

Original article

Evaluation of thermodynamic properties using GAB model to describe the desorption process of cocoa beans

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Summary The desorption isotherms and thermodynamic properties of cocoa beans were obtained during the drying process of this product. The isotherms were determined by dynamic method for various temperature (25, 35, 45 and 55 °C) and relative humidity (RH) conditions (30, 40, 50, 60, 70 and 80%). Equilibrium moisture content data were correlated by the Guggenheim–Anderson–de Boer (GAB) model, which presented good fit to the data, according to statistical procedures. Equilibrium moisture content ranged from 5.90 to 16.67 d.b.; it increased with an increment in the RH and decreased with increased temperature at a constant RH. Enthalpy values for each model coefficient were encountered, ranging from -90.05 to 545.96 kJ kg⁻¹. The integral isosteric heat of desorption and differential entropy increased with decreased equilibrium moisture content, a tendency also found for Gibbs free energy.

Keywords Entropy, gibbs free energy, isosteric heat, monolayer moisture content, *Theobroma cacao*.

Introduction

Brazil is one of the leading producers of cocoa beans in the world, being surpassed only by Côte d'Ivoire, Indonesia, Ghana and Nigeria. World production was estimated in approximately 4.3 millions of tons, and Brazil accounted for 210 000 tons in 2007 (FAO, 2007).

Agricultural products require several postharvest procedures aiming to prevent and minimise possible losses during their commercialisation. Regarding cocoa beans, these processes comprise the breaking of bean, fermentation, drying, selection and storage. Fermentation and drying are the main operations to the cure of cocoa beans (García-Alamilla *et al.*, 2007).

Drying is indispensable for the control and maintenance of the quality of the products. The drying process reduces moisture content (X) and water activity (a_w) to safe levels. High values of these two parameters may lead to the growth of microorganisms and deterioration of the

product; on the other hand, low values may lead to the use of excessive energy consumed during drying and undesired alterations to the product (Corrêa *et al.*, 2010a,b).

Sorption isotherms describe the relationship between the moisture content and relative humidity (RH) of the environment surrounding the product; this RH is equal to a_w of the product when the air and the product are in equilibrium. These isotherms are unique for each product and are necessary for understanding moisture variations during storage and preprocessing. Even though there is work with cocoa beans regarding desorption isotherms (Talib *et al.*, 1995; Sandoval & Barreiro, 2002), further analysis of different cultivars and conditions should be studied.

Several mathematical models are used to describe the sorption isotherms. They are divided into different groups: kinetic models based on monolayer (BET model); kinetic models based on multilayer (Guggenheim–Anderson–de Boer [GAB] model); semi-empirical models (Ferro-Fontan, Henderson, Halsey, etc.); and empirical models (Smith, Oswin, etc.). The GAB model was recommended by the European Project Group COST 90 (Wolf *et al.*, 1985) as a fundamental equation to characterise water sorption in foodstuff. The advantages of this model, when compared to the others, are its theoretical background and the physical meaning of its parameters. Furthermore, its suitability in describing the

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The present work was carried out in the Laboratory of Physical Properties and Quality Evaluation of Agricultural Products at the National Grain Storage Training Center – CENTREINAR, Federal University of Viçosa, Viçosa, MG, Brazil.

experimental data up to 0.90 is also an advantage (Oliveira *et al.*, 2010).

According to Corrêa *et al.* (2007), thermodynamic properties provide useful information for the development and improvement of dryers and for studies on water properties on food surface. Recently, thermodynamic parameters, such as enthalpy, entropy, Gibbs free energy and isosteric heat, among others, were investigated in different products (Kaya & Kahyaoglu, 2006; Togrul & Arslan, 2006; Corrêa *et al.*, 2007; Domínguez *et al.*, 2007; Samapundo *et al.*, 2007; Moreira *et al.*, 2008; Corrêa *et al.*, 2010b; Oliveira *et al.*, 2010; Goneli *et al.*, 2010a,b).

As a result of the importance of agricultural product hygroscopicity, the fact that cocoa thermodynamic studies were not studied in the wide range of drying conditions of this work and to the stated above, this work aimed to determine and model the desorption isotherms of cocoa beans using the GAB model. Furthermore, the model parameters and thermodynamic properties were obtained and correlated with the drying process of cocoa beans.

Materials and methods

The present work was conducted in the Laboratory of Evaluation of Physical Properties and Quality of Agricultural Products of the National Grain Storage Training Center – CENTREINAR, Federal University of Viçosa, Viçosa, MG, Brazil.

Raw material

Cocoa was harvested from an experimental unit sited at Bahia state. Cocoa beans were retrieved from the fruits, naturally fermented and dried until an approximate moisture content of 50% d.b. (dry basis). Before drying, the beans were separated in lots of 1 kg and stored at cold chambers (4 °C). The samples were retrieved from chambers after 12 h before the beginning of the treatments, allowing the thermal equilibrium with the environment.

Desorption isotherms

Drying conditions comprised four temperatures (25, 35, 45 and 55 °C) and six relative humidities (30, 40, 50, 60, 70 and 80%). These conditions were provided by an atmosphere control unit (Aminco-Aire 150/300). This equipment allows the control of temperature and RH, and an air flow of $10 \text{ m}^3 \text{ min}^{-1} \text{ m}^{-2}$ was employed. Temperature and RH were monitored with the aid of a psychrometer installed next to the trays containing the samples.

Approximately 300 g of cocoa beans were used for each of the five replications at each thin-layer drying

condition (thickness of 4 cm). Trays containing the product were periodically weighed during drying, and the hygroscopic equilibrium was reached when mass variation was kept constant during three consecutive readings.

The drying data were used to fit the GAB model to describe the desorption isotherms of cocoa beans. The GAB equation is expressed by the eqn 1, presented below.

$$X_{\text{eq}} = \frac{X_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (1)$$

In which: X_{eq} = equilibrium moisture content, %d.b.; X_m = monolayer moisture content, %d.b.; C , K = model constants that are related to monolayer and multilayer properties, respectively (van den Berg, 1984), dimensionless; and, a_w = water activity, decimal.

The GAB parameters were estimated using a nonlinear regression by the Gauss–Newton approximation method, which minimises the sum of square errors in a series of interactive stages.

The adequacy of the model was analysed based on the values of mean relative per cent deviation (P), the standard error (SE), determination coefficient (R^2) and residual plots:

$$P = \frac{100}{n} \sum_{i=1}^n \left(\frac{|Y - \hat{Y}|}{Y} \right) \quad (2)$$

$$SE = \sqrt{\frac{\sum_{i=1}^n (Y - \hat{Y})^2}{DF}} \quad (3)$$

In which: P is the mean relative per cent deviation, %; n is the number of observed data; SE is the standard error, %d.b.; Y is the observed value; \hat{Y} is the estimated value through the model; and DF is the degrees of freedom of the model.

Thermodynamic properties

After achieving the model coefficients, the enthalpy values for each GAB parameter were calculated using a simple regression procedure. It requires the representation of $\ln X_m$, $\ln C$ and $\ln K$ vs. the inverse of absolute temperature, as described by Simal *et al.* (2000).

$$C = C_0 \exp \left[\frac{\Delta H_1}{R(T + 273.16)} \right] \quad (4)$$

$$K = K_0 \exp \left[\frac{\Delta H_2}{R(T + 273.16)} \right] \quad (5)$$

$$X_m = X_0 \exp \left[\frac{\Delta H_3}{R(T + 273.16)} \right] \quad (6)$$

In which: C_0 and K_0 are parameters from eqns (4) and (5), dimensionless; X_0 is the parameters from eqn (6), decimal d.b.; T is the temperature, °C; ΔH_1 , ΔH_2 and ΔH_3 are enthalpies from the model coefficients, kJ kg^{-1} ; and R is the water vapour constant, $0.462 \text{ kJ kg}^{-1} \text{ K}^{-1}$. Remaining thermodynamic parameters, such as net isosteric heat of desorption (q_{st}), entropy of desorption (ΔS), Gibbs free energy (ΔG), activation energy (E_a) and enthalpy–entropy relationship, were obtained by means of a known methodology used by several researchers (Al-Muhtaseb *et al.*, 2004; Kaya & Kahyaoglu, 2006; Togrul & Arslan, 2006; Janjai *et al.*, 2009; Oliveira *et al.*, 2010; Goneli *et al.*, 2010a,b; Corrêa *et al.*, 2010b).

The net isosteric heat of desorption (or differential enthalpy) was calculated by means of eqn 7, known as Clausius–Clapeyron equation (Iglesias & Chirife, 1976).

$$\frac{\partial \ln(a_w)}{\partial T} = \frac{q_{st}}{RT_a^2} \quad (7)$$

In which: T_a is the absolute temperature, K ; q_{st} is the net isosteric heat of desorption or differential enthalpy, kJ kg^{-1} . Integrating eqn 7, and assuming that the net isosteric heat of desorption is independent of temperature, it was obtained the following equation, for each equilibrium moisture content (Wang & Brennan, 1991):

$$\ln(a_w) = -\left(\frac{q_{st}}{R}\right) \frac{1}{T_a} + C_1 \quad (8)$$

In which: C_1 is an integration constant, dimensionless. The integral isosteric heat of desorption was obtained by the sum of q_{st} and the latent heat of vapourisation of pure water, according to eqn 9.

$$Q_{st} = q_{st} + L \quad (9)$$

In which: L is the latent heat of vapourisation of pure water, kJ kg^{-1} ; Q_{st} is the integral isosteric heat of desorption, kJ kg^{-1} . The value of L was obtained using eqn 10 and the average temperature (\bar{T}) used in this work, in °C:

$$L = 2502.2 - 2.39\bar{T} \quad (10)$$

Alterations in differential entropy of desorption can be represented by eqn 11, known as the Gibbs–Helmholtz equation (Rizvi, 1995):

$$\Delta S = \frac{q_{st} - \Delta G}{T_a} \quad (11)$$

In which: ΔS is the differential entropy of desorption, $\text{kJ kg}^{-1} \text{ K}^{-1}$ and ΔG is the Gibbs free energy. Gibbs free energy during desorption is represented by eqn 12:

$$\Delta G = -RT_a \ln(a_w) \quad (12)$$

The effect of changes in moisture sorption over free energy is usually accompanied by alterations in enthalpy and entropy values. Thus, by replacing eqn 12 by eqn 11 and rearranging, it is obtained:

$$\ln(a_w) = -\frac{q_{st}}{RT_a} + \frac{\Delta S}{R} \quad (13)$$

The values of q_{st} and ΔS were calculated with eqn 13. In this procedure, the plotting of the water activity values vs. the inverse of absolute temperature (T_a^{-1}) is carried out at the respective values of equilibrium moisture content. The values of a_w , T and X_{eq} were obtained through the GAB model.

Values of differential enthalpy of desorption and entropy may be correlated by eqn 14 (Leffler & Grunwald, 1963):

$$q_{st} = T_B(\Delta S) + \Delta G_B \quad (14)$$

In which: T_B is the isokinetic temperature, K and ΔG_B is the Gibbs free energy associated with the isokinetic temperature, kJ kg^{-1} . The isokinetic temperature represents the temperature in which all reactions in series occur at the same rate. As enthalpy and entropy are highly correlated, it is assumed that the compensation theory is valid for the sorption process (Heyrovsky, 1970). To confirm the existence of compensation, the isokinetic temperature was compared with the harmonic mean temperature, defined according to eqn 15 (Krug *et al.*, 1976a,b).

$$T_{hm} = \frac{n}{\sum_{i=1}^n \left(\frac{1}{T_a}\right)} \quad (15)$$

In which: T_{hm} is the harmonic mean temperature, K and n is the number of temperatures used. An approximate interval of confidence, $(1-\alpha) 100\%$, to the isokinetic temperature was calculated by the following equations:

$$T_B = \hat{T}_B \pm t_{m-2, \alpha/2} \sqrt{\text{Var}(T_B)} \quad (16)$$

$$\hat{T}_B = \frac{\sum (q_{st} - \bar{q}_{st})(\Delta S - \bar{\Delta S})}{\sum (\Delta S - \bar{\Delta S})^2} \quad (17)$$

$$\text{Var}(T_B) = \frac{\sum (q_{st} - \Delta \bar{G}_B - \hat{T}_B \Delta S)^2}{(m-2)(\Delta S - \bar{\Delta S})^2} \quad (18)$$

In which: m is the number of data pairs of enthalpy and entropy; \bar{q}_{st} is the average net isosteric heat of desorption, kJ kg^{-1} ; and $\bar{\Delta S}$ is the average differential entropy of desorption, $\text{kJ kg}^{-1} \text{ K}^{-1}$.

Table 1 Parameter estimated values, mean relative error (P), standard error (SE), determination coefficient (R^2) and residual plots for GAB model to cocoa beans desorption in each temperature

Parameters	Temperature (°C)			
	25	35	45	55
X_m (%d.b.)	6.681	5.838	5.171	4.652
K	0.749	0.725	0.697	0.664
C	3749.457	3679.979	5258.779	3532.097
R^2	0.9806	0.9663	0.9618	0.9356
P (%)	2.94	3.73	3.85	4.32
SE (%d.b.)	0.41	0.43	0.37	0.39
Residual plots	Random	Random	Random	Random

Results and discussion

GAB model adequacy

Estimated parameters of the Guggenheim–Anderson–de Boer (GAB) and statistical parameters used to analyse

the degree of adequacy of this model are presented in Table 1.

It can be noticed that the values of R^2 were high (>93.56%). However, the adequacy of nonlinear models cannot be analysed solely by the determination coefficient. Therefore, values of P and SE were calculated, and they are low. According to Mohapatra and Rao (2005), P values below 10% indicate good adequacy of the model for practical purposes. This requisite was met at all temperatures studied at the present work. Regarding the SE, lower values indicate higher ability of the model to describe the studied phenomenon. Furthermore, an analysis of the residual plots is required for the correct evaluation of the model adequacy; if it presents a biased distribution, the model is ineffective to represent the experimental data, even when the remaining statistical parameters present opposite results. Residual plots were random at all temperatures, as observed in Fig. 1.

The GAB model is more advantageous than the other models because its coefficients present physical meaning

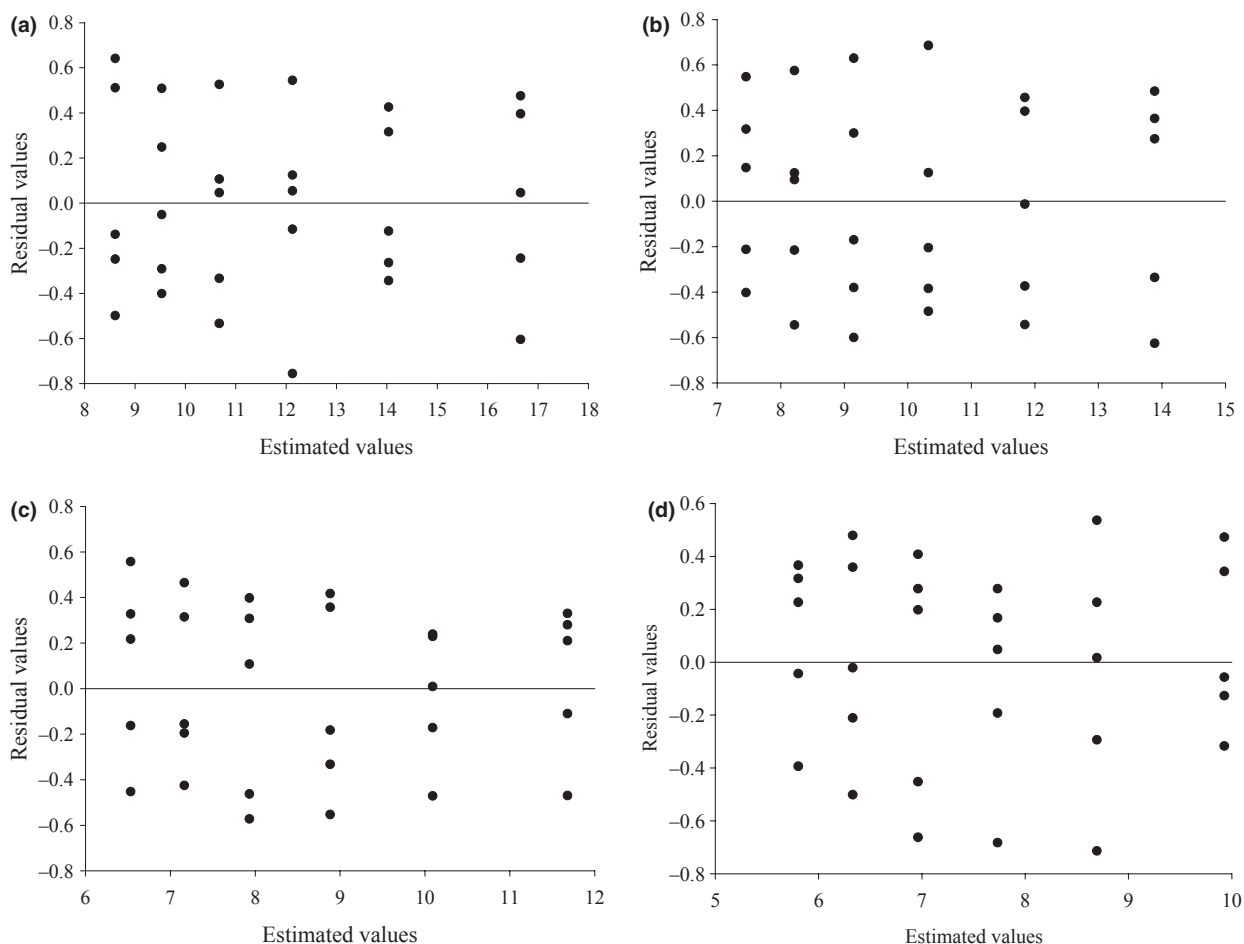


Figure 1 Residual plots of GAB model at temperatures of 25 °C (a), 35 °C (b), 45 °C (c) and 55 °C (d).

regarding the processes that occur during drying, thus allowing a more detailed study on heat and mass transfer, as explained below.

The monolayer moisture content indicates the amount of water molecules that are strongly adsorbed in specific sites at the food surface. The values of this parameter at the present work tended to decrease as temperature increased (Table 1), varying between 4.65% and 6.68% d.b. Several authors also observed this behaviour in different products (Togrul & Arslan, 2006; Samapundo *et al.*, 2007; Oliveira *et al.*, 2010). This phenomenon can be explained by the number of active sites that are reduced with increased temperature. It results from the modifications of the physical and chemical characteristics of the product (Perdomo *et al.*, 2009).

The C constant is associated with the chemical potential differences between the monolayer and superior layers (Timmermann *et al.*, 2001). This constant did not present a defined behaviour in the drying of cocoa beans.

The K constant corresponds to the difference at the chemical potential between the monolayer and free water (Duggan *et al.*, 2008). This parameter tended to decrease with increased temperature. This trend is possibly caused by temperature, because higher levels lead to a rapid desorption and water molecules transition between multilayer and free water.

Desorption isotherms

Desorption isotherms of cocoa beans may be observed in Fig. 2. It can be noticed an increased equilibrium moisture content with an increment of water activity (RH of equilibrium) at a constant temperature. A sigmoid-shaped type is observed for all temperatures studied. This shape is characteristic of amorphous materials rich in hydrophilic compounds (Al-Muhtaseb

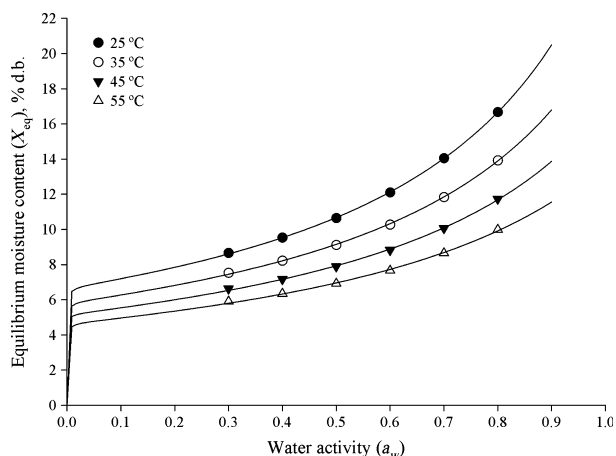


Figure 2 Desorption isotherms of cocoa beans.

et al., 2004). The sigmoid-shaped type can be explained by the binding of water molecule, which can be divided into three regions: $a_w < 0.3$; $0.3 < a_w < 0.7$; and $a_w > 0.7$ (Labuza, 1975). The moisture at the first region is because of structural water, presenting strong bonds with hydrogen, and monolayer moisture, adsorbed by polar and hydrophilic groups from the products components (Oliveira *et al.*, 2010). At this phase, structural water is not available owing to the high energy required to break the molecular connections, which present low or no insect and fungal development (Bewley & Black, 1994). These authors reported that fungal growth is interrupted by equilibrium moisture content values below the superior limit of the multilayer region (between 0.3 and 0.7 of a_w). At the second region, connections between the several layers with the first layer of water occur by means of hydrogen bonds. At the third region (above 0.7 of a_w), water molecules are easily stored in empty spaces of the product owing to a capillary region. This fact allows an easy access to water, which makes products susceptible to the attack of insects and microorganisms.

The equilibrium moisture content presented decreased values as temperature increased, at a constant value of RH. This fact is because of reduced available sites within the product to water molecules to bind; this is a result from the physical and/or chemical alterations promoted by temperature, as temperature affects the water molecule mobility.

Thermodynamic properties

C_0 , K_0 and X_0 and the enthalpies associated with each GAB model constant (ΔH_1 , ΔH_2 and ΔH_3) were obtained using the method proposed by Simal *et al.* (2000). These values are shown in Table 2.

Analysing Table 2, it can be noticed that enthalpy values were positive to the X_0 and C_0 constants, which indicates endothermic reactions, or in other words, reactions that require the absorption of energy from the environment in which products are inserted. This fact is expected, because during drying, the product absorbs energy from the environment in order to reach equilibrium with it, through heating (sensible heat) and later through the evaporation of free water (latent heat of vapourisation).

Table 2 Calculated values of GAB model constants (C_0 , K_0 and X_0) and its respective enthalpy values

Parameters	Values	Enthalpy (kJ kg^{-1})
X_0 (%d.b.)	0.1263	545.95
C_0	0.2029	180.51
K_0	7502.56	-90.95

Table 2 demonstrates that the enthalpy value for K_0 is negative. This signal indicates an energy release from the several layers that form the multilayer. This tendency may be explained by energy release as heat flow, because of the increasing level of molecular vibration of water molecules during drying.

The X_0 presented the highest enthalpy values (Table 2). This trend is expected, because the monolayer moisture content indicates the amount of water molecules that are strongly adsorbed by specific sites from the food surface; thus, significantly greater energy is required to remove these water molecules from the monolayer. This behaviour was also reported by Simal *et al.* (2000), in which the enthalpy from the monolayer was about ten times higher than the other enthalpies.

The latent heat of vapourisation (L), which represents the minimum amount of energy required to evaporate water molecules, was calculated according to the mean temperature of the present work (40 °C); its value was 2406.60 kJ kg⁻¹. This value was used to achieve the integral isosteric heat of desorption and the net isosteric heat of desorption. Fig. 3 presents the values of Q_{st} according to the equilibrium moisture content.

It can be observed that lower levels of equilibrium moisture content require higher energy to remove water from products. Moreira *et al.* (2008), working with loquat and quince fruits, reported the same trend for Q_{st} . These authors explain that a possible cause is that, at initial stages of desorption, there are polar sites highly active on food surface, which is covered by water molecules, forming the monomolecular layer. Al-Muhtaseb *et al.* (2004) reported that these layers require higher quantities of energy to remove water molecules from products. The same trend was found by researchers working with different products (Oliveira *et al.*, 2010; Goneli *et al.*, 2010a,b).

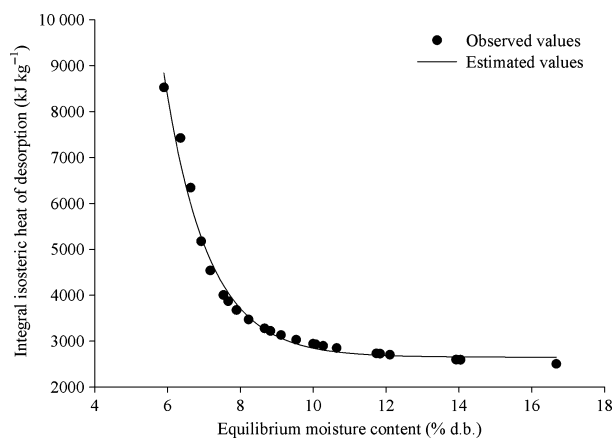


Figure 3 Observed and estimated values of integral isosteric heat of desorption in function of equilibrium moisture content of cocoa beans.

Figure 3 shows that Q_{st} values are higher than the latent heat of vapourisation. This indicates that the binding energies between water molecules and sorption sites are higher than the binding energy between water molecules at liquid phase (Masuzawa & Sterling, 1968). According to McMinn & Magee (2003), the knowledge of Q_{st} values at certain equilibrium moisture content indicates water molecules status, serving as a parameter for the physical, chemical and biological status; thus, this information is vital for studies on storage conditions.

Figure 4 presents the ΔS values according to the equilibrium moisture content. This figure shows that the differential entropy depends on the equilibrium moisture content, presenting tendency similar to Q_{st} . Entropy values decreased with increasing equilibrium moisture content. Similar results were reported for starch powder (Al-Muhtaseb *et al.*, 2004), sesame seeds (Kaya & Kahyaoglu, 2006), corn (Oliveira *et al.*, 2010), okra seeds (Goneli *et al.*, 2010b) and pearl millet grain (Goneli *et al.*, 2010a). The differential entropy of a material is proportional to the number of available sorption sites at a certain energy level (Madamba *et al.*, 1996), indicating water molecule mobility within the material. Therefore, this trend observed for differential entropy is expected, as there is lower amount of available sites of sorption in high values of moisture content, because these sites are already filled by water molecules; thus, lower mobility of water molecules is required to allow the occurrence of desorption.

Table 3 shows the regression equations of Q_{st} and ΔS found in the present work and their respective determination coefficients.

Gibbs free energy is related to the work needed regarding the product layers to become available to sorption (Nkolo Meze'e *et al.*, 2008); therefore, in higher

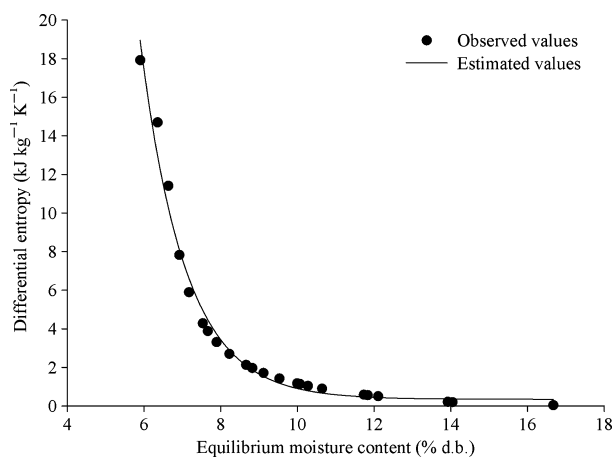


Figure 4 Observed and estimated values of differential entropy in function of equilibrium moisture content of cocoa beans.

Table 3 Regression equations of integral isosteric heat of desorption (Q_{st}) and differential entropy (ΔS) and their respective determination coefficients (R^2)

Thermodynamic property	Equation	R^2
Q_{st} (kJ kg^{-1})	$Q_{st} = 2650.1893 + 882345.0516 \exp(-0.8406^{**} X_{eq})$	98.56
ΔS ($\text{kJ kg}^{-1} \text{K}^{-1}$)	$\Delta S = 0.3471 + 2888.1361 \exp(-0.8551^{**} X_{eq})$	98.44

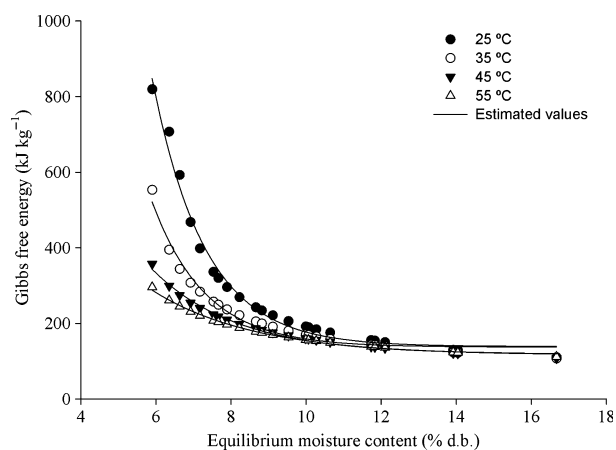


Figure 5 Observed and estimated values of Gibbs free energy in function of equilibrium moisture content of cocoa beans.

values of equilibrium moisture content, there will be fewer sites available to sorption. Therefore, ΔG values are expected, because in higher values of moisture content, there is lower necessity of work to make the sites available to sorption, because they are already available. This trend is observed by lower values of ΔG , in Fig. 5.

The decreasing tendency of Gibbs free energy together with increased temperature and moisture content was also reported by different authors (Kaleemullah & Kailappan, 2007; Oliveira *et al.*, 2010; Goneli *et al.*, 2010b). Positive values of this parameter are also expected, as it characterises endothermic reaction, or else, reactions that require energy from the environment to occur. It can also be noticed that around 11% of moisture of cocoa beans tend to present approximate values, regardless of the drying temperature, maintaining this characteristic with increased moisture content.

Table 4 contains the regression equations for Gibbs free energy, for each temperature studied in the present work, such as their respective values of determination coefficient.

Regarding the enthalpy–entropy compensation theory, the values obtained for harmonic and isokinetic temperature were, respectively, 321.7 K and 333.69 ± 1.31 K. According to Krug *et al.* (1976a,b), the linear chemical compensation only occurs when the isokinetic temperature is different from the harmonic mean temperature; thus, in the present work, this theory was corroborated for the desorption of cocoa beans.

Table 4 Regression equations for Gibbs free energy (ΔG), in each temperature analysed, and their respective determination coefficients (R^2)

Temperature ($^{\circ}\text{C}$)	Equation	R^2
25	$\Delta G = 138.8502 + 47251.9229 \exp(-0.7119^{**} U_e)$	98.71
35	$\Delta G = 137.2886 + 24390.8062 \exp(-0.7037^{**} U_e)$	97.60
45	$\Delta G = 118.2688 + 3045.0485 \exp(-0.4418^{**} U_e)$	99.08
55	$\Delta G = 115.7771 + 1490.2102 \exp(-0.3660^{**} U_e)$	99.48

Conclusions

Modelling and the thermodynamic parameters were encountered for desorption process of cocoa beans. Evaluation of these parameters during drying process of cocoa beans is of fundamental importance to the correct conservation of the product, as well providing parameters to design and develop the several equipments utilised on the main postharvest operations. When this machinery is wrongly constructed, it generates poor grain quality and consequently a reduction in the commercialisation prices.

According to the results, it can be concluded that desorption process was well represented by the GAB model. Also, monolayer moisture content decreased with increased temperature of drying.

Enthalpy values related to two GAB coefficients were positive, which indicates endothermic reactions; on the other hand, one coefficient from GAB model was negative, indicating an energy release from the several layers that form the multilayer. Isosteric heat, differential entropy and Gibbs free energy presented high correlation with the equilibrium moisture content of cocoa beans, and the enthalpy–entropy compensation theory exists for the desorption process of cocoa beans.

Acknowledgments

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