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Equilibrium Moisture and Thermodynamic Properties on Desorption Process of Jatropha Seeds

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Abstract

The equilibrium moisture content of Jatropha oilseeds was determined by the static method for different conditions of temperature and relative humidity. A diversity of mathematical models were fitted to the experimental data. The model that best fitted the data was used to calculate the thermodynamic properties enthalpy and entropy change, integral isosteric heat and the Gibbs free energy change in the desorption process. These properties were used to discuss the theory application of enthalpy-entropy compensation. The modified Henderson's model was considered adequate to represent and estimate the equilibrium moisture in the desorption process of Jatropha oilseeds. Equilibrium moisture content of Jatropha oilseeds is directly proportional to the relative humidity. Enthalpy and entropy changes were found to be positive, indicating that the desorption of Jatropha oilseeds is an endothermic and irreversible process. A negative change of free energy was obtained, indicating the spontaneous nature of the desorption process in Jatropha oilseeds for conditions evaluated.

Keywords: Water activity; Sorption; Moisture content

Introduction

Jatropha oilseed (*Jatropha curcas* L.) has been noted for its potential in oil production and the possibility of being used as a source of raw material for the production of biodiesel. Many studies have been conducted with the aim of taming the culture and encourage increased production of this oilseed. However, research related to jatropha grains post-harvest are still incipient. Jatropha grains and the oil contained in them during storage are constantly exposed to suffer changes in their physical, chemical and microbiological properties, which could be due to factors such as the presence of micro-organisms, insects, enzyme activity and respiratory activity of the grain itself [1]. The speed at which these changes occur is mainly determined by the water activity (Aw) in the product, ie, the grain water content in equilibrium with the relative humidity and ambient air temperature. The reduction of the water activity by drying operations is a widely used method which helps to reduce the growth of micro-organisms, enzyme activity and the respiratory rate of the grains and hence to delay these changes and loss of quality. The relationship of a given product water content and relative humidity at a particular temperature can be expressed by mathematical equations that are known as hygroscopic equilibrium curves or isotherms [2]. According to Hall [3], the hygroscopic equilibrium curves are useful for defining the product dehydration limits, estimate the changes of water under certain conditions of temperature level and ambient relative humidity and to set the water content suitable to beginning microorganism activity. Jamali et al. [4] added that these curves are useful for the development and optimization of processes and for the modeling and simulation of the drying process. In addition, through the hygroscopic equilibrium isotherms, you can determine the thermodynamic properties of water sorption, such as differential enthalpy (ΔH), differential entropy (ΔS), and variation of Gibbs free energy (ΔG), fundamental in the analysis energy demand and prediction of kinetic parameters in drying processes [5-7]. According Mulet et al. [8], to study the thermodynamic properties is sought to solve problems related to product stability to storage issues, design of equipment for drying and storage and optimization of these processes. The determination of these properties can be made by means of the sorption isotherms, by using equations such as the Clausius-Clapeyron and Gibbs-Helmholtz [9,10]. The enthalpy differential sorption is considered indicative of intermolecular forces of attraction between the water vapor and the solid sorbent-material [11]. It is an important property to design dryers capable of supplying an amount of heat greater than the water vaporization enthalpy (L) to dry the material until low water content [12].

According to Wang and Brennan [13], to remove moisture associated with a hygroscopic material, the energy required is greater than that used to vaporize the same amount of free water under the same conditions of pressure and temperature, by virtue of the bonding forces between water and the surface of the adsorbent substance. This additional energy corresponds to desorption differential enthalpy (ΔH) also called isosteric net desorption heat.

The total isosteric heat (Qst) is therefore the sum of the energy needed for desorption of chemically bounded water to the material (ΔH) with the energy required for the evaporation of free water in the product (L) [14]. The heat of adsorption is a measure of the energy required for water adsorption on the product while the heat of desorption is the energy requirement necessary to break intermolecular forces between the water vapor molecules and the adsorbent surface [10].

The differential entropy (ΔS) is related to the number of active sites of sorption for a given level of energy inherent in biological material [15]. According to McMinn et al. [16], the entropy characterizes or defines the degree of order or disorder in the existing water-sorbent system. According to Rizvi [10], the entropy for a given temperature quantifies the lost work and provides a measure of energy is not available to do work. The change in Gibbs free energy (ΔG) is a thermodynamic state function that represents the maximum amount

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of energy in a process, at constant temperature and pressure, which is free to perform useful work is therefore represented by the difference between the enthalpy differential and the product of differential entropy by the temperature. The change in water sorption process and the Gibbs free energy is generally accompanied by changes in enthalpy and entropy [17]. The change in Gibbs free energy of a product is a parameter that indicates the affinity between the product and the water, since it provides information as to the spontaneous ($\Delta G<0$) or non-spontaneous ($\Delta G>0$) of the sorption process.

Due to the importance of hygroscopicity and thermodynamic properties of the water sorption at drying and storage operations, a great deal of research is carried out to obtain equilibrium isotherms for the different agricultural products. However, data relating to the hygroscopic equilibrium and energy demand in the desorption process of jatropha grains they were rarely avaluated. Given the above-mentioned, the aims of the present work are to obtain hygroscopic equilibrium data of jatropha grains for different conditions of temperature and relative humidity, to adjust different mathematical models to experimental data and to select the one that best represented the phenomenon. Thermodynamic properties related to the desorption process (enthalpy and differential entropy, variation of Gibbs free energy and isokinetic temperature) were also evaluated.

Materials and Methods

Materials

They were used jatropha grains with 30% moisture content (dry basis, b.s.), extracted from fruits harvested manually in an experimental plantation located in Viçosa-MG. The seeds were kept in the fruits, which were packed in plastic bags and stored in a climate chamber with controlled temperature of 15°C until the beginning of the experiment (four days). This procedure was adopted to reduce the loss of water by seeds in the period before the start of data collection.

Equilibrium moiture data

Samples of 10 seeds for each treatment were separated and placed in organza bags. The bags containing the seeds were placed in glass containers with screw cap containing saturated salt solutions to control the desired relative humidity, according to Table 1. The seeds were kept suspended throughout the experiment to avoid direct contact with the saline solution. The jars were sealed with waterproof tape to prevent gas exchange with the external environment (Figure 1) and were stored in climate chambers with controlled temperatures of 20, 25, 30 and 35°C.

The seeds were weighed daily on an analytical balance accurate to four decimal places. When the sample weight remained constant in five consecutive weighings, the equilibrium moisture content was considered reached. The sample was removed, weighed and brought to a stove with forced air circulation at 105 ± 3°C for determining the equilibrium water content, according to the method recommended in the Rules for Testing Seeds [18], using an analytical balance of GEHAKA brand, AG 200 model with a precision of 0.0001 g. The experiment was conducted to 4 temperatures, 6 relative humidities and two replications.

Mathematical modeling for equilibrium moisture data

To obtain equilibrium data were used the static method. Mathematical models (Table 2) were tested to describe the behavior of equilibrium water content of jatropha grains in terms of relative humidity and temperature. For the adjustment of the models was performed a non-linear regression analysis, by the Gauss Newton method, using the computer program STATISTICA 8.0. wherein a, b and c are parameters of the model that depend on the product; UR is the relative humidity expressed as a decimal; T is the temperature, °C; T_{abs} is the temperature, K; *Ue** is the equilibrium water content,% b.s.

The models were selected considering the significance of the regression coefficients, the magnitude of the determination coefficient (R^2), the magnitude of the mean relative error (P) and estimated error (SE), and the residue analysis. The average relative error and the average error estimated for each model were calculated according to the following equations:

$$P = \frac{100}{n}\sum_{i=1}^{n}\left(\frac{\left|Y-\hat{Y}\right|}{Y}\right) \tag{7}$$

$$SE = \sqrt{\frac{\sum_{i=1}^{n}\left(Y-\hat{Y}\right)^2}{GLR}} \tag{8}$$

Wherein Y is the value experimentally observed; Ŷ is the value estimated by the model; n is the number of experimental observations and GLR are the degrees of freedom of the model (the number of observations minus the number of model parameters). The analysis of residues was performed by residues versus estimated values plots.

Thermodynamics properties

The enthalpy differential desorption (ΔH), also known as isosteric liquid heat, was determined for each equilibrium water content, from equation 9 [10], which is derived from Clausius-Clapeyron equation applied to pure water systems, under the following considerations:

1° - the system water content remains constant; and

Salts	**Temperature (°C)**			
	20	**25**	**30**	**35**
KOH	8.5	8.0	7.5	7.0
$MgCl_2$	33.0	32.5	32.5	32.5
K_2CO_3	44.0	43.0	42.0	41.0
NaCl	76.0	75.5	75.5	75.5
KCl	85.0	85.0	84.5	83.0
K_2SO_4	98.0	97.5	96.5	96.0

Table 1: Moisture values relative to saturated salts solutions kept under different temperature conditions.

Model (Reference)	**Equation**
Henderson [19]	$Ue* = \left[\ln\left(1-UR\right)/-a\,T_{abs}\right]^{\frac{1}{c}}$ (1)
Henderson Modificado [20]	$Ue* = \left[\ln\left(1-UR\right)/-a\,\left(T+b\right)\right]^{\frac{1}{c}}$ (2)
Halsey Modificado [21]	$Ue* = \left[\exp\,\left(a-b\,T\right)/-\ln\,\left(UR\right)\right]^{\frac{1}{c}}$ (3)
Sabbah [22]	$Ue* = a\left(UR^{b}/T^{c}\right)$ (4)
Copace [23]	$Ue* = \exp\left[a-\left(b\,T\right)+\left(c\,UR\right)\right]$ (5)
Sigma-Copace [23]	$Ue* = \exp\left[a-\left(b\,T\right)+\left(c\,\exp(UR)\right)\right]$ (6)

Wherein a, b and c are parameters of the model that depend on the product; UR is the relative humidity expressed as a decimal; T is the temperature, °C; T_{abs} is the temperature, K; *Ue** is the equilibrium water content, % b.s.

Table 2: Mathematical models used to adjust the hygroscopic equilibrium data of jatropha grains.

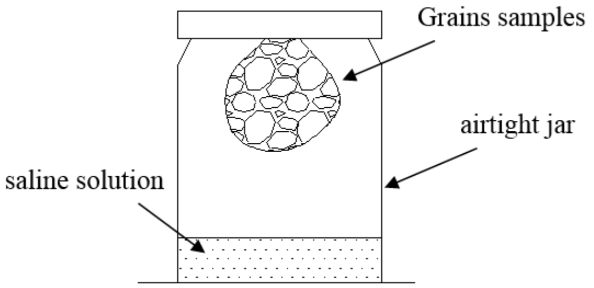

Figure 1: Experimental apparatus used in Jatropha grain packaging to determine the hygroscopic equilibrium of water content.

2° - heat of vaporization of pure water and excess heat (differential enthalpy) does not vary with temperature.

$$\frac{\partial \ln(Aw)}{\partial T} = \frac{\Delta H}{RT^2} \tag{9}$$

wherein Aw is the water activity equal to equilibrium relative humidity, decimal; T is the temperature, K; ΔH is the desorption enthalpy differential, kJ kg^{-1}; R is the universal gas constant, 8.314 kJ-mol^{-1} K^{-1} for water vapor 0.4615 kJ kg^{-1} K^{-1}; The integration of equation 9 whereas the enthalpy difference is independent of temperature, results in the following expression:

$$\ln(Aw) = -\frac{\Delta H}{R}\frac{1}{T} + C \tag{10}$$

where C is a constant of the model. Although it is assumed that ΔH is invariant with temperature, this method requires the measurement of sorption isotherms in more than two temperatures [14,24]. The water activity Aw to different equilibrium water content was obtained using the model that best represented the desorption isotherms at temperatures evaluated. For each equilibrium water content, it was adjusted a linear regression model to the data ln (Aw) versus 1/T. The slope of the straight line obtained, multiplied by the universal gas constant corresponds to the estimated value of ΔH. The ΔH values obtained for each equilibrium water content were used to assess their dependency relationship with the water content of jatropha grains.

The total isosteric heat of desorption (Qst) was then determined by adding the ΔH values, the value of the latent heat of vaporization of free water (W) according to the following equation:

$$Q_{st} = \Delta H + L \tag{11}$$

The latent heat of vaporization of free water (L) was obtained by the equation representing the variation of latent heat of vaporization of the free water in the temperature range under consideration, namely, from 15 to 40 ± 5°C:

$$L = 2501{,}5 + 2{,}37T_m \tag{12}$$

wherein T_m is the mean temperatures studied, °C.

The differential entropy of desorption (ΔS, kJ kg^{-1}K^{-1}) was calculated from the Helmholtz equation Gibbs (10):

$$\Delta G = \Delta H - T\Delta S \tag{13}$$

where ΔG is the change in Gibbs free energy (kJ kg^{-1}), which for the steady state can be obtained by the equation:

$$\Delta G = -RT\ln(Aw) \tag{14}$$

Substituting equation 14 in equation 13 and rearranging the terms, we have:

$$\ln(Aw) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{15}$$

Comparing equation 15 with equation 10, it is observed that the constant C obtained in equation 10, is the term ΔS/R of the equation 15. Thus, the differential entropy was obtained analogously to differential enthalpy, using a ln (Aw) versus 1/T plot. The compensation enthalpy-entropy theory or isokinetic relationship is used to evaluate the physical and chemical phenomena that prevail in sorption processes et al. [25,26]. In these processes, differential enthalpy values are correlated with the differential entropy values according to the following equation [27]:

$$\Delta H = \Delta G_B + T_B\Delta S \tag{16}$$

where T_B is the isokinetic temperature (K); ΔG_B is the change in Gibbs free energy to the isokinetic temperature. The ΔG_B and T_B values were obtained by linear regression representing the relationship between differential enthalpy and entropy differential. According Telis-Romero et al. [17], isokinetic temperature has an important physical significance, as it represents the temperature at which all phenomena occur at the same rate. Since the enthalpy and entropy are highly correlated, the theory of compensation can be considered valid for the process of desorption [27]. To confirm the existence of compensation, it was performed the test recommended by Krug et al. [28,29], which involves comparing the isokinetic temperature in relation to the harmonic mean temperature (T_{hm}), defined as:

$$T_{hm} = \frac{n}{\sum_{i=1}^{n}\frac{1}{T}} \tag{17}$$

where T_{hm} is the harmonic mean of temperature (K); n is the number of temperatures used in the study.

The compensation theory can only be applied if the isokinetic temperature (T_B) is different from T_{hm}. If $T_B > T_{hm}$ the change in enthalpy leads the process, otherwise the process of sorption is controlled by the variation of entropy [26].

According to Beristain et al. [27], if T_{hm} is in the range calculated for isokinetic temperature TB, the ratio of differential enthalpy and entropy values sorption is only experimental errors and not the existence of chemical and physical factors that govern the compensation theory.

Results and Discussion

Equilibrium data

Table 3 shows the parameters of the hygroscopic equilibrium models for jatropha grains obtained for desorption under different conditions of temperature and water activity. The Henderson Modified model showed the biggest adjustment coefficient, lower relative mean error (P) and lower estimated mean error (SE) when compared to others models. The full analysis of residues was applied to check for possible violation of any assumptions of the regression model. According to the results presented, the Halsey Modified, the Copace and the Sigma-Copace models, in addition to having the lowest coefficient of determination, presented, together with the Sabbah model, a tendentious residues distribution, and thus the assumptions that residues have zero mean and homogeneous variance are not valid. It is observed that the residual graphs that to the Sabbah model, the larger

Models	Parameters	R^2 (%)	P (%)	Residues Distribution	
Henderson	a 1.062E-5 c 2.3564	97.05	8.98	1.10	Random
Henderson Modificado	a 9.73E-5 b 1.8303 c 2.4108	98.88	5.84	0.68	Random
Halsey Modificado	a 10.1216 b 0.0505 c 4.0836	91.72	19.29	1.85	Tendentious
Sabbah	a 71.8892 b 0.7748 c 0.4201	96.74	9.27	1.16	Tendentious
Copace	a 1.663 b 0.015 c 1.781	92.73	6.39	1.73	Tendentious
Sigma-Copace	a 0.9174 b 0.0153 c 0.9474	88.84	11.42	2.15	Tendentious

Table 3: Estimation of model parameters adjusted to the hygroscopic equilibrium data of jatropha grains with the respective coefficients of determination, mean, relative and estimated errors and residues trend.

the predicted values the greater is the residues dispersion around the mean. This suggests that the variance is greater for greater equilibrium water content and therefore can not be considered constant. For the Halsey Modified, Copace and Sigma-Copace models the residues distribution does not occur randomly, i.e., follows a pattern, which suggests a correlation between successive residues and, consequently, the lack of independence thereof.

According to the results obtained in the analysis of residues and considering the values obtained for the average relative error, estimated average error and the coefficient of determination, Henderson and Henderson Modified models may be appropriate to represent the variation of the equilibrium water content as a function of relative humidity and temperature. The Henderson Modified model was chosen to estimate the water activity of the Jatropha grains to be used for the determination of thermodynamic properties. In addition to not violate the assumptions of the regression model, this model had lower mean relative error (P) (5.84%), lower estimated average error (0.68) and higher coefficient of determination (98.88%).

Mohapatra and Rao [30] used as a criterion for selecting models the average relative error (P) and considered that this should not exceed 10%. According to Draper and Smith [31], the ability of a model to describe a particular physical phenomenon is inversely proportional to the estimated average error (SE). Gely and Santalla [32], to obtain hygroscopic equilibrium data for peanut kernels and castor beans, respectively, also concluded that the Henderson Modified model was the most appropriate to describe the dependency ratio of the water content factors and temperature with a water activity of those oilseeds. Figure 2 shows the Henderson Modified model adjusted to the equilibrium water content data as a function of relative humidity and temperature.

The temperature effect on the sorption isotherm is useful since the grains are exposed to different temperature conditions during pre-processing operations, storage and processing [33]. Setting a relative humidity value, the equilibrium water content is higher at lower temperature. Ferreira and Pena [34] explained this behavior based on increased water vapor pressure in the air and on the surface of the product. Higher temperature results in higher water vapor pressure in air, which in turn leads to higher loss of water by the grains until they reach a new state of equilibrium water content. For a given temperature, the higher water activity, the greater the product equilibrium water content, following the same trend of other agricultural products studied [25,35-38]. Moreover, it is found that the temperature dependence varies with the water activity, while the smaller the water activity value is the lower effect of temperature on equilibrium water content values of the grains. This behavior can be well represented by a sigmoidal curve, which reflects a Type II isotherm according to the Brunauer classification [39].

According to Labuza [40], sigmoidal isotherm can be divided into three distinct regions:

- Region I is the monolayer region on which the existent water is tightly bound to protein molecules, carbohydrates, and other components of the grain;

- Region II is the region in which the water molecules in the grains begin to be found in free form due to the decrease in number of active sites of chemical bonds with water molecules; and

- Region III is the region of condensing following by the dissolution of soluble materials. In this region, mass transfer of water from the grains to the environment or from the environment to the grains are more intense and consequently the product is exposed to the action of micro-organisms due to high water activity. In this work, the region II is delimited by the interval at which the second derivative of the Henderson Modified equation is constant and less than 0.001. Thus, it was determined the intervals corresponding to other regions. The region I for equilibrium isotherms of Jatropha grains was delimited by average water activity between 0 and 0.28 (0.28<Aw ≤ 0.61). The region II by 0.28<Aw ≤ 0.61, and the region III by 0.61<Aw<1. The corresponding mean values of equilibrium water content (% b.s.) were 0 ≤ Ue ≤ 6.75, 6.75<Ue ≤ 10.07 and Ue>10.07 for regions I, II and III, respectively. After the average water activity of 0.28, the values Ue increases slowly with increasing Aw to about 0.61, from which a small increase Aw causes a more significant increase in water content equilibrium of the grains. This observation suggests that water activity values below 0.28 may have minimal effects on the stability of the components of Jatropha grains during storage.

The minimum water activity for the development of fungi in stored grain is 0.7 [41,42]. For jatropha, most recommended water content for storage of jatropha grains should be the one in equilibrium with relative humidity up to 61%. According to the Henderson Modified equation to Jatropha grains, these values vary from 10.1 to 12.5% (b.s.), as the temperature varies from 35 to 20°C. At high temperatures, water molecules reach higher energy levels and this allows them to break bonds with sorption sites, thereby lowering the equilibrium moisture [43]. The water content values for safe storage of jatropha grains in the evaluated temperature range were higher than those observed for the castor beans (6.1 and 8.4% bs, for temperatures of 40 and 20°C, respectively) [32] and peanuts (6.9% and 7.4 bs, for temperatures of 40 and 20°C respectively) [44].

Thermodynamics properties

The differential enthalpy values were calculated using hygroscopic equilibrium data at different temperatures by using equation 10. The variation of the differential enthalpy of desorption in terms of the water content of Jatropha grains is shown in Figure 3.

The differential entalpy of desorption for jatropha grains increased by reducing the water content. It is observed a tendency for differential enthalpy values becoming constant at high water contents. This confirms that for high levels of water content of Jatropha grains, as well as other agricultural products, there is a decrease in bond forces of the water molecules with other hydrophilic constituent of grains due to the saturation of active sites bond. According Cadden [45], since the differential enthalpy of desorption is the amount of energy required to remove the water from the solid, the higher these values, the more strongly the water molecules are linked to these constituents. This variation can be represented by a sigmoidal four parameter model, wich coefficient of determination R^2 was equal to 0.99:

$$\Delta H = y_0 + \frac{a}{1+\exp\left(\frac{-1}{b}(U-c)\right)} \qquad (18)$$

in which y_0, a, b and c are parameters of the regression equation (y_0=-48.75, a=1597.33; b=-3.77 and c=12.41) and U is the water content of the grains. Similar behavior was reported by Toğrul and Arslan [33], Idlimam et al. [46] for seed nuts, *Z. gaetulum,* and rice seeds, respectively.

Several authors have found that the exponential model can be used to represent the variation of the differential enthalpy in terms of the water content of various agricultural products [35,47-51]. For the desorption of Jatropha grains exponential model was tested and, however, does not adequately represented dependency relationship between differential enthalpy and water content, at the temperature range evaluated. The differential enthalpy of desorption was lower compared to the latent heat of vaporization of pure water (2566.67 kJ kg^{-1}) in of the average temperature of this study, indicating that the bond energy between water molecules and active sorption sites is less than the energy which retains water molecules bound at liquid state [48]. The total energy required for removing water from the Jatropha grains in drying processes at different temperatures can be determined by substituting T_m (27.5°C) of the equation 12 by the drying temperature (T) and adding to the differential enthalpy (equation 11). Estimated values of isosteric heat of desorption for drying temperatures of 30, 35, 40 and 45°C are presented in Table 4.

It is noted (Table 4) that the amount of energy required to remove a unit mass of water Jatropha grains with initial water content of 20% b.s. is 139.44 kJ kg^{-1}, 7 times lower than the energy required to remove the same mass unit of water when the product is an initial water content of 10% b.s. (996.84 kJ kg^{-1}). For the initial water content of 8 and 6% (b.s.) the amount of energy required increases to 1170.18 and 1301.90 kJ kg^{-1}, respectively, equivalent to an increase of 17 and 30%, respectively, regarding the needed energy to remove a unit mass of water the product in initial water content of 10%. The differential entropy of desorption values for Jatropha grains according to water content are shown in Figure 4.

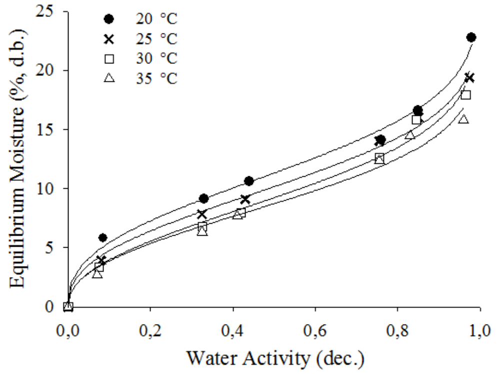

Figure 2: Values observed and estimated by Henderson Modified model of moisture equilibrium of jatropha grains obtained by desorption under different conditions of temperature and water activity.

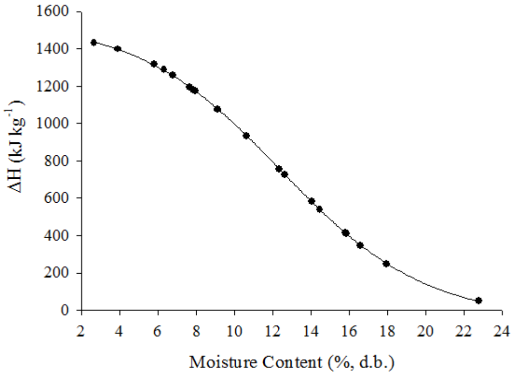

Figure 3: Differential enthalpy of desorption for different water contents of jatropha grains.

The entropy increase may be an indication of the irreversible energy consumption for the clutter and movement of water molecules, while reducing the differential entropy can be related to the entrapment of water in microcapillaries and porous matrix [52]. The differential entropy of sorption is proportional to the number of sorption sites available at a particular energy level [33]. The differential entropy of desorption of Jatropha grain increased with increasing water content up to a maximum of 3.56 kJ $\text{kg}^{-1}\text{K}^{-1}$, which corresponds to a value of 5.73% b.s. water content, and from this point decreases with increasing water content. This phenomenon may occur due to demonstrate the heterogeneity of the composition of the surface functional groups, and consequently, the heterogeneity in the distribution of energy on the surface as it reduces the water content. The differential entropy of desorption (ΔS) according to the water content (U) can be represented by a cubic polinomial regression model (equation 20) with a coefficient of determination r^2 equal to 99.90%:

$$\Delta S = y_0 + aU + bU^2 + cU^3 \qquad (20)$$

wherein y_0, a, b and c are regression equation parameters (y_0=2.04; a=0.5791; b=-0.0634; and c=0.0015). Idlimam et al. [46] found similar results for the differential entropy of *Z. gaetulum* in adsorption and desorption processes.

Umidade (% d.b.)	ΔH kJ kg^{-1}	Q_{ST} (kJ kg^{-1}) Temperatura de secagem (°C)			
		30	35	40	45
4	1393.61	3966.21	6550.66	9146.96	11755.11
6	1301.90	3874.50	6458.95	9055.25	11663.40
8	1170.18	3742.78	6327.23	8923.53	11531.68
10	996.84	3569.44	6153.89	8750.19	11358.34
12	793.30	3365.90	5950.35	8546.65	11154.80
14	583.95	3156.55	5741.00	8337.30	10945.45
16	396.00	2968.60	5553.05	8149.35	10757.50
18	246.77	2819.37	5403.82	8000.12	10608.27
20	139.44	2712.04	5296.49	7892.79	10500.94
22	67.61	2640.21	5224.66	7820.96	10429.11
24	21.82	2594.42	5178.87	7775.17	10383.32

Table 4: Estimated value of total isosteric heat of desorption in different temperature.

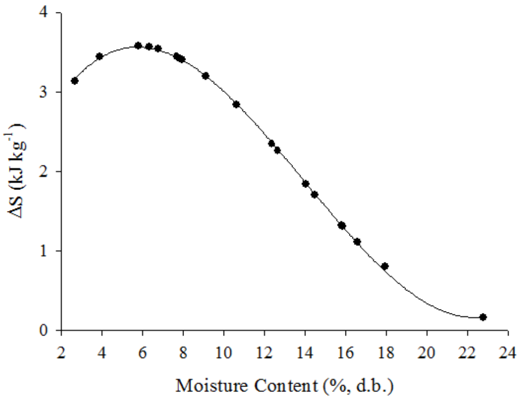

Figure 4: Differential entropy of desorption for different water contents of jatropha grains.

Above 5.73% water content, the behavior is similar to what has been observed for most agricultural products, ie, with the saturation of active links sites by water molecules, there is a reduction of the differential entropy. Kaya and Kahyaoglu [5] and Aviara et al. [35] suggested that the decrease of ΔS is assigned to the lowering movement of water molecules as the available adsorption sites are saturated. Positive values for the enthalpy and differential entropy indicates that the desorption process of jatropha grains is endothermic (occurs with energy consumption) and irreversible. The ΔH and ΔS values of the desorption process, to different water contents were obtained by means of a linear regression equation (Equation 9) assuming that for a specific water content, ΔH and ΔS does not vary with temperature. A graph ΔH vs ΔS is shown in Figure 5.

To the water content range from 5.8 to 22% b.s., the theory of linear chemical compensation between the enthalpy and entropy of desorption can be applied once the data is properly correlated according to the equation 15, i.e., the variation in differential enthalpy is a linear function of the differential entropy, with r^2=99.35%. The T_B parameters, called isokinetic temperature, and variation in Gibbs free energy (ΔG) were calculated by linear regression for all data sets within a 95% confidence interval. The harmonic mean temperature (T_{hm}) was calculated from Equation 17. The isokinetic temperature for desorption was equal to 364.51 ± 15.87 K. T_{hm} was equal to 300.54 K, significantly different value of all T_B possible values, confirming the adequacy of isokinetic theory. According Krug et al. [28,29], the chemical linear compensation standard exists only if T_B is different from T_{hm}.

According to Leffler [53], if $T_B > T_{hm}$ the process is driven by enthalpy, whereas if it is observed the opposite condition ($T_B < T_{hm}$), the process is considered as controlled by entropy. As this study, possible T_B values are greater than T_{hm}, the desorption process is controlled by varying the enthalpy indicating that the amount of energy required for the removal of water attached to the constituents of the grain is greater than the energy consumed for reorganization of the system molecules. According Apostolopoulos and Gilbert [54], ΔG indicates the energy spontaneous interaction of the water-sorbent, providing a measure of the useful or available energy to the process. When ΔG is negative, the process is said spontaneous, otherwise, the process is non-spontaneous. The ΔG obtained for the desorption process of jatropha grains was -61.80 kJ kg^{-1}, which indicates that the process occurs spontaneously [55].

Conclusions

For the desorption process of jatropha grain, setting a relative humidity value, the equilibrium water content is greater the lower the temperature. For a given temperature, the higher water activity, the greater the product equilibrium water content, following the same trend of most agricultural products. The Henderson Modified model is suitable for representing the variation of the equilibrium water content as a function of relative humidity and temperature. The lower the water content of Jatropha grains, the higher the differential enthalpy, i.e., the greater the energy requirements for the process of removing water. The variation of the differential enthalpy with the water content of the grains can be adequately represented by a sigmoidal four parameter model.

The differential enthalpy of desorption is smaller than the latent heat of pure water vaporization, indicating that the binding energy between water molecules and the active sites for sorption is less than the energy which holds the water molecules bound liquid state. The differential entropy of desorption of Jatropha grains increases with the decrease of the water content to a level of 5.73% b.u., indicating the increase of the irreversible energy consumption for mobility and disruption of water molecules in the grain. The differential enthalpy and entropy are correlated according to a linear model, confirming the validity of the application of linear chemical compensation theory. T_{hm} was significantly lower than all possible values of T_B, confirming the adequacy of isokinetic theory and indicating that the process is controlled by enthalpy. Positive values of enthalpy and differential entropy and the negative value of ΔG indicated that the desorption process of jatropha grains is endothermic and irreversible and occurs spontaneously.

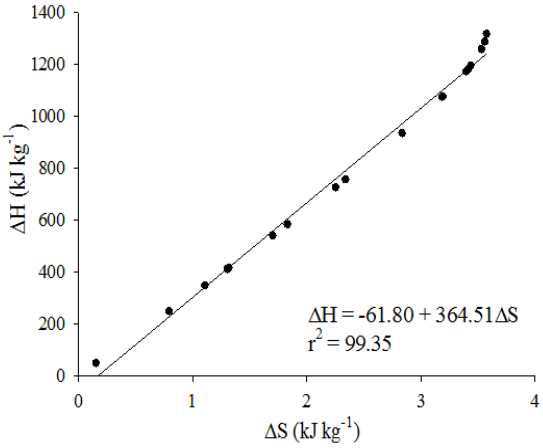

Figure 5: Relationship between the enthalpy and differential entropy in the desorption process of jatropha grains.

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