

## Desorption Isotherms and Isosteric Heats of Fermented Cocoa Beans (*Theobroma cocoa*)

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### Abstract

Water desorption isotherms of fermented cocoa beans from Ivory Coast were determined using the gravimetric static method of saturated salts solutions at 30 °C, 40 °C and 60 °C, and isosteric heats of desorption were calculated from Clausius-Clapeyron equation. The experimental data were fitted to several isotherm equations. The best fittings were obtained for the BET equation for  $a_w < 0.50$  (with an average mean relative deviation (MRD) value of 1.56%) and for the Harkins-Jura equation for  $a_w \geq 0.50$  (with an average value MRD equation of 4.17%). The isotherms obtained at 30 °C and 40 °C are practically coincident and overlapped for  $a_w$  below 0.40. Fermented cocoa beans presented a monolayer moisture content of 0.083 dry basis (d.b.) at 30 °C and this value decreases with increasing temperature. The net isosteric heats of desorption for fermented cocoa beans for the temperature range studied (30-60 °C) were estimated as a function of moisture content. The maximum net isosteric heat of desorption for fermented cocoa beans was estimated at around 13.51 kJ/mol corresponding to a moisture content value of 2.85%. The energy requirement for maintaining the moisture content low of 8.7% (d.b.) or 8% wet basis (w.b.) for safe storage of this product or for reducing the moisture content during drying was estimated at around 9.58 kJ/mol.

**Keywords:** cocoa beans, isosteric heat, mathematical model; water sorption isotherm

### 1. Introduction

Cocoa production is the main activity of smallholders. They provide 95% of the world production on surfaces lower than 10 ha with a weak average yield estimated from 350 to 400 kg/ha cocoa beans (Barel, 2005). Ivory Coast is the world's largest cocoa grower. Its production represents 10% of GDP (Gross Domestic Product) and 40% of export earnings (Banzio, 2003). However since some years, the quality of cocoa beans has decreased slowly and gradually on the world market. Quality of cocoa beans for export-market is significantly affected by post-harvest processing method (i.e. fermentation and drying) and the problems of cocoa beans stability during storage (Anonymous, 2006; Sandoval & Barreiro, 2002; Fowler, 1995). In most cases the aerothermic conditions of storage area are unfavourable affecting beans moisture content and water activity. Water activity influences particularly micro-organisms growth, enzymatic reactions kinetic and the lipids oxidation in biological products. To maintain the stability of dried cocoa beans during storage, it is necessary to know product physical properties, in particular the relationship between water activity and equilibrium moisture content at room temperature and the relative humidity. This relationship is represented by product sorption isotherms. The effect of temperature on sorption isotherm is very important due to the fact that cocoa beans packaged in permeable jute bags are exposed to variable temperatures during storage and processing. In another hand, water activity changes with temperature (Al Muhtaseb, McMinn, & Magee, 2002). Furthermore, sorption isotherm is used in drying to determine the final moisture (Cassini, Marczak, & Norena, 2006; Noumi et al., 2004).

Unfortunately, few works is found in literature about water sorption isotherms of cocoa beans (Sandoval et al., 2002). Mercier, Tusa and Guaiquirian (1982) determined moisture desorption isotherms of cocoa beans at three temperatures (33.3 °C, 41.8 °C and 52.4 °C) using a gravimetric method. The monolayer water content and the average sorption enthalpy were calculated using the BET equation. Talib, Daud and Ibrahim (1995) determined

moisture desorption isotherms of cocoa beans using a constant environment chamber for various combinations of air relative humidity (30 to 90%) and temperature (20 °C to 70 °C). The new modified Hasley, Henderson, and Chung equations, whose parameters are fitted to a fifth-order polynomial with respect to temperature, was used to represent satisfactorily the isotherms of cocoa beans in the temperature range investigated.

Sandoval et al. (2002) obtained no statistical differences ( $p < 0.01$ ) among the water sorption isotherms of non fermented cocoa beans (Venezuelan fine second grade) at 25 °C, 30 °C and 35 °C. All data were adjusted with a single isotherm in this temperature range and the best fit were found for BET ( $a_w < 0.50$ ) and Harking –Jura ( $a_w \geq 0.50$ ) models.

More recently, GAB model gave the best fit of the sorption isotherms of cocoa and cupuassu products at 15 °C, 30 °C and 35 °C (Medeiros, 2006).

Although several mathematical models exist to describe water sorption isotherms of food materials (Iglesias, Chirife, & Lombardi, 1975), none of them gives accurate results throughout the whole range of water activities, or for all types of foods.

The main purposes of this work were to provide experimental data for the sorption characteristics of fermented cocoa beans originated from Ivory Coast to model the desorption isotherms, determine their dependence on temperature, and estimate the differential heat of sorption which is importance when designing equipment for dehydration processes of cocoa beans.

## 2. Material and Methods

### 2.1 Material

The experiments were achieved on fresh cocoa beans previously fermented. About 20 kg fermented cocoa beans with an initial moisture content around 55-60% (by wet weight) supplied by an organic agricultural farm were used.

### 2.2 Measurement of Water Sorption Isotherms

The method for determining water desorption isotherms was static gravimetric technique in which the weights were followed discontinuously until the equilibrium. This method was based on the COST 90 project method (Wolf, Spiess, & Jung, 1985). About  $25 \pm 0.001$  g sample of cocoa beans was put in an open shallow glass container inside a glass jar containing diluted solutions of sulphuric acid. Each experiment was carried out in triplicate. Sulphuric acid (Fisher Scientific, UK) solutions were used to maintain the specified relative humidity inside the glass jars.

The glass jars with the samples were kept in temperature-controlled cabinets ( $\pm 0.5$  °C) at 30 °C, 40 °C and 60 °C. The samples were allowed to equilibrate until there was no discernible weight change, as evidenced by constant weight values ( $\pm 0.001$  g). This involved a period of approximately 9 – 12 days for 60 °C, 15 – 21 days for 40 °C and 21 – 27 days for 30 °C. The long stabilization time of samples constitutes main disadvantage of this method (Medeiros, Ayrosa, Pitombo, & Lannes, 2006). To prevent microbial spoilage of samples, a small dish containing crystalline tymol was placed in the glass jar where high water activities occurred ( $a_w > 0.7$ ) (Wolf et al., 1985; Cassini et al., 2006). In order to avoid disrupting the degree of atmospheric moisture sorption, the sample was weighted only every third day in five seconds or less. After the equilibrium had been reached, the samples were dried using the oven method at 105 °C during 24 h (AOAC, 1990; Augier, 1999). Moisture determinations were done by triplicate and the averages were calculated. Seven (7) equilibrium points were obtained in these experiments.

The isotherm models used to fit the data are presented in Table 1. The goodness of fit of each model was evaluated using the correlation coefficient ( $r$ ) and the mean relative deviation (MRD). The MRD value is given in percentage and may be estimated as follows:

$$MRD(\%) = \frac{100}{N} \sum_{i=1}^N \frac{|X_{Exp,i} - X_{Cal,i}|}{X_{Exp,i}} \quad (13)$$

where values below 10% are indicative of good fit (Lomauro, Bakshi, & Labuza, 1985).

Table 1. Isotherm equations for experimental data fitting

| Model                                  | Mathematical expression   | $a_w$ range         |
|--|---|---------------------|
| BET (Brunauer et al., 1938)            | $X_{eq} = X_m C a_w / [(1 - a_w)(1 + (C - 1)a_w)]$ (1)  | $a_w < 0.50$        |
| GAB (Van den Ben & Bruin, 1981)        | $X_{eq} = X_m C K a_w / [(1 - K a_w)(1 + C_G K a_w - K a_w)]$ (2)<br>$C = c_0 \exp(\Delta H_C / RT)$ (3)<br>$K = k_0 \exp(\Delta H_K / RT)$ (4) | $0.05 < a_w < 0.95$ |
| Chung and Pfof (1967)                  | $X_{eq} = \frac{1}{B} [\ln A - \ln(-\ln a_w)]$ (5)  | $0.20 < a_w < 0.90$ |
| Hasley (1948)                          | $X_{eq} = (-A / \ln a_w)^{\frac{1}{B}}$ (6)   | $0.05 < a_w < 0.80$ |
| Harkins and Jura (1946).               | $X_{eq} = [-B / (\ln(a_w) - A)]^{\frac{1}{2}}$ (7)  | $a_w > 0.50$        |
| Henderson (1952)                       | $X_{eq} = [-\ln(1 - a_w) / A]^{\frac{1}{B}}$ (8)  | $0.50 < a_w < 0.95$ |
| Kuhn (Labuza, Mizrahi, & Kasel, 1972.) | $X_{eq} = A / \ln a_w + B$ (9)  | $a_w < 0.5$         |
| Oswin (1946)                           | $X_{eq} = A [a_w / (1 - a_w)]^B$ (10)   | $0.05 < a_w < 0.90$ |
| Smith (1947)                           | $X_{eq} = A + B \ln(1 - a_w)$ (11)  | $0.50 < a_w < 0.95$ |
| Freundlich (1906)                      | $X_{eq} = A (a_w)^{\frac{1}{B}}$ (12)   | $a_w < 0.90$        |

Variables to measure experimentally:  $X_{eq}$ = equilibrium moisture content (% d.b.);  $T$ = temperature (K) ;  $a_w$ = water activity.

Parameters to be estimated from the data:  $A$ =constant (dimensionless),  $B$ = constant (dimensionless),  $C$ = GAB or BET model parameter (dimensionless),  $c_0$ = constant (adjusted to the temperature effect) (dimensionless),  $\Delta H_C$ = difference in enthalpy between mono-layer and multi-layer sorption (Kj/mol),  $\Delta H_K$ = difference between the heat of condensation of water and the heat of sorption of the multilayer (Kj/mol),  $K$ = GAB model parameter (dimensionless),  $k_0$ = constant (adjusted to the temperature effect) (dimensionless),  $R$ = universal gas constant (0.00831Kj/(mol.K)),  $X_m$ = Monolayer moisture content (% d.b.).

### 2.3 Measurement of Net Isothermic Heats

The net isothermic heat of desorption ( $q_{st}$ ) was calculated from the Clausius-Clayperon equation (Labuza, Kaanane, & Chen, 1985; Tsami, 1991; Hossain, Bala, Hossain, & Mondol, 2001; Veltchev & Menkov, 2000; Igbabul, Ariaahu, & Umeh, 2013):

$$q_{st} = -R \left( \frac{\partial \ln(a_w)}{\partial (1/T)} \right) \quad (14)$$

where  $T$  is the absolute temperature (K) and  $R$  is the universal gas constant (0.00831Kj/(mol.K)) and  $a_w$  is the water activity.

This relationship required previously that sorption isotherms were determined at the study temperatures, in order to calculate the logarithmic variation in water activity as a function of temperature inverse at constant moisture content. In practice, it is easier to determine the slope of regression lines  $\ln(a_w)$  vs  $1/T$  for a specific moisture content, and then deduce the net isosteric heat of sorption ( $q_{st}$ ).

The heat of desorption is a measure of the energy requirement to break the intermolecular forces between water vapour molecules and adsorbent surface (AL-Muhtaseb et al., 2002; Rao & Rizvi, 1995 ).

In an attempt to describe the relationship between the net isosteric heat of sorption and the equilibrium moisture content, Tsami, Maroulis, Morunos and Saravacos.(1990) proposed an empirical exponential correlation, which can be written as:

$$q_{st} = q_0 \exp(-X / X_0) \quad (15)$$

where  $q_0$  is the net isosteric heat of sorption of the first molecules of water in the food and  $X_0$  is the characteristic moisture content of food material. The values of  $q_0$  and  $X_0$  were determined by adjustment of net isosteric heat  $q_{st}$  data with the Equation (15).

### 3. Results and Discussion

#### 3.1 Water Sorption Isotherms

The experimental data obtained for water desorption isotherms of fermented cocoa beans at 30 °C, 40 °C and 60 °C are shown in Figure 1. The desorption isotherms reveal an increase in equilibrium moisture content with increasing water activity, at a constant temperature. The effect of temperature on desorption isotherm for the total range of water activities can be observed. The Figure 1 shows clearly that the moisture contents decrease while the temperature increases at constant water activity. This behavior is typical of many food products (Vazquez, Chenlo & Moreira, 2003). Moisture sorption isotherms of most foods are nonlinear, generally sigmoidal in shape, and have been classified as Type II isotherms (Akkad et al., 2008; AL-Muhtaseb et al., 2002; Sandoval et al., 2002; Kouhila, Belghit, & Daguenet, 1999).

The isotherms obtained at 30 °C and 40 °C are practically coincident and overlapped for  $a_w$  below 0.40. Indeed many researchers have observed that the sorption isotherms vary very little for temperature differences lower than 10°C. A similar behavior was observed for non fermented cocoa beans at 25 °C to 35 °C (Sandoval et al., 2002), for sultana raisin at 20 °C to 30 °C (Saravacos, Tsiourvas, & Tsami, 1986).

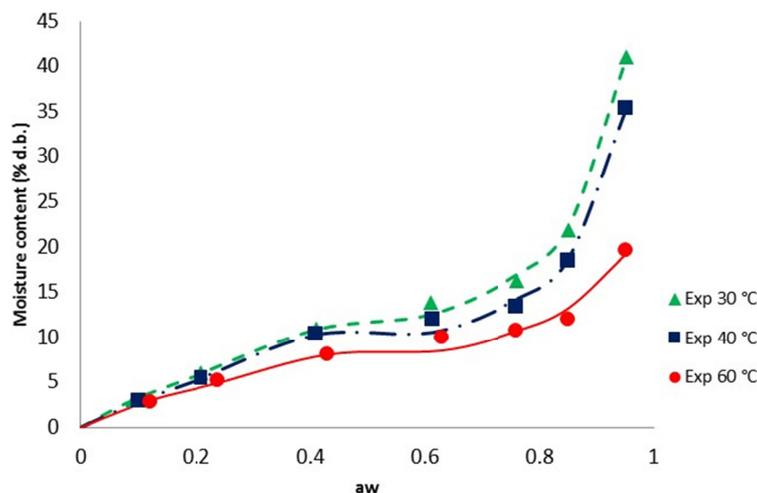


Figure 1. Desorption isotherms of fermented cocoa beans at different temperatures

Table 2 shows the fitting constants of models (presented in table 1), the correlation coefficient (r) and the mean relative deviation (MRD).

Table 2. Estimated values of constants, correlation coefficient (r) and the mean relative percentage deviation modulus (MRD) obtained for the models

| Model        | Constants | 30 °C   | 40 °C   | 60 °C       |
|--------------|-----------|---------|---------|-------------|
| GAB          | Xm        | 0.0543  | 0.0455  | 0.0464      |
|              | C         | 27.0155 | 44.0684 | 22.5443     |
|              | K         | 0.9117  | 0.9151  | 0.7930      |
|              | r         | 0.990   | 0.985   | 0.972       |
|              | MRD(%)    | 14.30   | 16.46   | 13.27       |
| BET          | Xm        | 0.0828  | 0.0822  | 0.0554      |
|              | C         | 5.0030  | 4.1163  | 6.5404      |
|              | r         | >0.999  | >0.999  | 0.997       |
|              | MRD(%)    | 0.24    | 0.64    | 3.81        |
| Chung-Pfost  | A         | 2.3626  | 2.4923  | 3.2081      |
|              | B         | 8.8321  | 10.5798 | 17.4761     |
|              | r         | 0.883   | 0.868   | 0.962       |
|              | MRD(%)    | 32.71   | 31.82   | 10.88       |
| Hasley       | A         | 0.1436  | 0.1439  | 0.1442      |
|              | B         | 1.7608  | 1.7510  | 1.7595      |
|              | r         | 0.972   | 0.955   | 0.910       |
|              | MRD(%)    | 339.29  | 393.60  | 519.41      |
| Harkins-Jura | A         | -0.0051 | -0.0080 | 0.049420715 |
|              | B         | 0.0077  | 0.0054  | 0.0037      |
|              | r         | 0.998   | 0.996   | 0.970       |
|              | MRD(%)    | 3.85    | 4.77    | 3.90        |
| Henderson    | A         | 8.4469  | 10.2375 | 58.2966     |
|              | B         | 1.0830  | 1.1008  | 1.7338      |
|              | r         | 0.979   | 0.969   | 0.974       |
|              | MRD(%)    | 23.02   | 24.74   | 9.73        |
| Kuhn         | A         | -0.1103 | -0.1071 | -0.0708     |
|              | B         | -0.0137 | -0.0163 | -0.0025     |
|              | r         | 0.998   | 0.999   | 0.989       |
|              | MRD(%)    | 7.51    | 2.58    | 6.81        |
| Oswin        | A         | 0.1050  | 0.0844  | 0.0752      |
|              | B         | 0.4568  | 0.4864  | 0.3191      |
|              | r         | 0.995   | 0.990   | 0.985       |
|              | MRD       | 9.86    | 11.13   | 11.54       |
| Smith        | A         | 0.0222  | 0.0220  | 0.0361      |
|              | B         | -0.1199 | -0.1012 | -0.0516     |
|              | r         | 0.982   | 0.926   | 0.976       |
|              | MRD       | 13.15   | 14.89   | 14.70       |
| Freundlich   | A         | 0.3939  | 0.3311  | 0.1673      |
|              | B         | 0.4440  | 0.4655  | 1.0183      |
|              | r         | 0.934   | 0.917   | 0.925       |
|              | MRD       | 43.29   | 43.74   | 17.05       |

All models present correlation coefficient very close to unity indicating good fit to experimental data. However, considering the MRD, the best fittings were obtained for the BET equation for  $a_w < 0.50$  (with an average value of 1.56%) and for the Harkins-Jura equation for  $a_w \geq 0.50$  (with an average value of 4.17%). The isotherms graphical representation at 30 °C, 40 °C and 60 °C with these equations and experimental data are presented in Figure 1 Sandoval et al. (2002) reported that the BET equation ( $a_w < 0.50$ ) and the Harkins-Jura equation ( $a_w \geq 0.5$ ) provide good description of cocoa beans isotherms.

The fittings of these equations to experimental data generated the lowest MRD values, due probably, to the fact that these equations describe water sorption isotherms of food materials in limited range of water activities where as some models are involved in overall range. Labuza (1975) noted that no sorption isotherm model could fit data over the entire range of water activities because water is associated to food matrix by different mechanisms in different water activity regions. Furthermore Iglesias and Chirife (1982) recommended to divide in two domains the water activities range to realize sorption isotherms of food materials.

Using the Harkins-Jura equations, the high values of moisture contents, corresponding to a water activity of 0.70, for which cocoa beans remained safe for microbiological stability after drying or in storage, were 14.83%, 12.47% and 9.56% at 30 °C, 40 °C and 60 °C, respectively. Different studies reported adsorption and/or desorption isotherms of cocoa beans (Cassini et al., 2006; Sandoval et al., 2002; Talib et al., 1995). Concerning desorption isotherms of fermented cocoa beans, the values estimated from the data presented by Talib et al. (2002) for the same water activity value were 26.56%, 18.52% and 11.09% at 30 °C, 40 °C and 60 °C, respectively. These values of moisture contents were higher than the results obtained herein at the same temperatures. This could be explained by the excessive initial moisture content of cocoa beans used by these researchers for their experimentation.

The monolayer moisture content values ( $X_m$ ) of fermented cocoa beans estimated with BET equation at 30 °C, 40 °C and 60 °C can be observed in Table 3. Fermented cocoa beans presented a monolayer moisture content of 0.083 (d.b.) at 30 °C and this value decreases with increasing temperature. This fact on  $X_m$  is a characteristic of type II isotherms. Similar results were found by others researchers for protein (Cassini et al., 2006), for starch powders (AL-Muhtaseb et al., 2002) and for tomatoes (McLaughlin & Magee, 1998). This decrease in monolayer moisture content reflects the reduction in product's hygroscopicity which accompanies the increasing temperature. This can be explained by the reduction of the degree of hydrogen bonding in such products with the increasing temperature, thereby decreasing the availability of active sites for water binding and thus, the monolayer moisture content (AL-Muhtaseb et al., 2002).

Considering the values of monolayer moisture content estimated with BET equation, a more detailed analysis of GAB parameters can provide further valuable information about desorption. Therefore a direct non-linear regression technique was adopted, with Equations 3 and 4 being substituted into Equation 2. The results of regression analysis are summarized in Table 3. These parameters ( $c_0$ ,  $\Delta H_C$ ,  $k_0$  and  $\Delta H_K$ ) have also physical meaning in terms of sorption processes (Van den Berg, 1984).  $\Delta H_C$  represents the difference in enthalpy between mono-layer and multi-layer sorption (Van den Berg, 1984). The values of  $\Delta H_C$  are negatives (with an average value of -25.125 KJ/mol). These negative values show that the reaction of the water removal associated with the food matrix is endothermic. This indicates the need to bring energy to achieve the optimum moisture content of the food, for which stability is maximum. For some authors (Brunauer et al., 1938; Rockland, 196.), this optimum moisture content corresponds to the mono-layer moisture content of BET.  $\Delta H_K$  represents the difference between the heat of condensation of water and the heat of sorption of the multi-layer (Van den Berg, 1984). The positive value of  $\Delta H_K$  indicates that the heat of sorption of the multi-layer is lower than the heat of condensation of water, in the case of fermented cocoa beans.

Table 3. Characteristic GAB parameters for Equation 3 and Equation 4 at different temperatures

| T(°C) | $X_m$ | $c_0$   | $\Delta H_C$ (Kj/mol) | $k_0$ | $\Delta H_K$ (Kj/mol) | r     | MRD(%) |
|-------|-------|---------|-----------------------|-------|-----------------------|-------|--------|
| 30 °C | 0.083 | 9057.49 | -24.331               | 0.285 | 2.843                 | 0.985 | 18.97  |
| 40 °C | 0.082 | 8956.29 | -25.514               | 0.198 | 3.838                 | 0.977 | 19.36  |
| 60 °C | 0.055 | 8871.27 | -25.531               | 0.195 | 3.946                 | 0.966 | 16.90  |

$c_0$ = constant (adjusted to the temperature effect) (dimensionless),  $\Delta H_C$ = difference in enthalpy between mono-layer and multi-layer sorption (Kj/mol),  $\Delta H_K$ = difference between the heat of condensation of water and the heat of sorption of the multi-layer (Kj/mol),  $k_0$ = constant (adjusted to the temperature effect) (dimensionless),  $X_m$ = Monolayer moisture content (d.b.).

### 3.3 Net Isosteric Heats of Desorption

A graphical representation of the net isosteric heats of desorption for fermented cocoa beans is shown in Figure 2. The results illustrate a progressive increase in the heat of desorption with decreasing moisture content. Our results agrees with observations by many researchers (Cassini et al., 2006; Magda, Ana, Ronaldo, & Suzana, 2006; Fasina & Sokhansanj, 1993), since the lower the moisture content, the higher the energy required to remove water from product.

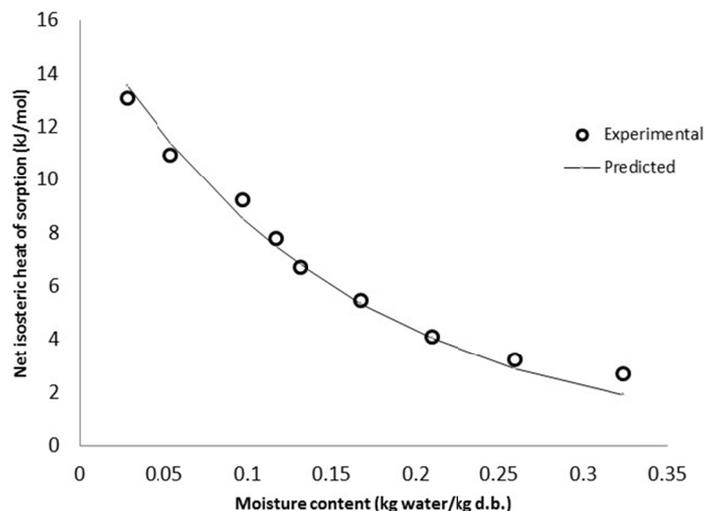


Figure 2. Net Isosteric heat of sorption of fermented cocoa beans estimated between 30 and 60 °C

The net isosteric heats of sorption have been modeled by an empirical exponential correlation given by Tsami et al. (1990):

$$q_{st} = 16.34 \exp(-X / 0.15) \quad (\text{with } r = 0.996 \text{ and } \text{MRD} = 18.89\%).$$

Thus, the maximum net desorption isosteric heat of fermented cocoa beans was estimated at around 13.51 kJ/mol corresponding to a moisture content value of 2.85%.

The energy required for maintaining the moisture content at 8.7% (d.b.) or 8% (w.b.) for safe storage of this product (Braudeau, 1970) or for reducing the moisture content during drying was estimated at around 9.58 kJ/mol.

### 4. Conclusions

The experimental data for water desorption isotherms of fermented cocoa beans (Ivory Coast) were determined for three temperatures (30 °C; 40 °C and 60 °C) and adjusted to several equations. Considering the MRD, the best fittings were obtained for the BET equation for  $a_w < 0.50$  (with an average value of 1.56%) and for the Harkins-Jura equation for  $a_w \geq 0.50$  (with an average value equation of 4.17%). Using the Harkins-Jura equation, the values of moistures contents considering safe for microbiological stability ( $a_w = 0.70$ ) were deduced at each temperature studied. Fermented cocoa beans presented a monolayer moisture content of 0.083 (d.b.) at 30 °C and this value decreases with increasing temperature.

The net isosteric heats of desorption for fermented cocoa beans for the temperature range studied (30-60 °C) were estimated as a function of moisture content. The energy requirement for maintaining the moisture content at 8.7% (d.b.) or 8% (w.b.) for safe storage of this product or for reducing the moisture content during drying was estimated at around 9.58 kJ/mol.

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