\log(Aw)]\}^{1/c}$	(12)
Halsey modificado	$Xe = \{\exp(a - bT)/[-\ln(Aw)]\}^{1/c}$	(13)
Harkins	$Xe = [\exp(a - b.T)]/[c - \log(Aw)]$	(14)
Iglesias	$Xe = (a + b.T).[Aw/(1 - Aw)] + c$	(15)

Xe: water content in equilibrium, decimal, d.b.; Aw: water activity, decimal; a, b and c: models' adjustment parameters; and T: temperature in °C.

$$MRE = \frac{100}{n}\sum_{i=1}^{n}\frac{\left|Y_i - \hat{Y}_i\right|}{Y_i} \tag{16}$$

$$SDE = \sqrt{\frac{\sum_{i=1}^{n}\left(Y_i - \hat{Y}_i\right)^2}{GLR}} \tag{17}$$

where:
Y_i: value observed experimentally, %, d.b.;
$\hat{Y}_i$: value estimated by the model, %, d.b.;
n = number of observed data; and
RDF = residual degrees of freedom (number of observed data minus the number of parameters of the model).

After the choice of the model was made, the isotherms were constructed for each temperature, to represent the desorption phenomenon of the sunflower seeds under the conditions studied. From the values determined by the chosen mathematical model, the other thermodynamic properties were determined.

The liquid isosteric heat of sorption (or differential enthalpy), for each equilibrium water content, was used the Clausius-Clayperon equation (Equation 18) (Iglesias; Chirife, 1976):

$$\frac{\partial \ln\left(A_w\right)}{\partial T} = \frac{\Delta h_{st}}{RT_a^2} \tag{18}$$

Where A_w = water activity (decimal), Ta = absolute temperature (K), Δhst = differential enthalpy (kJ kg^{-1}) and R = universal gas constant (8.314 kJ kmol^{-1} K^{-1} for gases and 0.4619 kJ kg^{-1} K^{-1} for water vapor).

Integrating Equation 18 and assuming that the isosteric liquid heat of sorption is independent of temperature, the equilibrium water content was obtained according to Equation 19 (Wang; Brennan, 1991):

$$\ln\left(A_w\right) = -\left(\frac{\Delta h_{st}}{R}\right).\frac{1}{T} + C \tag{19}$$

where C = coefficient of the model.

The integral isothermal heat (Qst) of sorption was obtained by the addition of the differential enthalpy and latent heat of vaporization of free water, according to Equation 20.

$$Q_{st} = \Delta h_{st} + L = a.\exp\left(-b.Xe^*\right) + L \tag{20}$$

Where Qst = integral isosteric heat of sorption (kJ kg^{-1}), L = latent heat of vaporization of free water (kJ kg^{-1}), and Δhst = differential enthalpy (kJ kg^{-1}), which can be estimated by mathematical model above, where Xe* = equilibrium water content (d.b.) and "a" and "b" = coefficients of the model.

At the equilibrium temperature (°C), the latent heat of vaporization of the free water (kJ kg^{-1}) was calculated using the mean temperature (T) in the range under study, with the aid of Equation 21:

$$L = 2502.2 - 2.39 \, . \, T \tag{21}$$

The differential entropy of sorption was calculated from the Gibbs-Helmholtz equation (Equation 22) (Rivizvi, 1995):

$$\Delta S = \frac{\Delta h_{st} - \Delta G}{T_a} \tag{22}$$

where ΔS = differential sorption entropy (kJ kg-1K^{-1}) and ΔG = free energy of Gibbs (kJ kg^{-1}).

For spontaneity analysis of the water gain and loss process between product and environment, as indicated by Oliveira et al. (2017), the Gibbs free energy calculation was applied. For the negative Gibbs free energy values, the process is spontaneous and, for positive values, it is not spontaneous, but when it is zero, the equilibrium has been reached in relation to the spontaneity of the process (Correa et al., 2010). According to Oliveira et al. (2013), the free energy of Gibbs can be estimated by means of Equation 23:

$$\Delta G = R \, . \, T \, . \, \mathrm{Ln}\left(A_w\right) \tag{23}$$

The effects of changes in sorption of water on free energy are usually accompanied by changes in enthalpy and entropy values. Thus, by substituting Equation 23 in 22, we have Equation 24:

$$\ln\left(A_w\right) = \frac{\Delta h_{st}}{R.T} - \frac{\Delta S}{R} \tag{24}$$

The calculated enthalpy values of sorption (Δhst) and entropy (ΔS) were correlated by Equation 25 (Beristain, Garcia and Azuara, 1996):

$$\Delta hst = TB \left(\Delta S\right) + \Delta GB \tag{25}$$

where TB = isokinetic temperature (K) and ΔGB = Gibbs free energy at isokinetic temperature (kJ kg^{-1}).

The isokinetic temperature represents the temperature at which all the series reactions occur at the same rate. Since enthalpy and entropy are highly correlated, it is assumed that the compensation theory may be valid for sorption (Beristain; Garcia; Azuara, 1996). In order to confirm the existence of the compensation, the isokinetic temperature was compared with the harmonic mean of the temperatures used to determine the sorption isotherms, according to Equation 26 (Krug; Hunter; Griger, 1976a, 1976b).

$$T_{hm} = \frac{n}{\sum\left(\frac{1}{T}\right)} \tag{26}$$

Where, T_{hm} = harmonic mean of the temperature (K) and n = number of temperatures used.

According Krug, Hunter and Grieger, (1976a, 1976b), linear chemical compensation or compensation theory only exists if the isokinetic temperature (TB) is different from the harmonic mean of the temperature (Thm). An approximate confidence interval (1-α, 100%) for the isokinetic temperature was calculated by Equations 27, 28 and 29.

$$T_B = \widehat{T_B} \pm t_{m-2,\alpha/2\sqrt{var(TB)}} \tag{27}$$

where

$$\widehat{T_B} = \frac{\sum\left(\Delta h_{st} - \overline{\Delta h_{st}}\right)\left(\Delta S - \overline{\Delta S}\right)}{\sum\left(\Delta S - \overline{\Delta S}\right)^2} \tag{28}$$

$$Var\left(T_B\right) = \frac{\sum\left(\Delta h_{st} - \overline{\Delta G_B} - \widehat{T_B}.\Delta S\right)^2}{\left(m-2\right)\sum\left(\Delta S - \overline{\Delta S}\right)^2} \tag{29}$$

where m = number of enthalpy and entropy data pairs, Δh_{st} = mean enthalpy (kJ kg^{-1}) and ΔS = mean entropy (kJ kg^{-1}).

If the harmonic mean temperature (T_{hm}) is within the range calculated for the isokinetic temperature (T_B), the relationship between the enthalpy values and differential sorption entropy reflects only experimental errors and not the existence of chemical and physical factors that react to compensation theory (Beristain; Garcia; Azuara, 1996). For TB, a 99% confidence interval was adopted for the entire observed data range.

RESULTS AND DISCUSSION

Table 2 shows the estimates of the parameters of the models adjusted to the data of water content in the hygroscopic balance of sunflower seeds for different temperature and relative humidity conditions, their respective coefficient of determination (R^2), estimated mean error (SDE), mean relative error (MRE) and trend of residuals.

Among the models used, Smith showed better adaptation to the experimental data. This was verified through the statistical analyzes studied. That is, MRE of 5,415% (less than 10%); SDE of 0.726; R^2 of 0.986 and random dispersion of residues. Several authors argue that a model fits well with the data if the relative mean error (MRE) value is less than 10% (Corrêa et al., 2014; Silva et al., 2015; Rosa; Moraes; Pinto, 2010). According to Kashaninejad et al. (2007), the values of the relative mean error indicate deviations of the observed values, in relation to the curve estimated by the model. It is observed that the mathematical models used to describe the hygroscopicity of sunflower seeds generally have a good fit with R^2 greater than 95%. It is important to emphasize that the coefficiente of determination cannot be used as an exclusive criterion for model evaluation, but as an auxiliary criterion (Kashaninejad et al., 2007).

Thus, the models that would best suit such conditions would be Copace, Sigma-Copace, COP, Scop, Chung-Pfoste and Smith. The last two presented the best statistical values that determined a good fit to the experimental data.

In order to ensure that the selected model is able to describe the phenomenon, it is indicated that the residue dispersion analysis is performed for the different models tested, because, according to Baptestini et al. (2015), even when the statistical parameters show good results, the model can be ineffective if it presents biased residue distribution. For Correa et al. (2014) the chosen model must present the residual values close to the horizontal range, around zero, and not form definite or geometric figures, not indicating bias of the results. If it exhibits biased distribution, presenting regions in which the model underestimates or overestimates the real condition, or tends to accumulate off-axis, the model is considered inadequate to represent the phenomenon under study. Thus, Chung-Pfoste model presented a bias in relation to the distribution of the residues, and therefore, it is verified that the Smith

Table 2: Estimates of the parameters of the hygroscopic equilibrium models of sunflower seeds, their respective coefficients of determination (R^2), estimated mean error (SDE), relative mean error (MRE) and residue trend, in the temperature range from 10 to 55 °C.

Models	Estimates of the parameters			Statistical parameters			
	a	b	c	R^2	MRE (%)	SDE	Residual distribution
Copace	1.062	0.007	0.020	0.975	10.500	0.977	Random
Sigma-copace	0.263	0.006	1.049	0.980	10.009	0.869	Random
Sigma-copace II	-0.311	-0.052	-0.238	0.924	17.139	1.675	Blased
Copace 3	1.470	1.285	1.579	0.953	15.666	1.331	Random
Henderson modified	0.019	607.383	0.012	0.883	76.294	2.053	Blased
Chung-Pfoste	20.887	3.696	36.269	0.980	9.760	0.874	Blased
COP	1.062	0.007	1.976	0.975	10.500	0.977	Random
Frend	14.816	0.909	-	0.898	33.875	1.924	Blased
Oswin modified	7.626	-0.032	3.069	0.971	11.352	1.055	Random
Scop	0.263	0.006	1.049	0.980	10.009	0.869	Random
Smith	4.627	0.056	4.889	0.986	5.415	0.726	Random
Sabbab	4.723	0.010	2.562	0.958	13.188	1.261	Blased
Halsey modified	4.723	0.010	2.562	0.958	13.188	1.261	Blased
Harkins	2.103	0.006	0.374	0.958	11.243	0.951	Random
Iglesias	0.514	0.014	5.075	0.958	24.490	2.155	Random

model was the one that best described the hygroscopicity of the sunflower seeds, presenting a better fit in the set of parameters analyzed. The Smith model presented R^2 value of 0.986, SDE of 0.726 and MRE of 5.415%.

The sorption isotherms, estimated by the Smith model, at temperatures of 10, 25, 40 and 55 °C are shown in Figure 1.

As can be seen in Figure 1, with the increase of water activity, there was an increase in water content, and the same effect was observed with increasing temperature. The generated Smith model is presented in Equation 30.

$$Xe = 4.627 - 0.056.T - 4.889.\ln\left(1 - a_w\right) \qquad (30)$$

According to Araújo, Corrêa and Silva (2001), the Smith model can also be used to describe the hygroscopic equilibrium curves of sweet corn seeds of the cultivars Supersweet and Sweet Cristal. Ramos, Mancini and Medeiros (2014) also found that this model was the one that best adjusted the balance isotherms of the *Jatropha*, with a determination coefficient equal to 98.23% and a mean relative deviation of 14.72%.

The water activity estimated by the Smith model (Equation 30), for the temperatures of 10 °C, 25 °C, 40 °C and 55 °C and for the equilibrium water contents from 5.18% to 19.80% (d.b.) is shown in Table 3.

As can be seen from Table 2, as temperature and water content increase, water activity increases. The water activity values (Table 2) were used to determine the values of the differential enthalpy and differential desorption entropy, as shown in Figure 2.

As can be seen from Figure 2, the slope of the straight lines increases as the equilibrium water content is reduced. This slope was used for isosteric heat calculations.

The isosteric heat values of sunflower seeds ranged from 1.787 to 2.670 kJ kg^{-1} for the water content range of 19.8 to 5.18% (d.b.) as shown in Figure 3.

As indicated in Figure 3, it was verified that, with the reduction in the water content, there was an increase in the energy required for the removal of water from the product, represented by the values of the integral isothermal desorption heat (Qst), as observed by Oliveira, Resende and Devilla (2017) and Teixeira, Andrade and Devilla (2018) studying corn and pumpkin seed respectively. The isosteric heat values of Jatropha seeds varied from 3.035 to 2.632 kJ kg^{-1} for the water content range of 13.6 to 6.4% (d.b.), respectively (Chaves et al., 2015).

For Brooker, Bakker- Arkema and Hall (1992), a higher amount of energy is required for the removal of water in products with low water content when compared to wet products. According to Al-Muhtaseb, McMinn and Magee (2004), this occurs because, in the initial sorption phase (lower water content), there are monomolecular layers that require high amounts of energy to remove these water molecules from the product.

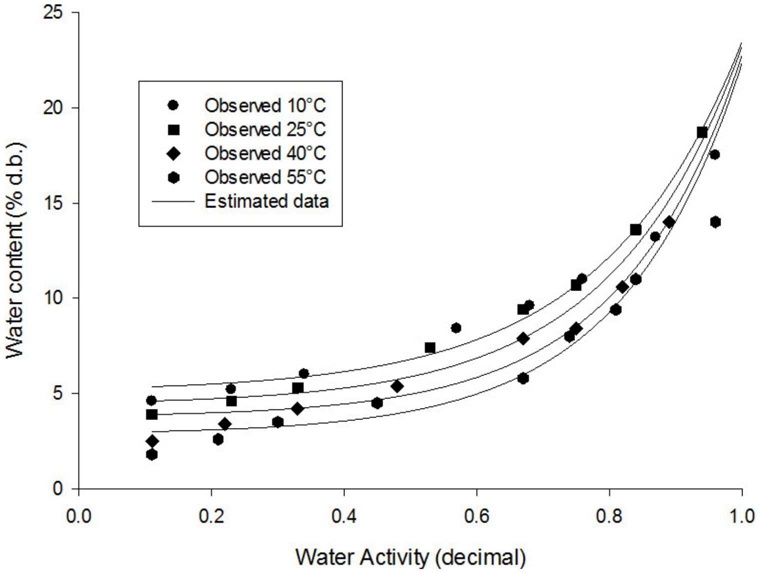

Figure 1: Observed and estimated values of the sorption isotherms, determined Smith model, for sunflower seeds at temperatures of 10, 25, 40 and 55 °C.

Table 3: Water activity values (decimal) estimated by the Smith model, as a function of temperature and equilibrium water content (Xe).

Xe (% d.b.)	Temperatures (ºC)			
	10	25	40	55
5.1805	0.2037	0.3294	0.4353	0.5244
5.5768	0.2657	0.3816	0.4792	0.5614
6.0968	0.3398	0.4440	0.5318	0.6057
6.9139	0.4414	0.5296	0.6038	0.6664
7.8001	0.5340	0.6076	0.6695	0.7217
8.1917	0.5699	0.6378	0.6950	0.7431
8.6430	0.6078	0.6697	0.7219	0.7658
9.1575	0.6470	0.7027	0.7496	0.7892
9.6564	0.6812	0.7315	0.7739	0.8096
10.4967	0.7316	0.7739	0.8096	0.8397
10.7636	0.7458	0.7860	0.8197	0.8482
11.0428	0.7599	0.7978	0.8297	0.8566
12.1824	0.8098	0.8399	0.8651	0.8864
13.1715	0.8447	0.8692	0.8898	0.9072
14.0404	0.8700	0.8905	0.9078	0.9223
16.9779	0.9287	0.9400	0.9494	0.9574
19.8032	0.9600	0.9663	0.9716	0.9761

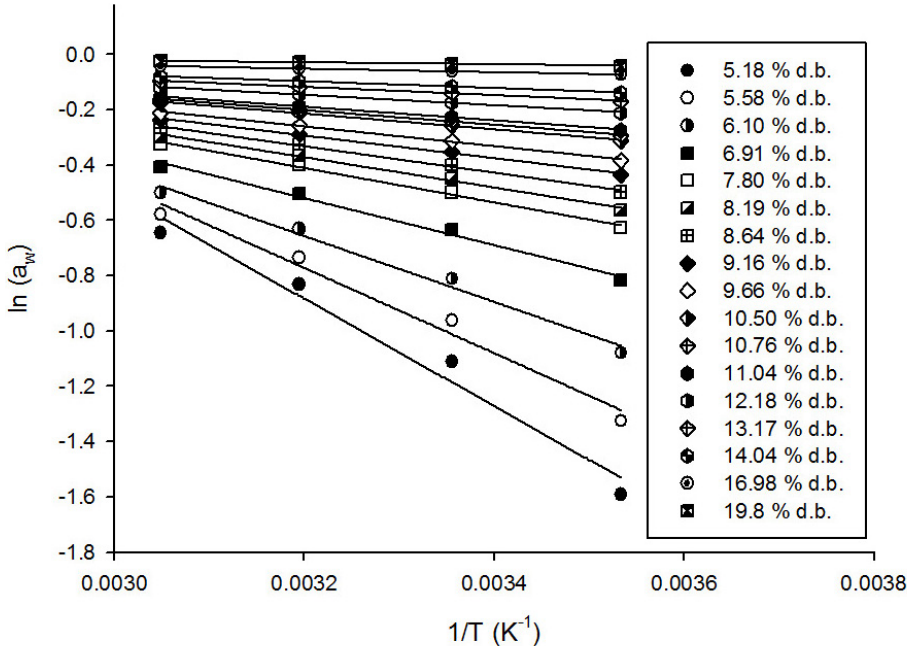

Figure 2: Curves of the neperian logarithm of water activity (decimal), for specific values of equilibrium water content (% d.b.), as a function of values of 1/T (K^{-1}), for sunflower seeds.

It was verified that the differential entropy is strongly related to the water content of the seeds, presenting values of 0.0373 to 2.4646 kJ kg^{-1} K^{-1} (Figure 4).

According to Figure 4, with the increase in water content, there was a decrease in the differential entropy. This behavior is related to the mobility of the water molecules present during the desorption process. With high water activity, there are fewer sites available for the bonds between molecules, implying a lower mobility demand for water molecules (Goneli et al., 2010). Similar behavior was observed by Teixeira, Andrade and Devilla (2018) and Silva et al. (2016) studying pumpkin and pepper seeds, respectively.

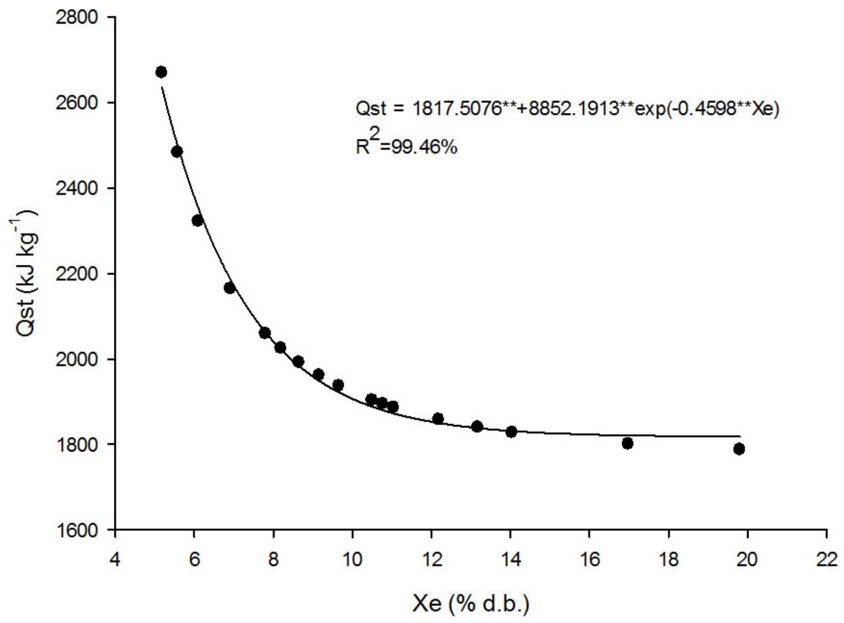

Figure 3: Isosteric heat values of sunflower seeds (**significant at 1%, by the t-test).

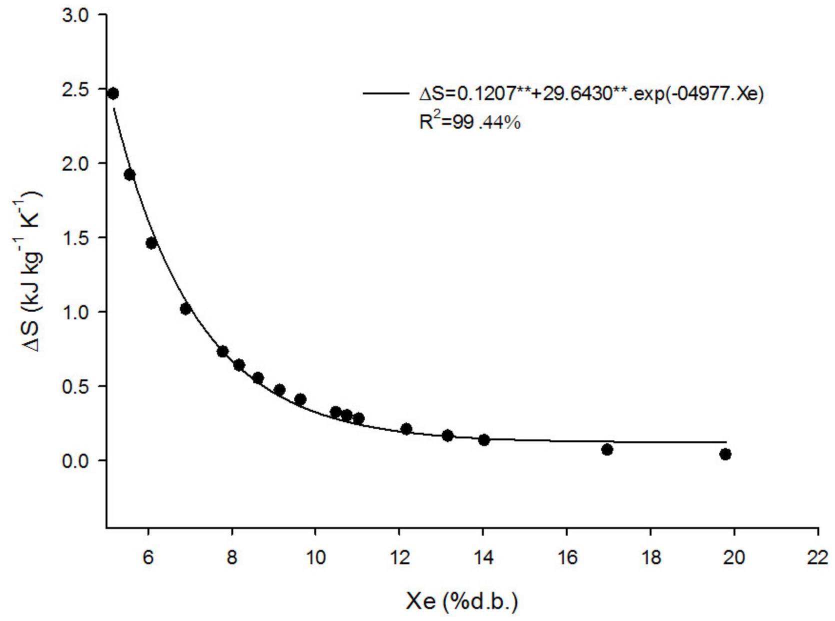

Figure 4: Differential entropy of sunflower seeds (**significant at 1%, by the t-test).

The enthalpy and entropy relationship for the sunflower seeds in the desorption process was adjusted according to a linear regression, with a high coefficient of determination (99.92%) (Figure 5).

With the linearity between the differential enthalpy ratio and the differential entropy of sorption, as showed at Figure 5, the isokinetic theory, or enthalpy-entropy compensation theory, can be considered valid for the phenomenon of water desorption.

To test the validity of the enthalpy-entropy compensation theory, the isokinetic temperature was compared to the harmonic mean (T_{hm}) of the temperature range studied, used to determine the desorption process in sunflower seeds. In the linear enthalpy-entropy compensation, it was found that, if $T_B > T_{hm}$, the process is controlled by enthalpy, otherwise ($T_B < T_{hm}$), the process is controlled by entropy (Ryde, 2014).

The isokinetic temperature for the desorption of sunflower seeds was 364.13 ± 15.11 K and the range of 349.02 K to 379.25 K. The calculated harmonic mean was 304.58 K, being significantly different of the described isokinetic temperature values, confirming the enthalpy-entropy compensation phenomenon, for the desorption process.

It was found that the harmonic mean was outside the isokinetic temperature range and was different from the isokinetic temperature. The isokinetic temperature was higher than the temperature of the harmonic mean, evidencing that the process is controlled by the enthalpy. These results are in agreement with what has been observed by several researchers, who have successfully applied the isokinetic theory on the sorption of various agricultural products (Oliveira; Resende; Devilla, 2017; Silva et al., 2016).

It was observed that the free energy of Gibbs increased with the decrease of the water content, being positive for all studied temperatures, tending to stabilize, at higher levels of equilibrium water content (Figure 6). This tendency was also observed by Oliveira et al. (2013) and Oliveira et al. (2014), studying corn and jatropha, respectively.

Nkolo Meze'e, Noah Ngamveng and Bardet (2008) report that Gibbs free energy is related to the work required to make sorption sites available. The free energy values of positive Gibbs are characteristic of an exogenous reaction, that is, one that requires an external agent supplying energy to the environment. These positive values were already expected, since desorption is a non-spontaneous process, as observed in the present work, for sunflower seeds.

It was found that the coefficient α decreased with increasing temperature, and that the coefficient β increased with increasing temperature as shoed at Figure 7. Both presented linear adjustment with high coefficient of determination, being possible to determine the free energy of Gibbs to any temperature, within the studied range.

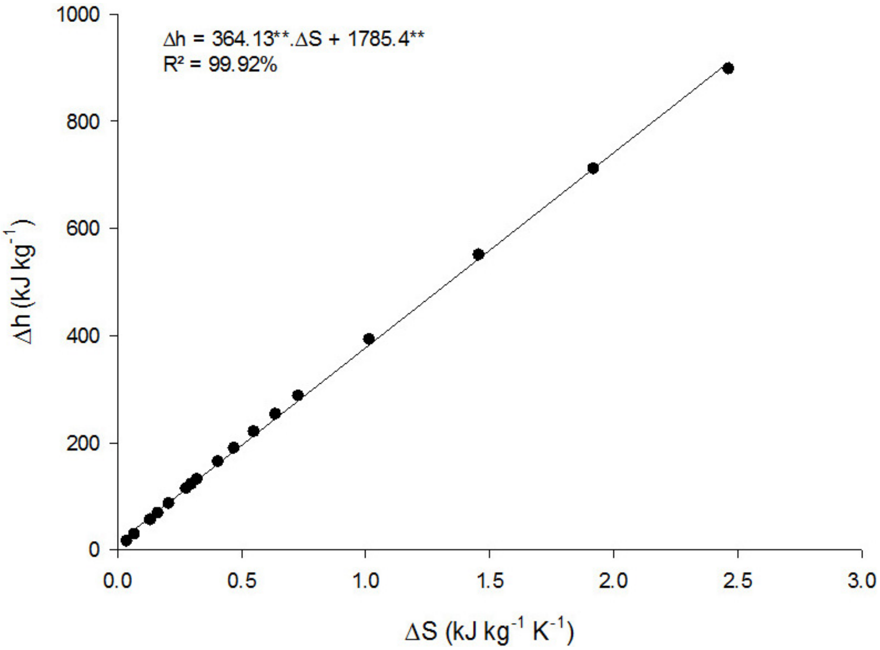

Figure 5: Desorption process, as a function of equilibrium water content, for sunflower seeds (**significant at 1%, by the t-test).

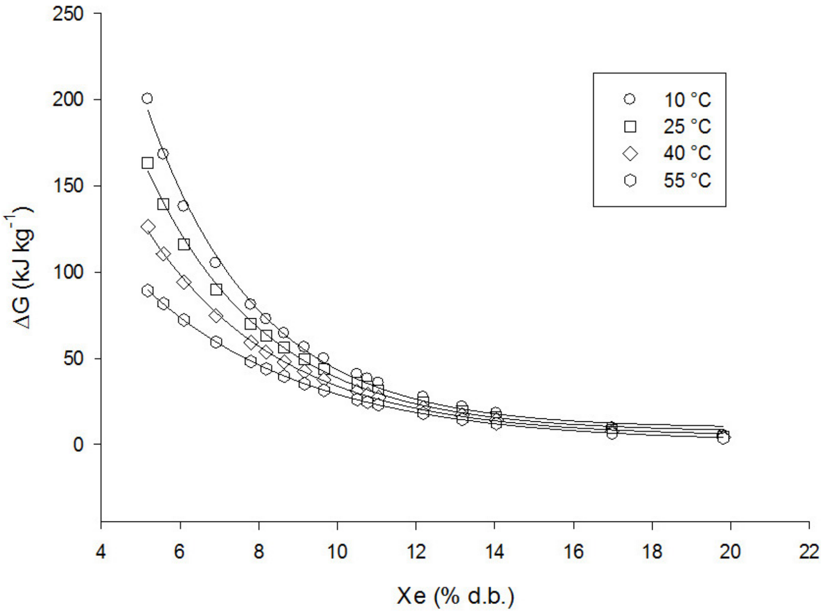

Figure 6: Gibbs free energy, depending on the water content of sunflower seeds.

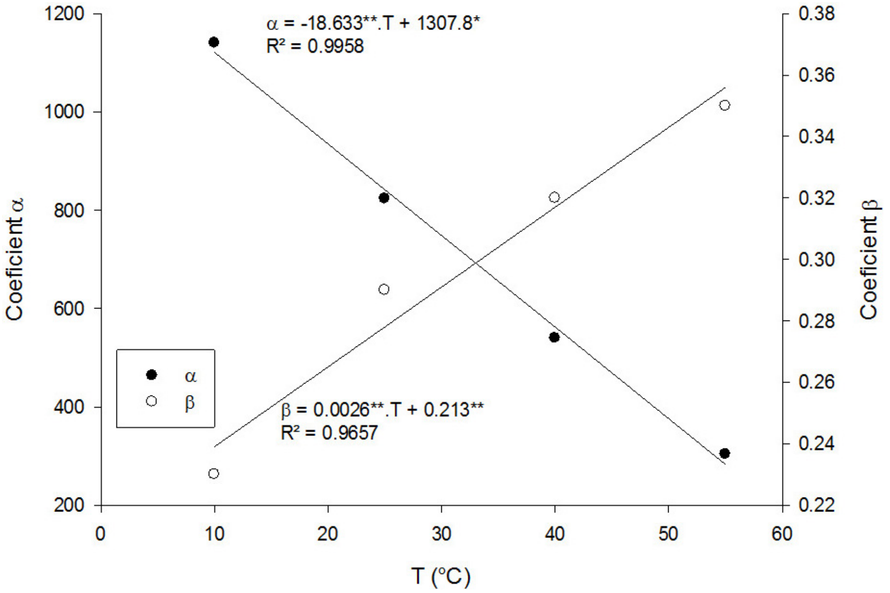

Figure 7: α and β coefficients of Gibbs free energy regression equation. ** and *: 1% and 5%, respectively, by the t-test.

CONCLUSIONS

Among the mathematical models applied to the experimental data, the one that presented the best fit was that of Smith. It was also verified that the thermodynamic properties were influenced by the water content of the seeds, increasing the energy needed to remove water from the product, as desorption occurred. Integral isosteric desorption heat was found to increase with decreasing water content, ranging from 1,787 to 2,670 kJ kg^{-1}, for the water content range of 19.8% to 5.18% (bs), increasing the energy required to remove water from the product. Differential entropy also increased with decreasing water content, ranging from 0.0373 to 2.4646 kJ kg^{-1} K^{-1}. Furthermore, it was found that the sunflower seeds desorption process was controlled by enthalpy, Gibbs free energy was positive for the studied temperatures and increased along the desorption process, proving to be a non-spontaneous process.

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