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Thermodymnamic properties of crambe fruits

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ABSTRACT. This study aimed to determine and evaluate the thermodynamic properties of crambe fruit at different equilibrium moisture contents. The dynamic-gravimetric method was used to collect experimental data. Crambe fruits with an initial moisture content of approximately 26% db (dry basis) were used. The thin-layer desorption of the product was conducted at different controlled temperatures (25, 30, 35, 40, and 45°C) and at water activity levels ranging from 0.10 to 0.89 until the product reached the equilibrium moisture content at the specified air condition. In conclusion, the thermodynamic properties of crambe fruit are affected by temperature and moisture content. The isokinetic theory is valid for the desorption process, which is controlled by enthalpy, and the Gibbs free energy is positive at all of the tested temperatures, which indicates that water desorption is not a spontaneous process.

Keywords: *Crambe abyssinica*, enthalpy, entropy, Gibbs free energy.

Propriedades termodinâmicas dos frutos de crambe

RESUMO. O objetivo no presente trabalho foi determinar e avaliar as propriedades termodinâmicas para diferentes teores de água de equilíbrio dos frutos de crambe. Para obter os dados experimentais utilizou-se o método dinâmico-gravimétrico. Foram utilizados frutos de crambe, com teor de água inicial de, aproximadamente, 26 % b.s. (base seca). A dessorção do produto em camada delgada foi realizada para diferentes condições controladas de temperatura (25, 30, 35, 40 e 45°C) e atividades de água entre 0,10 e 0,89, até que o produto atingisse seu teor de água de equilíbrio com a condição do ar especificada. Conclui-se que as propriedades termodinâmicas dos frutos de crambe são influenciadas pelas temperaturas e pelos teores de água. A teoria da isocinética é válida para o processo de dessorção, sendo este controlado pela entalpia. A energia livre de Gibbs é positiva para todas as temperaturas estudadas, indicando que a dessorção da água é um processo não espontâneo.

Palavras-chave: *Crambe abyssinica*, entalpia, entropia, energia livre de Gibbs.

Introduction

Nowadays concerns about climate change and sustainability along with the need for development and the increasing demand for energy resources have driven researchers to discover new fuel sources that can replace fossil fuels. Thus, the crop potential of crambe (*Crambe abyssinica*) fruit has been investigated in Brazil because of high concentrations of oil (44.10±1.46%) and proteins (21.3±1.86%), what make it an excellent alternative for biodiesel production (Souza, Fávaro, Ítavo, & Roscoe, 2009).

Following harvest, crambe fruit should bedried to reduce moisture content to suitable levels, and to enable preservation during storage. However, the existing relationship between the product and surrounding air must be understood to establish the best drying and storage conditions for agricultural products (Goneli, Corrêa, Oliveira, Gomes, & Botelho, 2010a; Corrêa, Botelho, Botelho, & Goneli, 2014), including crambe fruits.

The relationship between the product and the surrounding air may be best understood using sorption isotherms or hygroscopic equilibrium curves that depict the relationship between the hygroscopic equilibrium moisture content of a particular product and the relative humidity at a specific temperature (Resende, Corrêa, Goneli, & Ribeiro, 2006; Cladera-Olivera, Marczak, Noreña, & Pettermann, 2011).

Sorption isotherms are a valuable and widely used tool in preventing possible changes in food stability during storage, packaging development and the design and optimization of drying equipment (Cladera-Olivera, Pettermann, Noreña Wada, & Marczak, 2008).

In several agricultural product studies, researchers used sorption isotherms to determine certain thermodynamic properties to describe the water sorption of a material and the energy requirements involved in the drying processes (Kaya & Kahyaoglu, 2006; Corrêa, Oliveira, Botelho, Goneli, & Carvalho, 2010; Smaniotto, Resende, Oliveira, Sousa, & Campos, 2012; Oliveira, Resende, Campos, & Sousa, 2014a; Koua, Koffi, Gbaha, & Toure, 2014).

Additionally, thermodynamic properties are required and used in drying equipment projects; in the study of the adsorbed water properties; and in the evaluation of food microstructure and understanding of physical phenomena that occur on the surface of foods (Kaya & Kahyaoglu, 2006; Corrêa et al., 2010).

The latent heat of vaporization (Corrêa et al., 1998; Ojediran, Raji, & Owamah, 2013; Oliveira, Resende, Chaves, Sousa, & Smaniotto, 2014b), differential entropy and enthalpy (Rosa, Moraes, & Pinto, 2010; Cladera-Olivera et al., 2011), the theory of enthalpy-entropy compensation or isokinetic theory (Thys, Noreña, Marczak, Aires, & Cladera-Olivera, 2010; Oliveira et al., 2014a) and Gibbs free energy (Goneli et al., 2010a; Goneli, Corrêa, Oliveira, & Botelho, 2010b) are the most studied thermodynamic parameters. Thus, this study aimed to determine and analyze the thermodynamic properties of crambe fruit at different temperatures and equilibrium moisture contents.

Material and methods

This study was carried out at Postharvest Laboratory of Plant Products of the Instituto Federal de Educação, Ciência e Tecnologia Goiano - *Campus* Rio Verde, located in Rio Verde, Goiás State, Brazil. Crambe (*Crambe abyssinica*) fruit was harvested in experimental area of IF Goiano - Câmpus Rio Verde were used to perform the experiment executed in this study.

Crambe fruits with a moisture content of approximately 26 (% db) were hand-picked. The moisture contents were measured by gravimeter method using an oven at 105±3°C for 24 hours (Brasil, 2009).

The dynamic-gravimetric method was used to determine hygroscopic equilibrium moisture content of crambe fruits. A thin-layer desorption of the product was investigated at different controlled temperatures (25, 30, 35, 40, and 45°C) and water activity range from 0.10 to 0.89 until product reached equilibrium moisture content at a specific air conditions.

The environmental conditions required to perform hygroscopicity tests were achieved using an environmental chamber, which controls the temperature and relative humidity. Samples containing 10 g of product were wrapped in a permeable fabric (i.e., voile) to allow air circulation through the product; the samples were then placed inside of the device.

The Sigma Copace model, which showed the best experimental data fit, was used to calculate the thermodynamic properties of the crambe fruits (Costa, Resende, & Oliveira, 2015). Water activities were determined using the Equation 1:

$$\mathrm{Xe} = \mathrm{Exp}\left\{0.571297^{**} - \left(0.011807^{**} \cdot \mathrm{T}\right) + \left[0.967917^{**} \cdot \mathrm{Exp}\left(\mathrm{a_w}\right)\right]\right\} \quad (1)$$

where: $\mathrm{Xe}^{\star}$ = equilibrium moisture content, % db; $\mathrm{a_w}$ = water activity, decimal; and T = temperature, °C.

**Significant at 1% based on a Student's t-test.

Based on Clausius-Clapeyron, Othmer (1940) studies, it was established the Equation 2 to calculate partial vapor pressure contained in porous systems:

$$\mathrm{Ln}\left(\mathrm{Pv}\right) = \left(\frac{\mathrm{L}}{\mathrm{L'}}\right) \cdot \mathrm{Ln}\left(\mathrm{Pvs}\right) + \mathrm{C} \quad (2)$$

where: Pvs = Saturation vapor pressure of free water at a specific equilibrium temperature (°C); Pv = vapor pressure of free water at a specific equilibrium temperature (°C); L = latent heat of vaporization of the product water (kJ $\mathrm{kg^{-1}}$); L' = latent heat of vaporization of free water at the equilibrium temperature (kJ $\mathrm{kg^{-1}}$); and C = constant of integration.

Based on the sorption isotherms of crambe fruits, the value of the L/L' ratio of Equation 3 was assessed at different equilibrium moisture contents, Xe (decimal), which adjusted the equation to the enthalpy of vaporization of water, as reported by Rodrigues - Arias (Brooker, Bakker-Arkema, & Hall, 1992). This equation also includes an additional coefficient to improve the estimation of L/L' ratio (Corrêa, Christ, Martins, & Mantovani, 1998):

$$\frac{\mathrm{L}}{\mathrm{L'}} - 1 = \mathrm{a} \cdot \mathrm{Exp}\left(-\mathrm{b} \cdot \mathrm{Xe^m}\right) \quad (3)$$

where: a, b and m = estimated coefficients.

The latent heat of vaporization of free water (kJ $\mathrm{kg^{-1}}$) at the equilibrium temperature (°C) was calculated using the mean temperature (T) of the range tested in °C using the Equation 4:

$$\mathrm{L'} = 2502.2 - 2.39 \cdot \mathrm{T} \quad (4)$$

The saturation vapor pressure of free water, Pvs, was calculated using the Thétens equation 5 (Corrêa et al., 1998):

$$\mathrm{Pvs} = 0.61078 \cdot 10^{((7.5 \cdot T)/(273.3+T))} \tag{5}$$

The vapor pressure (Pv) was determined according to Equation 6:

$$\mathrm{Pv} = a_w \cdot \mathrm{Pvs} \tag{6}$$

The combination of Equations 3 and 4 results in the Equation 7, which is used to estimate the latent heat of vaporization of the product (Corrêa et al., 1998):

$$L = (2502.2 - 2.39 \cdot T) \cdot \left[1 + a \cdot \mathrm{Exp}\left(-b \cdot Xe^{m}\right)\right] \tag{7}$$

The differential sorption entropy was calculated using the Gibbs-Helmholtz equation 8 (Rizvi, 1995):

$$\Delta S = \frac{\Delta h_{st} - \Delta G}{T_a} \tag{8}$$

where: ΔS = differential sorption entropy (kJ kg^{-1} K^{-1}); Δh_{st} = differential enthalpy (kJ kg^{-1}); T_a = absolute temperature (K); and ΔG = Gibbs free energy (kJ kg^{-1}).

Gibbs free energy was assessed using the following Equation: 9

$$\Delta G = -R \cdot T_a \cdot \mathrm{Ln}(a_w) \tag{9}$$

where: R = universal gas constant, 8.314 kJ kmol^{-1} K^{-1}, which is 0.4619 kJ kg^{-1} K^{-1} for water vapor.

The effects of the changes in water sorption on Gibbs free energy are typically followed by changes in the values of the enthalpy and entropy. Thus, the following equation 10 results from substituting Equation 8 into Equation 9 and rearranging:

$$\mathrm{Ln}(aw) = \frac{\Delta h_{st}}{R \cdot T_a} - \frac{\Delta S}{R} \tag{10}$$

The differential sorption entropy (ΔS) and differential enthalpy (Δ_{hst}) were estimated using Equation 11 and were correlated using the Equation below (Beristain, Garcia, & Azuara, 1996):

$$\Delta h_{st} = T_B(\Delta S) + \Delta G_B \tag{11}$$

where: T_B = isokinetic temperature (K); and ΔG_B: Gibbs free energy at isokinetic temperature (kJ kg^{-1}).

The isokinetic temperature is the temperature at which reactions in series occur at the same rate. The theory of enthalpy-entropy compensation is presumed to be valid for sorption because enthalpy and entropy are highly correlated (Beristain et al., 1996). To confirm the existence of compensation, the isokinetic temperature was compared to the harmonic mean temperatures used to assess the sorption isotherms based on Equation 12 (Krug, Hunter, & Grieger, 1976):

$$T_{hm} = \frac{n}{\sum\left(\frac{1}{T}\right)} \tag{12}$$

where: T_{hm} = harmonic mean temperature (K); and n = number of temperatures used.

Based on Krug et al. (1976), linear chemical compensation or enthalpy-entropy compensation theory will occur if the isokinetic temperature (T_B) is different from the harmonic mean temperature (T_{hm}). An approximate confidence interval of (1-α) 100% was established for the isokinetic temperature using the following equations 13-15 :

$$T_B = \hat{T} \pm t_{m-2,\alpha/2\sqrt{\mathrm{Var}(T_B)}} \tag{13}$$

where:

$$\hat{T}_B = \frac{\sum\left(\Delta h_{st} - \overline{\Delta h}_{st}\right)\left(\Delta S - \overline{\Delta S}\right)}{\sum\left(\Delta S - \overline{\Delta S}\right)^2} \tag{14}$$

and:

$$\mathrm{Var}(T_B) = \frac{\sum\left(\Delta h_{st} - \overline{\Delta G}_B - \hat{T}_B \Delta S\right)^2}{(m-2)\sum\left(\Delta S - \overline{\Delta S}\right)^2} \tag{15}$$

where: m = number of data pairs of enthalpy and entropy; $\overline{\Delta h}_{st}$ = mean enthalpy, kJ kg^{-1}; $\overline{\Delta S}$ = mean entropy, kJ kg^{-1}.

If the harmonic mean temperature T_{hm} falls within the calculated range of the isokinetic temperature T_B, the ratio between the values of differential sorption entropy and enthalpy only describes the experimental errors and not the existence of chemical and physical factors that react based on the theory of compensation (Beristain et al., 1996). A 99% confidence interval was used for T_B in the experimental range.

Results and discussion

Table 1 shows the water activity data estimated using the Sigma Copace model (Equation 1) at 25, 30, 35, 40, and 45°C and at equilibrium moisture contents range from 3.9 to 10.9 (% db).

Table 1. Water activity values (decimal) estimated using the Sigma Copace model based on the temperature and equilibrium moisture content (Xe) of crambe (*Crambe abyssinica*) fruits.

Xe (% db)	Temperature (°C)				
	25	30	35	40	45
3.9	0.1036	0.1572	0.2080	0.2563	0.3025
4.0	0.1293	0.1815	0.2312	0.2784	0.3236
4.1	0.1661	0.2165	0.2644	0.3102	0.3539
4.3	0.1919	0.2410	0.2878	0.3326	0.3754
4.6	0.2628	0.3086	0.3524	0.3944	0.4347
4.8	0.2964	0.3407	0.3832	0.4239	0.4631
4.9	0.3037	0.3477	0.3899	0.4303	0.4692
5.5	0.3931	0.4335	0.4722	0.5096	0.5456
6.1	0.4626	0.5003	0.5366	0.5717	0.6055
6.2	0.4714	0.5088	0.5448	0.5795	0.6131
6.3	0.4745	0.5118	0.5477	0.5823	0.6158
7.0	0.5468	0.5815	0.6151	0.6475	0.6789
7.4	0.5775	0.6112	0.6438	0.6753	0.7059
7.7	0.6003	0.6332	0.6651	0.6960	0.7259
7.8	0.6026	0.6355	0.6673	0.6981	0.7280
8.0	0.6252	0.6573	0.6884	0.7186	0.7479
8.4	0.6473	0.6788	0.7092	0.7388	0.7675
9.7	0.7260	0.7551	0.7833	0.8108	0.8376
10.9	0.7789	0.8065	0.8333	0.8595	0.8850

When studying the thermodynamic properties of corn kernels and oil radish seeds, respectively, Oliveira, Resende, Smaniotto, Sousa, and Campos (2013) and Sousa, Resende, Goneli, Smaniotto, and Oliveira (2015) observed a decrease in equilibrium moisture content at the same water activity with temperature increase. Increases in water activity and temperature are related considering the same moisture content. These results are similar to those found for crambe fruit.

Table 2 outlines values of L/L' ratios for different moisture contents. Decreases in moisture content lead to increases in L/L' ratios of crambe fruits.

Table 2. L/L' ratios for different moisture contents of crambe (*Crambe abyssinica*) fruit.

Moisture content (% db)	L/L' ratio	Moisture content (% db)	L/L' ratio
3.9	1.9544	6.3	1.2353
4.0	1.8199	7.0	1.1954
4.1	1.6786	7.4	1.1812
4.3	1.6027	7.7	1.1716
4.6	1.4533	7.8	1.1707
4.8	1.4022	8.0	1.1619
4.9	1.3923	8.4	1.1538
5.5	1.2957	9.7	1.1292
6.1	1.243	10.9	1.1154
6.2	1.2373		

The L/L' ratio noticeably increases as the moisture content decreases, reaching values near 1.0 at high moisture contents. Corrêa et al. (1998) and Ojediran et al. (2013) assessed similar performances in their studies of popcorn seeds and cottonseeds, respectively.

Table 3 shows "a", "b" and "m" parameters used to estimate the ratio between the latent heat of vaporization of water in agricultural products and the latent heat of free water through non-linear regression.

Table 3. Parameters "a", "b" and "m" used to calculate the ratio between the latent heat of vaporization of water in agricultural products and the latent heat of free water (L/L').

A	B	m	R^2 (%)
0.102989**	-39.40607**	-2.13472**	99.87

**Significant at 1% based on Student's t-test.

The following Equation (16) to calculate the latent heat of vaporization of water for crambe fruit results from changing the values of "a", "b" and "m" in the equation proposed by Corrêa et al. (1998):

$$L = (2502.2 - 2.39 \cdot T) \cdot \left[1 + 0.102989 \cdot \exp\left(39.40607 \cdot Xe^{-2.13472}\right)\right] \quad (16)$$

Figure 1 shows the curves of the latent heat of vaporization of water of crambe fruits at 25, 30, 35, 40, and 45°C.

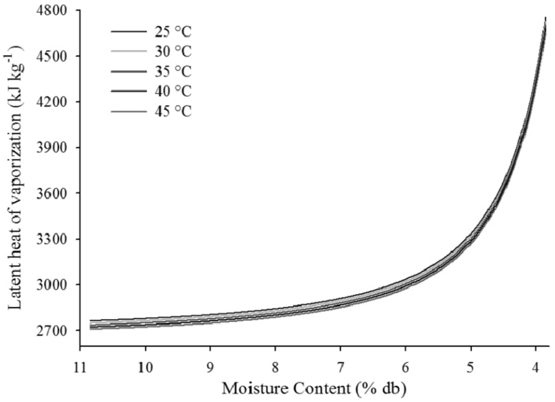


Figure 1. Experimental and estimated values of the latent heat of vaporization of water as a function of the equilibrium moisture content of crambe fruits (*Crambe abyssinica*).

The latent heat of vaporization is indirectly proportional to the moisture content of crambe fruits, and the increase in temperature at the same moisture content reduced the latent heat of vaporization.

Based on Wang and Brennan (1991), the latent heat of vaporization is indicative of the intermolecular forces of attraction between the water vapor adsorption sites of the product. Thus, the analysis of Figure 1 shows the existence of water molecules in a free state when crambe fruits have high moisture contents because the latent heat of vaporization of water in the product is near the latent heat of vaporization of pure water (2,418.55 kJ kg^{-1}).

The latent heat of vaporization of crambe fruits ranged from 4,733.47 to 2,708.87 kJ kg^{-1}, with moisture contents ranging from 3.9 to 10.9 (% db). Oliveira et al. (2014b) reported lower latent heats of vaporization, which ranged from 2,762.92 to 2,495.56 kJ kg^{-1}, for physic nut seeds, which had moisture contents ranging from 5.61 to 13.42 (% db). Smaniotto et al. (2012) observed that the latent heat of vaporization ranged from 2,775.87 to 2,468.14 kJ kg^{-1} in corn kernels with moisture contents ranging from 12.76 to 23.26 (% db). The most significant variation in the latent heat of vaporization of crambe fruit is related to the chemical composition and moisture content used. Brooker et al. (1992) emphasized that the latent heat of vaporization of a product is primarily affected by moisture content and temperature.

Figure 2 shows the values of differential desorption entropy (ΔS) and enthalpy (Δhst) as a function of the equilibrium moisture content (% db).

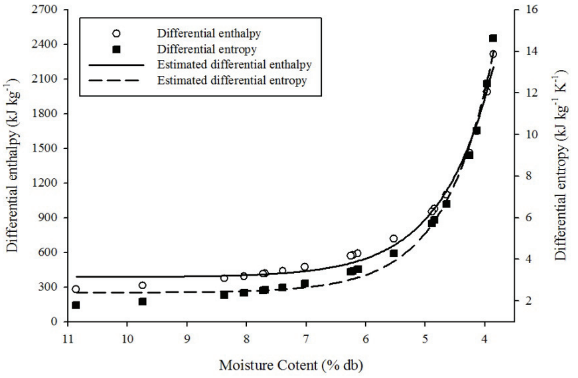


Figure 2. Experimental and estimated values of the differential sorption entropy and enthalpy of crambe (*Crambe abyssinica*) fruits.

The values of differential enthalpy and entropy noticeably increase as the moisture content of crambe fruits decreases (Figure 2), corroborating the results assessed using sesame seeds (Kaya & Kahyaoglu, 2006), okra seeds (Goneli et al., 2010b), Brazilian pine seeds (Cladera-Olivera et al., 2008; Thys et al., 2010), cocoa beans (Oliveira, Corrêa, Santos, Treto, & Diniz, 2011) and physic nut seeds (Oliveira et al., 2014b). Additionally, the differential enthalpy and entropy varied from 279.81 to 2,313.19 kJ kg^{-1} K^{-1} and from 1.7827 to 14.612 kJ kg^{-1} K^{-1}, respectively, as moisture content varied from 3.9 to 10.9 (% db). The high variations of differential enthalpy and entropy are related to the analysis of the equilibrium moisture content range and are also functions of the chemical composition of the crambe fruits.

Additionally, Figure 2 shows that the differential enthalpy and entropy showed similar trends in relation to the moisture content, and the magnitudes also showed a tendency to stabilize at high moisture contents. Tunç and Duman (2007), Thys et al. (2010) and Oliveira et al. (2014b) reported the same behavior in cottonseeds (*Gossypium hirsutum* L.), Brazilian pine (*Araucaria angustifólia*) and physic nut seeds (*Jatopha curvas* L.), respectively.

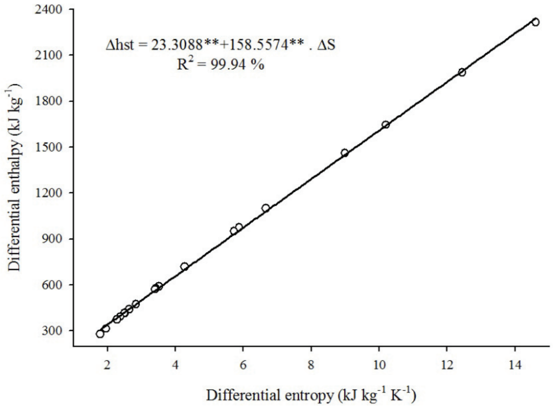
Table 4 shows the equations used to assess the differential enthalpy and entropy and the coefficients of determination of crambe fruits. All equation parameters were significant at the 1% significance level based on Student's t-test and showed high coefficients of determination (R^2 > 99%), highlighting the suitability of the equations to represent the experimental data.

Table 4. Equations and coefficients of determination of differential desorption entropy (ΔS) and enthalpy (Δhst) of crambe (*Crambe abyssinica*) fruit.

Thermodynamic Properties	Equations	R^2 (%)
Differential enthalpy	$\Delta hst = 386.6590^{\star\star} + 144724.4935^{\star\star} . \exp(-1.1345^{\star\star} . Xe)$	99.09
Differential entropy	$\Delta S = 2.4014^{\star\star} + 1300.8145^{\star\star} . \exp(-1.2243^{\star\star} . Xe)$	99.16

★★Significant at 1% based on a t test.

Figure 3 shows that the curve representing the relationship between enthalpy and entropy regarding the desorption process, which were assessed using Equation 11 for each moisture content, was linear, considering that the differential enthalpy and entropy are invariable with temperature at a specific moisture content.



★★Significant at 1% based on a t test.

Figure 3. Relationship between enthalpy and entropy regarding the water desorption process of crambe (*Crambe abyssinica*) fruits.

This relationship may be represented by a linear equation, which showed a high coefficient of determination (99.94%). Thus, the theory of enthalpy-entropy compensation or isokinetic theory is valid to describe the water sorption phenomena of crambe fruits because a high degree of linearity exists between the values of enthalpy and entropy. Goneli et al. (2010a) and Oliveira et al. (2013) observed the same behavior when studying the thermodynamic properties of millet and corn kernels, respectively.

The isokinetic temperature was compared with the harmonic mean (T_{hm}) of the studied temperature range used to determine the desorption process of crambe fruits towards testing the validity of the theory of enthalpy-entropy compensation. As reported by Telis-Romero, Kohayakawa, Silveira Júnior, Pedro, and Gabas (2005), linear enthalpy-entropy compensation is typically observed when $T_B \neq T_{hm}$. This process is controlled by enthalpy if $T_B > T_{hm}$; otherwise, the process is controlled by entropy (Telis-Romero et al., 2005).

The isokinetic temperature, which is the regression slope of the relationship between the enthalpy and entropy regarding the desorption process of crambe fruits, was 343.27 ± 5.11 K, and the isokinetic temperature ranged from 336.54 to 350.00 K. Conversely, the calculated harmonic mean temperature was 306.68 K, which is significantly different and higher than values of the reported isokinetic temperature, confirming the enthalpy-entropy compensation phenomenon regarding the desorption process of crambe fruits and that the process is controlled by enthalpy. Similar behaviors were observed in other agricultural products (Telis-Romero et al., 2005; Tunç & Duman, 2007; Goneli et al., 2010a; Oliveira et al., 2014a).

Figure 4 shows experimental and estimated values of Gibbs free energy as a function of the moisture content at each temperature during the desorption process of crambe fruits.

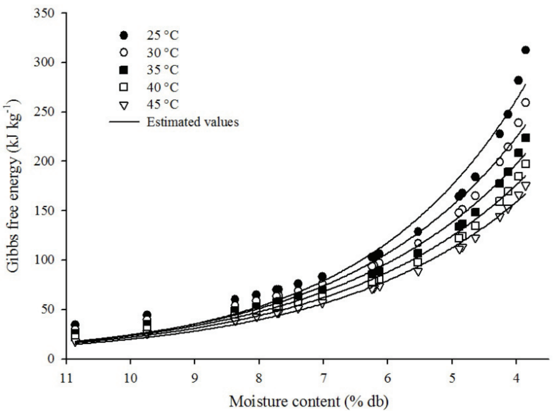


Figure 4. Gibbs free energy as a function of the moisture content (Xe) and temperature (T) of crambe fruits (*Crambe abyssinica*).

Changes in Gibbs free energy are related to the amounts of energy required to transfer water molecules from a solid state to a vapor state (Corrêa et al., 2010). Thus, the Gibbs free energy significantly increases with moisture content decreases and tends to stabilize at high levels of equilibrium moisture content and as temperature increases. Additionally, Gibbs free energy was noticeably positive at all tested temperatures, thus indicating that water desorption is a non-spontaneous process (Oliveira et al., 2013). These results corroborate the findings of Goneli et al. (2010b), Oliveira et al. (2011) and Goneli et al. (2013) in their studies of okra seeds, coconuts and coffee cherries, respectively.

Figure 5 shows that the parameters α and β of Gibbs free energy decrease as temperature increases, and both equations showed high coefficients of determination and the coefficients were significance.

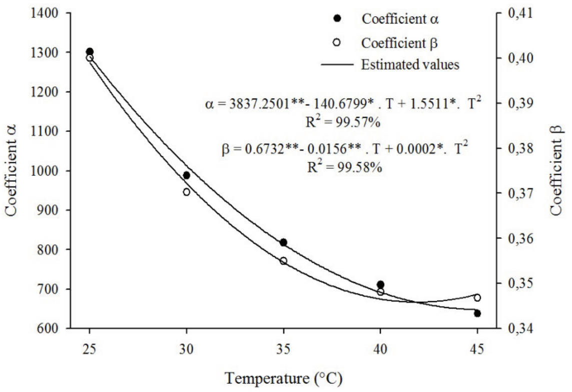


Figure 5. Coefficients α and β of the regression equation of Gibbs free energy for crambe (*Crambe abyssinica*) fruits.

Thus, Equation 17, which may be used to calculate the Gibbs free energy of crambe fruits in the studied temperature range, is created by substituting the equations of parameters α and β (Figure 5) into Equation 9:

$$\Delta G = \left(3837.2501 - 140.6799 \cdot T + 1.5511 \cdot T^2\right) \\ \mathrm{Exp}\left[\left(0.6732 - 0.0156 \cdot T + 0.0002 \cdot T^2\right) \cdot Xe \star\right] \qquad (17)$$

Conclusion

The thermodynamic properties of crambe fruits are affected by equilibrium moisture content and temperature.

The isokinetic theory is valid for the desorption process, which is controlled by enthalpy.

Gibbs free energy is positive at all studied temperatures, indicating that water desorption is not a spontaneous process.

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