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Kinetics of moisture adsorption during simulated storage of whole dry cocoa beans at various relative humidities

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ABSTRACT

A simple combined model involving semi-infinite slab geometry with Fickian diffusion and the Harkin-Jura adsorption isotherm, adjusted to the final equilibrium experimental moisture content given by the model, was developed to predict the kinetics of moisture adsorption of dried cocoa beans under simulated external storage temperature and relative humidity. This model was able to predict accurately the moisture gain by individual beans during storage ($R^2 > 0.994$). Experimental moisture adsorption kinetics of whole cocoa beans were determined for a relative humidity range of 64–93% at 25 °C (298 K). A diffusion coefficient at 298 K of $3.30 \times 10^{-11} \pm 0.56 \times 10^{-11}$ m^2/s was determined and found independent of moisture concentration in the experimental range considered. An operational storage map was proposed to predict the average moisture content of whole cocoa beans of any commercial thickness ($0.600 \leq l \leq 1.200$ cm) ($6.00 \times 10^{-3} \leq l \leq 1.200 \times 10^{-2}$ m) during storage under atmospheres of constant relative humidity (64% ≤ RH ≤ 93%) and temperatures from 5 to 35 °C (278–308 K).

1. Introduction

The cocoa bean is a tropical product obtained from the pods of the cocoa tree (*Theobroma cacao L.*) that are used in the manufacture of chocolate and other products, representing an important exportation commodity in many countries. After harvesting, the pods are opened and the cocoa beans are subjected to fermentation, drying and packaging in new permeable jute or sisal bags, or sometimes handled in bulk for storage and transportation.

When the dried beans are packed in permeable bags, they can gain or lose moisture during storage or transportation, depending on the psychrometric conditions of the surrounding air, until an equilibrium state is reached. The rate at which water vapor from air is adsorbed from the air depends mainly on factors such as the bean moisture, temperature, external air relative humidity and time. Moisture sorption isotherms, correlating moisture and water activity of cocoa beans have been presented in several studies (Akmel et al., 2015; Sandoval et al., 2002, 2020; Sandoval and Barreiro, 2002; Koua et al., 2016). Water activity regulates the growth of deteriorative molds that could affect the product quality and condition. Therefore, the storage potential and stability of cocoa beans depend mainly on their moisture content and the factors affecting water activity such as ambient relative humidity and temperature.

There are several studies in the scientific literature regarding the moisture desorption kinetics of cocoa beans during mechanical drying using dryers with hot forced air, among others those of García-Alamilla et al. (2007); Hii et al. (2009); and Páramo et al. (2010). Some of these research works studied the drying process of cocoa beans using models adapted to simple geometry such as a plane sheet (García-Alamilla et al., 2007) and a sphere (Hii et al., 2009). Páramo et al. (2010) used ellipsoidal cylindrical coordinates to model the drying process. Other authors, as Koffi et al. (2018), presented empirical models for moisture loss during solar drying based on a mass flow equation and semi empirical models in order to fit experimental drying data, without implying the bean geometry in the analysis. All of them reported reasonable adjustment of the experimental drying data to the models used. Hii et al. (2009) modelled the geometry as a sphere and proposed variable diffusion coefficients adjusted to empirical equations. García-Alamilla et al. (2007) used a slab geometry following the model developed by Herman-Lara et al. (2005), to model the theoretical moisture evolution during cocoa fixed bed drying, while Páramo et al. (2010) used ellipsoid geometry and ellipsoidal coordinates to study the change in acidity,

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volatile fatty acids and water diffusivity of cocoa beans dried artificially. Mass diffusivity was estimated from the fitting of experimental kinetics to a theoretical model that takes into consideration the beans' shape.

No reference to studies about the rate of moisture adsorption of cocoa beans during storage was found in the literature reviewed. Therefore, the objective of this work was to study the rate of water vapor adsorption during storage of cocoa beans under atmospheres with different relative humidity without the presence of temperature gradients, and to determine the apparent mass diffusivity during adsorption. Also, to develop a simple mathematical model to predict the rate of moisture adsorption of individual beans under external conditions of constant temperature and relative humidity.

2. Model development

The form of the cocoa bean is basically flat with a length/thickness ratio of 2.51 ± 0.31 and width/thickness ratio of 1.43 ± 0.22, as found by Sandoval et al. (2019b) for the Trinitario variety. The length to thickness ratio suggests that the thickness is the critical dimension for mass transfer. For this reason the slab geometry was selected, being similar to that adopted by García-Alamilla et al. (2007) with cocoa beans, based on the work of Herman-Lara et al. (2005) modelling drying processes. The geometry selected implies that the predominant mass flow is unidirectional from both large sides of the bean. On the other hand, moisture adsorption data is usually fitted to different models to obtain the diffusion coefficient. Roca et al. (2008), studied the effective moisture diffusivities in model food systems for several initial and boundary conditions, concluding that analytical solutions of Fick's second law to simple geometries as a slab, are normally used whatever the food material considered in their study, because they are simpler and no particular knowledge about the food properties are required. Therefore, in the present work, the geometry of cocoa beans was assimilated to that of a solid bound by two parallel planes (semi-infinite slab) and not to a more complex geometry, following the principle of parsimony.

The unidirectional mass flow from the surface of an isotropic solid of thickness l (m) can be described by the Fick's law (equation (1)), assuming a constant diffusivity coefficient (D in m^2/s), independent of concentration (Crank, 1975):

$$\frac{\partial M(x,t)}{\partial t} = D\frac{\partial^2 M(x,t)}{\partial x^2} \tag{1}$$

Being $M(x,t)$ the moisture content (dry basis, d. b.) at any position (x in m) measured from the surface and time t (s). Equation (1) has been solved using the following initial and boundary conditions: The initial moisture in the whole bean is uniform and equal to zero ($M(x,0) = 0$). The surface moisture content $M(0,t)$ remains constant for $t > 0$, and equal to that in equilibrium with the ambient relative humidity M'_∞. Mass flow was assumed to be symmetrical, taking place from both large surfaces of the bean. Additionally, the model considers constant temperature and no change in volume due to variations in moisture. The solution of equation (1) for these initial and boundary conditions is well known (equation (2)) and has been presented by Crank (1975):

$$\frac{M'_{av}}{M'_\infty} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\left(\frac{1}{(2m+1)^2}\right)e^{\left(-D(2m+1)^2\pi^2 t/l^2\right)} \tag{2}$$

Where M'_{av} is the average moisture content integrated over the volume of the bean.

Since the initial condition assumed is not found in real life, in order to solve this normalized equation for the average moisture content and to meet the initial condition ($M(x,0)=M'_0 = 0$), a change of variable is required. The estimated initial moisture content (M_0) must be deducted from all the moisture values involved in the equation in order to have zero initial moisture content. After solving the equation for these conditions, this change must be reverted by adding the initial moisture content to the result as indicated by Charm (1971) and Carslaw and Jaeger (1959). Thus, after reverting this change, equation (2) turns into equation (3):

$$M_{av} = M_0 + (M_s - M_0)\left[1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\left(\frac{1}{(2m+1)^2}\right)e^{-D(2m+1)^2\pi^2 t/l^2}\right] \tag{3}$$

Where M_{av}, M_o and M_s are the average, initial and surface equilibrium moisture content (d. b.).

The boundary condition used considering the surface moisture content as constant for $t > 0$, and equal to that in equilibrium with the ambient relative humidity is justified on the basis of the fact that the external cuticle of the cocoa cotyledon is thin (0.310 ± 0.076 mm) and highly hygroscopic (Sandoval et al., 2020). Roca et al. (2008) pointed out that this boundary condition, was an acceptable approximation as far as hydrophobic materials are concerned since the water uptake rate in these products is very slow. Cocoa beans can be considered as hydrophobic due to the large amount of fat they contain.

3. Materials and methods

3.1. Sample collection

A composite sample of about 10 kg of dry cocoa beans (*Theobroma cacao* L.) was drawn from exportation lots at the port of La Guaira, Venezuela. The beans in these lots were packed in new and clean 60-kg jute bags. The cocoa beans were graded as Fine Second grade (*Fino de Segunda)*, according to the Venezuelan standard for cocoa beans (Covenin, 1995). The laboratory sample was formed by mixing and dividing the primary samples of cocoa beans. The sample so prepared was kept in a dry place in plastic bags at an average temperature of 25 °C (298 K) until it was used for analyses and further testing.

3.2. Dimensions of cocoa beans

A 100-bean sample was randomly selected and the characteristic perpendicular dimensions of each bean measured using a Scienceware™ type 6914 vernier caliper (±0.1 mm or 1 × 10^{-4} m). The characteristic dimensions: length (L), width (W) and thickness (T) are indicated in Fig. 1.

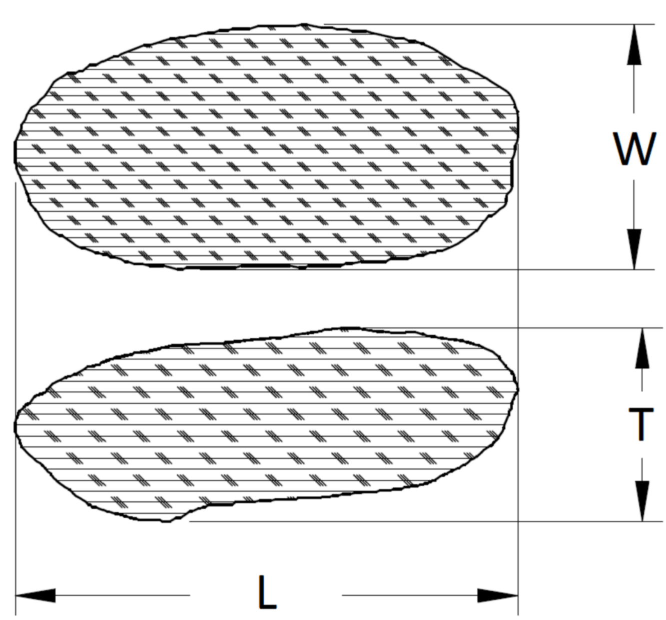

Fig. 1. Dimensions of cocoa beans (L: length, W: width, T: thickness).

3.3. Moisture analysis

The moisture content of the whole beans was determined using the atmospheric oven method at 100–102 °C (373–375 K) for 16 h (57600 s) until constant weight, following the procedure indicated in the A. O. A. C. (1996). The water activity of the samples was determined using a Decagon CX-1 equipment previously calibrated according to the operation manual (Anonymous, 1984).

3.4. Moisture adsorption kinetic studies

In order to determine the rate of moisture adsorption during storage of the whole dry cocoa beans, a static gravimetric technique was followed. The samples with original moisture ranging from 7.19 to 7.52% (wet basis: w. b.) were conditioned to a lower moisture of around 3–5% (w. b.), by drying in an oven at atmospheric pressure at 45 °C (318 K) for 5 days. The moisture content determined for the conditioned samples (M_0, in % d. b.) were: 3.46 ± 0.16, 3.46 ± 0.35 and 4.32 ± 0.74 for testing the relative humidities of 64, 75 and 93%, respectively. Samples of about 50 g (5.0×10^{-2} kg) of beans, selected at random, were placed on a tray equipped with a plastic mesh so that all the surface of the beans was exposed to the ambient. The tray was placed on an electronic Ohaus™ balance (±0.0001 g or 1×10^{-7} kg) inside a hermetic chamber (Precision™ chromatography cabinet) 0.64 x 0.64 × 0.49 m with an established storage relative humidity kept at a temperature of 25 ± 1 °C (298 ± 1 K). A wide range of relative humidity was chosen covering values normally found during storage conditions of cocoa beans (65–90%) including maritime transportation. Different oversaturated salt solutions of known equilibrium relative humidity (Greenspan, 1977) were placed in the drawer of the chamber for this purpose: $NaNO_2$ (64%), NaCl (75%) and KNO_3 (93%). The temperature and relative humidity inside the chamber was regularly checked using a Vaisala™ equipment (HMI33), provided with a probe installed inside. The evolution in the weight of the sample as a function of time was determined using the electronic balance installed inside the chamber. The experiment proceeded until the weight gain in two consecutive measurements was about 0.001 g (1×10^{-6} kg). The initial moisture content of each sample was determined by triplicate and the moisture content at any moment was calculated knowing its moisture gain. At the end of the experiment the moisture content was determined by the oven method in triplicate in order to check its agreement with the final moisture calculated based on the weight gain.

3.5. Statistical analysis

Non-linear and linear regression analyses were done using Matlab R2016a (The MathWorks, Inc.). For the non-linear regression, the curve fitting tool (cftool) was used. Also, the measures of central tendency and dispersion, correlation and Student t-tests were calculated using the same software. The adequacy of the regression was evaluated using the coefficient of determination (R^2) and the root mean square error (RMSE).

4. Results and discussion

4.1. Cocoa bean dimensions

The cocoa bean average dimensions measured were (±standard deviation): Length: 23.04 ± 1.76 mm ($2.304 \times 10^{-2} \pm 0.176 \times 10^{-2}$ m); Width: 13.13 ± 1.28 mm ($1.313 \times 10^{-2} \pm 0.128 \times 10^{-2}$ m); Thickness: 7.07 ± 0.96 mm ($7.07 \times 10^{-3} \pm 0.96 \times 10^{-3}$ m). This thickness was used for calculations. In this case, the length/thickness ratio was 3.25 and width/thickness ratio was 1.88, confirming the flat form of the beans. Also, this confirms that the smaller dimension for mass transfer was the bean thickness.

4.2. Rate of moisture adsorption

The moisture adsorption curves obtained representing the moisture content (d. b.) as a function of time during storage at the relative humidity of 64, 75 and 93% are presented in Fig. 2a, b and 2c, respectively.

The non-linear fitting of equation (3) was carried out with D as variable and known M_0 and $M_s = M_\infty$, with M_∞ being the equilibrium moisture taken from the moisture sorption isotherm for cocoa beans (cocoa powder) at 25 °C (298 K), presented by Sandoval and Barreiro (2002). In order to guarantee the convergence and precision of the results, 20 terms of the summation in equation (3) (m = 19) were used for the calculations. In all cases, it was found that the curves predicted by equation (3) approached equilibrium to values lower than those given by the sorption isotherm previously presented in the literature for cocoa powder. This unexpected result was also observed by Pixton and Griffiths (1971) working with moisture adsorption of wheat kernels.

Instead, equation (3) was adjusted using non-linear regression with the software presented before, with known M_0 and using M_s and D (hereafter named as D_{eff}) as fitting parameters. The Trust-Region algorithm, which handle bound constraints, was utilized so that only positive values for M_s and D_{eff} were managed during calculations. A tolerance of 1×10^{-6} and starting points close to zero as guessing values were used. In all cases, excellent fitting of equation (3) to the experimental data was found, as evidenced by the elevated R^2 and low RMSE values obtained (See Fig. 2a through 2c and Table 1). The model for moisture uptake, using the slab geometry with Fickian diffusion with the initial and boundary conditions established, fitted accurately the experimental data obtained.

As can be observed, the final equilibrium moisture content (M_s) for cocoa beans in surrounding storage environments of 64, 75 and 93% relative humidity was 5.03 ± 0.03, 6.23 ± 0.08 and 11.02 ± 0.12 g water/100 g dry solids respectively (Table 1), as compared with the values given by the sorption isotherm (M_∞) of 6.11, 7.90 and 15.48 g water/100 g dry solids reported by Sandoval and Barreiro (2002) for cocoa powder.

In Fig. 3, the moisture differential given by the equilibrium moisture content calculated using the best-fit to equation (3), (M_s-M_0) was represented against the differential given by the isotherm (M_∞-M_0). The trivial point (0,0) was included in this analysis. An elevated linear regression coefficient ($R^2 = 0.999$) was found, with a ratio of (M_s-M_0)/(M_∞-M_0) = 0.302 that in theory should have been equal to one.

Several reasons could be considered for the discrepancy between the theoretically controlling moisture differential (M_∞-M_0) and the experimental differential (M_s-M_0) calculated with the best-fit values. Pixton and Griffiths (1971), who found a similar behavior working with moisture adsorption in wheat, proposed reasons such as: a) Possible occurrence of hysteresis in the equilibrium adsorption curves in the elevated water activity zone; b) Eventual leakage of ambient air in the testing chamber which would alter the relative humidity. However, in the present work, hysteresis does not seem to be the cause since it is known that it is usually small at high moisture content and on the other hand, no hysteresis has been reported in cocoa bean isotherms as far as we are aware. Leakage is also unlikely, since in our case the temperature and relative humidity inside the chamber were regularly measured and no abnormalities were evidenced. There are other possible sources for the discrepancy that could be postulated such as the additional drying to which the sample was subjected for conditioning for these experiments. Besides the expected loss of moisture in this process, melting of fat present in the bean could result because of the fact that the temperature experienced exceeded its melting range. This fact was evidenced in the thermal analysis of cocoa beans using differential scanning calorimetry technique carried out by Sandoval et al. (2019c), showing bimodal endothermic events with peaks at 18.9 and 31.4 °C (291.9 and 304.4 K) for whole cocoa beans. Melted hydrophobic fat could block and disrupt the access to active sites and also block or reduce the diameter of the original pathways for water vapor diffusion within pores in the bean.

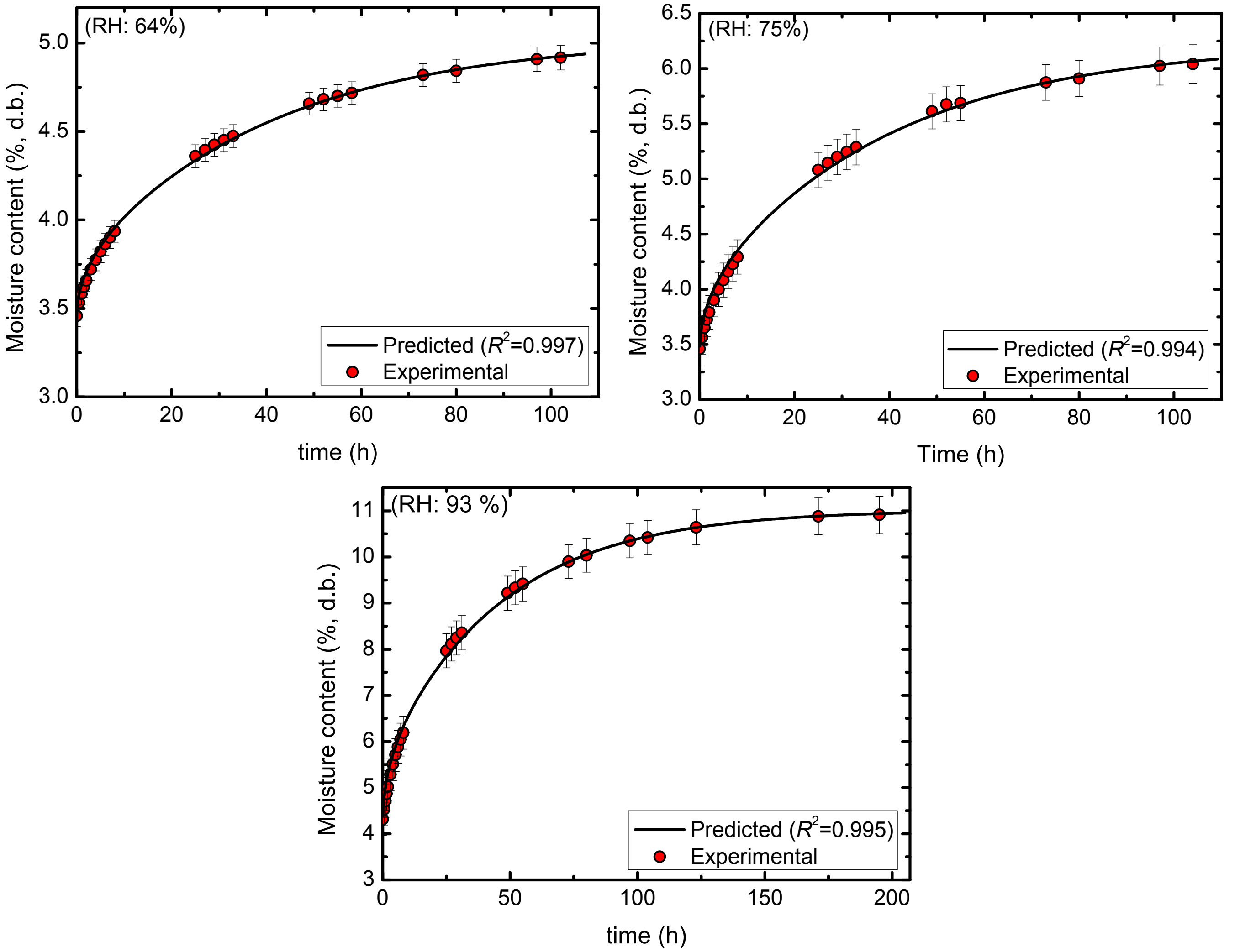

Fig. 2. Experimental and predicted moisture gain as a function of time for whole cocoa beans stored at 25 °C in storage environments at (a) 64%, (b) 75% and (c) 93% relative humidity using equation (3).

Table 1
Values obtained for the effective mass diffusivity (D_{eff}) and surface equilibrium moisture (M_s), using a non-linear regression adjustment to equation (3) for environments of 64, 75 and 93% relative humidity at 25 °C (The ± 95% confidence interval is indicated).

Parameter	Air relative humidity (%)		
	64	75	93
D_{eff} (m^2/s) x 10^{11}	3.42 ± 0.43	3.54 ± 0.61	3.03 ± 0.35
M_s (%, d. b)	5.03 ± 0.07	6.23 ± 0.17	11.02 ± 0.24
R^2	0.997	0.994	0.995
RMSE	0.029	0.073	0.170

This, probably reduces the water vapor diffusion during moisture adsorption. On the other hand, many studies to determine the cocoa bean moisture sorption isotherm data were done by grinding the beans (i.e., cocoa powder) in order to accelerate the equilibration process. In this way, as a result of the grinding process, the surface area of the sample and the exposure of active sites increase, while the length of pathways for diffusion in pores within the pieces decreases, probably resulting in higher moisture contents in the isotherm. In order to explore this theory further research at microscopic level is needed.

Regardless, there is an experimental fact observed: the cocoa beans approached equilibrium during adsorption to a moisture content M_s,

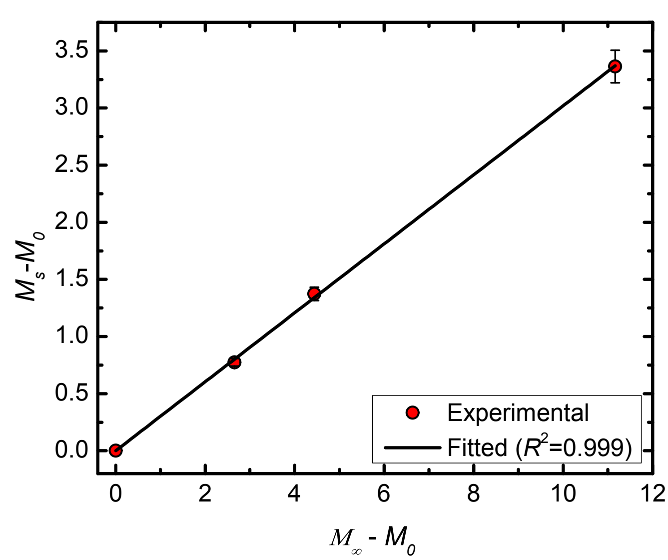

Fig. 3. Experimental relationship between (M_s-M_0) and (M_∞-M_0) during moisture adsorption of whole cocoa beans.

obtained by the best-fit adjustment determined for equation (3) and not to the equilibrium given by the sorption isotherm (M_∞) for cocoa powder (Table 1). The equilibrium was assessed by the asymptote reached for very long times, which was determined with equation (3).

4.3. Equilibrium moisture

In order to predict the real equilibrium moisture (M_s) as a function of the external air relative humidity, an adsorption isotherm was required. It has been found that for water activity values greater than 0.50 (a_w>0.50), the sorption isotherm can be described well using the Harkins and Jura (1944) model giving by equation (4) (Sandoval and Barreiro, 2002; Akmel et al., 2015), with A and B as fitting parameters.

$$\ln a_w = A + B/M_s^2 \tag{4}$$

The Harkins and Jura model was preferred in this case because it has been proved to be accurate in predicting water activity in the range of practical interest in the cocoa trade ($a_w > 0.50$). Also, because it was used before for the same raw material studied in the present work (Sandoval and Barreiro, 2002; Sandoval et al., 2002).

The data of M_s presented in Table 1 were adjusted to the linearized Harkins and Jura model (Fig. 4). A significant linear relationship ($p < 0.05$) with a linear regression coefficient $R^2 = 0.993$ was found. A and B values for equation (4) were 0.0302 (dimensionless) and −11.836 (g water/100 g dry solids)^2 respectively.

Rearranging equation (4), the equilibrium surface moisture M_s can be estimated using the Harkins and Jura model, considering that the water activity (a_w) of the surface in equilibrium with the external air relative humidity (RH) can be expressed as RH/100:

$$M_s = \sqrt{-11.836\Big/\left(\ln\left(\frac{RH}{100}\right) - 0.0302\right)} \tag{5}$$

4.4. Mass diffusivity

In order to evaluate the effective mass diffusivity (D_{eff}) and test its dependence with moisture concentration at the temperature studied (25 °C) (298 K), the procedure described by Crank (1975) was followed, calculating the initial arithmetic mean of the moisture content in the process $M_{mean}=(M_s + M_0)/2$, and plotting $D_{eff}.M_{mean}$ as a function of M_{mean}. Graphical or numerical differentiation of this curve with respect to M_{mean} gives an approximation of the relationship between D_{eff} and the moisture content. The equation for the effective average diffusivity ($\overline{D}$) was presented by (Crank, 1975):

$$\overline{D} = \frac{1}{(Ms - M0)} \int_{M_0}^{M_s} D_{eff}\, d\ \mathrm{M_{mean}} \tag{6}$$

In this case, a linear relationship ($R^2 = 0.993$) shown in Fig. 5 was obtained, including the trivial point (0,0). Therefore, the mass effective diffusivity D_{eff} was constant and independent of the moisture concentration in the range of moisture and temperature studied and given by the slope of the straight line, with $\overline{D} = 0.0012$ cm^2/h (3.30×10^{-11} m^2/s).

The statistical analysis showed that there were no significant differences ($p > 0.05$) between the D_{eff} values obtained for the different relative storage environments presented in Table 1. Since the D_{eff} values were constant and independent of the moisture concentration in the moisture range and temperature studied, the values were averaged and the 95% confidence interval obtained: $\overline{D} = 0.0012 \pm 0.0002$ cm^2/h ($3.30 \times 10^{-11} \pm 0.56 \times 10^{-11}$ m^2/s). This value for moisture adsorption is lower than the one reported by Páramo et al. (2010) of $4.61 \pm 0.55 \times 10^{-11}$ m^2/s for moisture desorption of cocoa beans during drying. Constant diffusivity is one of the assumptions required in the Fick's model given by equation (3).

4.5. Proposal of a generalized moisture adsorption relationship during storage

The adsorption data was plotted using the non-dimensional group (M_{av}-M_0)/(M_s-M_0) as a function of time (Fig. 6). The curve predicted with equations (3) and (5) was also represented in this Figure.

In all cases it was found that equation (3) with the initial and boundary conditions and assumptions specified, using the surface bean equilibrium moisture M_s given by equation (5), and the initial moisture M_0, was capable of fitting the experimental data satisfactorily. The semi-infinite slab geometry assumed represents a simple model to predict moisture adsorption by whole cocoa beans during storage in an environment of constant relative humidity and temperature of 25 °C (298 K). Since moisture sorption of cocoa beans is independent of temperature in the range 5–35 °C (278–308 K) (Sandoval and Barreiro, 2002; Sandoval et al., 2002; Akmel et al. 2015), it can be considered that the data obtained in this work for 25 °C (298 K) could be used in this range.

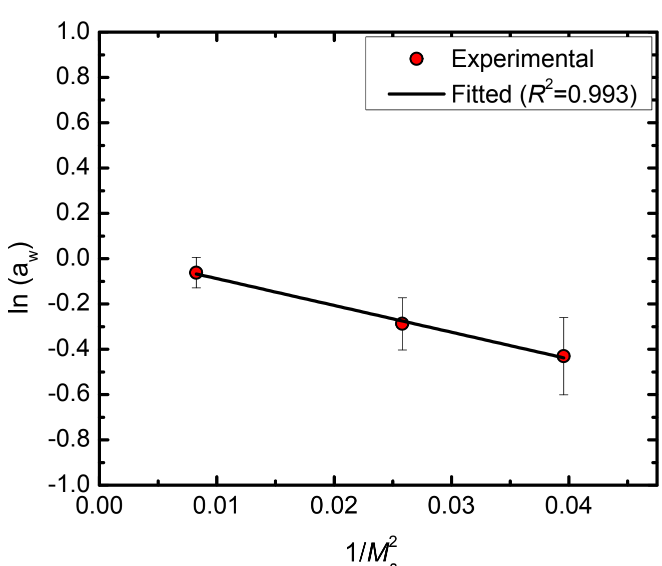

Fig. 4. Linearized Harkins and Jura isotherm for moisture adsorption of whole cocoa beans at 25 °C, using the M_s values calculated.

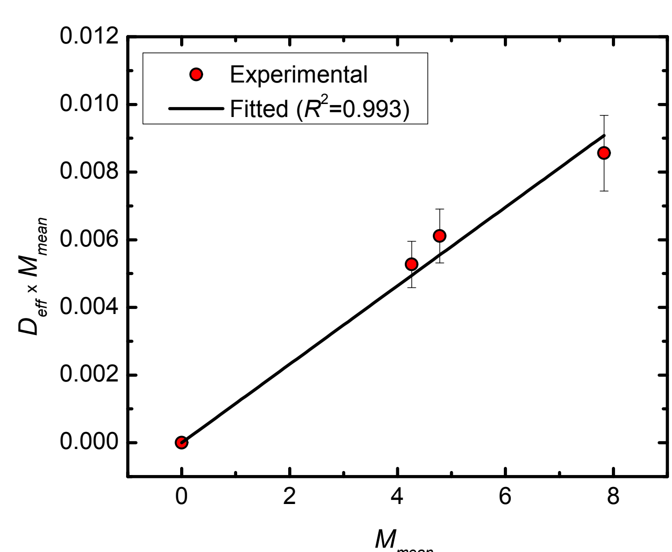

Fig. 5. $D_{eff}.M_{mean}$ as a function of M_{mean} to estimate $\overline{D}$, according to Crank (1975).

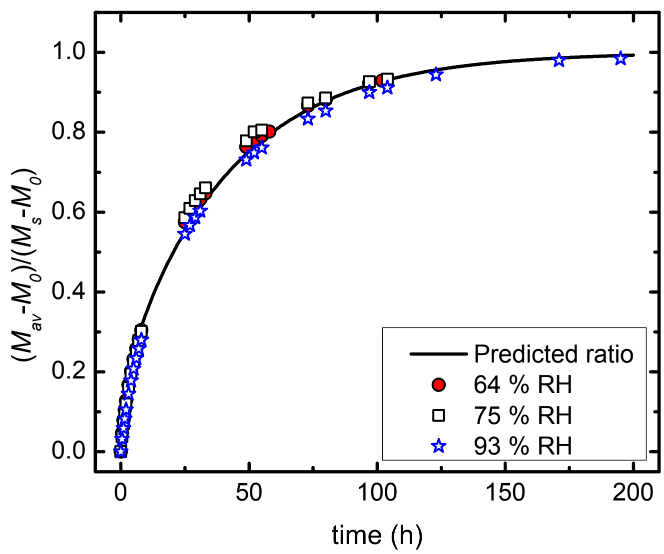

Fig. 6. Non dimensional ratio (M_{av}-M_0)/(M_s-M_0) as a function of time for water adsorption of cocoa beans (l = 0.707 cm or 7.07 × 10^{-3} m) at 25 °C.

4.6. Model validation

The model to predict the equilibrium surface moisture and the moisture content of the whole cocoa beans during storage under an environment of constant temperature and relative humidity, when the mass diffusivity $\overline{D}$ and the bean thickness l are known, is represented by equations (3) and (5).

In order to test the model developed, equations (3) and (5) were used with $D = \overline{D} = 0.0012$ cm^2/h (3.30 × 10^{-11} m^2/s) and $l = 0.707$ cm (7.07 × 10^{-3} m), both determined in this work. The model was tested for whole dry cocoa beans stored in an environment of 75.3% relative humidity in an independent experiment using an oversaturated solution of NaCl at 25 ± 1 °C (298 ± 1 K). In this experiment, the initial moisture content of cocoa beans was $M_0 = 3.37\%$ (d. b.) and $M_s = 6.14\%$ (d. b.), calculated with equation (5) with RH = 75.3%.

The results obtained for the moisture experimental and predicted values using the model are shown in Fig. 7a. An elevated determination coefficient between the experimental and predicted moisture values of $R^2 = 0.997$ was obtained, with a statistically highly significant relationship ($p < 0.0001$) between them, according to the analysis of variance (F-test) conducted. Average prediction error was 2.24%. The 95% confidence and prediction intervals for the relationship between the experimental and predicted values are presented in Fig. 7b. These results reflect in this case, the predictive capacity of the model.

4.7. General theoretical storage map for cocoa beans

A theoretical operational storage map for whole cocoa beans was prepared by plotting the non-dimensional parameters (M_{av}-M_0)/(M_s-M_0) as a function of the dimensionless Fourier number (Dt/l^2), using the model represented by equations (3) and (5) and taking $D = \overline{D} = 0.0012$ cm^2/h (3.30 × 10^{-11} m^2/s) at 25 °C (298 K). The model was calculated for cocoa bean thickness of 0.600 (6.00 × 10^{-3} m), 0.800 (8.00 × 10^{-3} m), 1.000 (1.000 × 10^{-2} m) and 1.200 cm (1.200 × 10^{-2} m). This range covers the commercial dimensions reported elsewhere for the thickness of cocoa beans. The results obtained are shown in Fig. 8.

As can be observed in Fig. 8, the curves practically overlapped for the four thicknesses studied, particularly for values of (M_{av}-M_0)/(M_s-M_0) >0.40. Therefore, in principle, the graph could be used to predict the average moisture content of whole cocoa beans of any thickness during storage under atmospheres of constant relative humidity ($0.600 \le l \le 1.200$ cm) ($6.00 \times 10^{-3} \le l \le 12.00 \times 10^{-3}$ m) and 64% ≤ RH ≤ 93%) and a temperature of 25 °C (298 K) (valid for the range of 5–35 °C or 278–308 K).

When taking the target moisture (M_{av}) as the critical moisture (M_{crit}), generally recognized for microbiological stability of cocoa beans, between 6 and 8% (w. b.) (Sandoval and Barreiro, 2002; Scharnow, 1986; Mabett, 2013), the storage time required to reach that moisture can be predicted using the storage map. For example, for *Trinitario* fermented cocoa beans with the storage parameters presented in Table 2 values of (M_{av}-M_0)/(M_s-M_0) = 0.772 and (D t/l^2) = 0.13 (read from Fig. 8) are obtained. From the Fourier number the time to reach the critical moisture content can be calculated (t = 3.59 × 10^5 s or 99.8 h). In this case, the cocoa beans with initial moisture content of 6.5% d. b. would reach the critical moisture content of 8.70% d. b. when exposed to an ambient of 90% relative humidity, in about 100 h (3.60 × 10^5 s).

4.8. Model limitations

This theoretical storage map is based on a model that can have

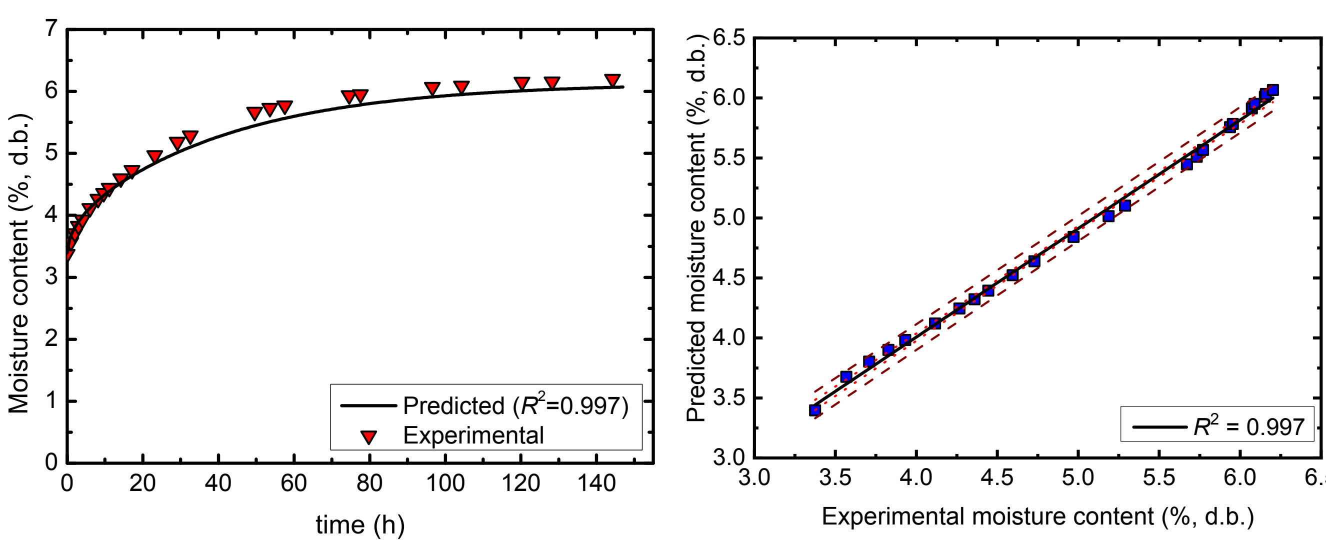

Fig. 7. (a) Predicted and experimental moisture content values as a function of time obtained in an independent test for whole cocoa beans (l = 0.707 cm or 7.07 × 10^{-3} m) stored in an atmosphere of 75.3% relative humidity and 25 °C. (b) Correlation between experimental an predicted moisture values presented in Fig. 7a. Dotted lines represent the 95% confidence bands and dashed lines show the 95% prediction bands.

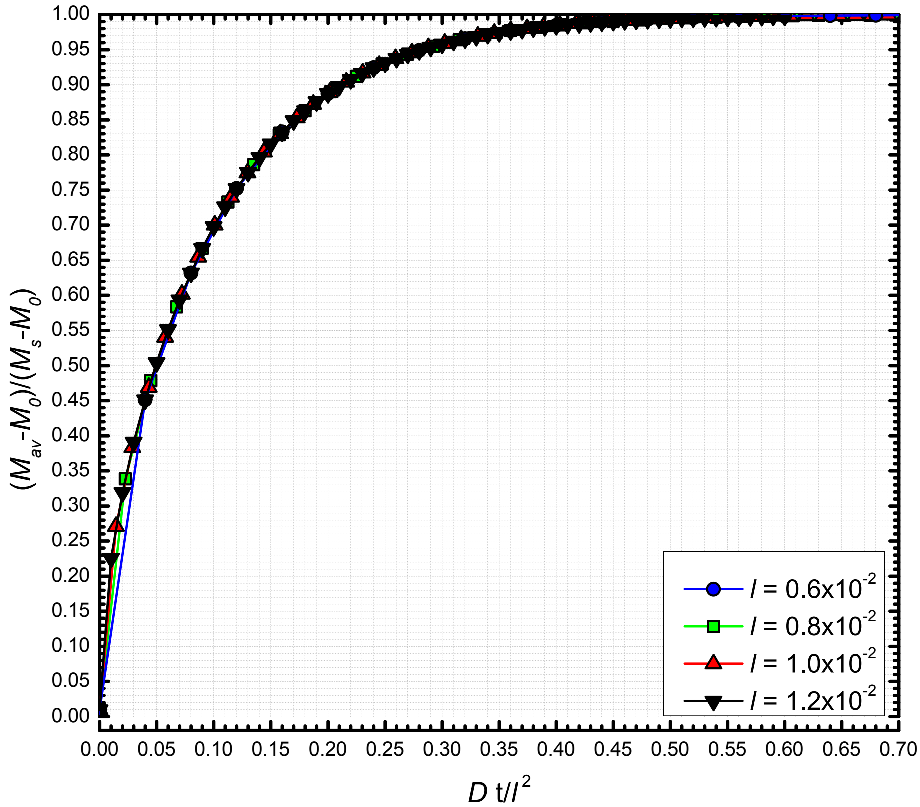

Fig. 8. Storage map for whole cocoa beans of various thickness (l in m) exposed to air relative humidity in equilibrium with the surface moisture M_s (equations (3) and (5)).

Table 2
Parameters used to illustrate the theoretical storage map (Fig. 8) for cocoa beans.

Parameter	Value
Average thickness (l in m)	9.6×10^{-3}(*)
Storage relative humidity (RH in %)	90
Storage temperature (T in K)	298
Apparent mass diffusivity at T ($\overline{D}$ in m^2/s)	3.30×10^{-11}
Initial moisture content (M_0 in %, d.b.)	6.50
Equilibrium moisture (M_s in %, d.b.)	9.34(**)
Critical moisture (M_{crit} in %, d.b.)	8.70(***)

* From Sandoval et al. (2019b).
** Calculated from equation (5).
*** Taken as the critical moisture for microbiological stability 8% (w.b.).

several limitations. The storage time estimated can be considered a minimum since the model assumes that the surface moisture turns instantly in equilibrium with the relative humidity of the atmosphere and this can take some time to occur in real conditions. Although the model developed allows the estimation of the rate of water adsorption by whole cocoa beans exposed to an ambient of constant relative humidity on their entire surface, this could not be the case when the beans are surrounded by other beans in a bag during storage. When the cocoa beans are stowed in bulk or bagged, mass transfer to the inner parts of the stowage could be impaired since the water vapor would have to diffuse through the interstitial space between the stored bags and beans, and then into the beans. This process will require the development of a more complex model, taking into consideration this fact. The model in the present work should be considered a first approximation, applicable to the beans exposed to the external air in the surface of the bagged product that are usually the more affected. Further research would be required to test the model.

5. Conclusions

The kinetics of water adsorption during simulated storage of whole cocoa beans under different constant relative humidity values and temperature of 25 °C (298 K) was studied. A simple combined model was developed involving semi-infinite slab geometry with Fickian diffusion and the Harkins and Jura adsorption isotherm adjusted to the final equilibrium experimental moisture content. This model was able to predict satisfactorily the moisture gain by individual beans during storage ($R^2 > 0.994$). An effective mass diffusivity coefficient $\overline{D} = 0.0012 \pm 0.0002\ cm^2/h$ ($3.30 \times 10^{-11} \pm 0.56 \times 10^{-11}\ m^2/s$) was found. It was constant and can be considered independent of the bean moisture content for the experimental conditions studied. An operational storage map was developed for commercial thicknesses of cocoa beans. With this map, the average moisture content of whole cocoa beans can be predicted for different bean thickness ($0.600 \le l \le 1.200$ cm) ($6.00 \times 10^{-3} \le l \le 12.00 \times 10^{-3}$ m) during storage under atmospheres of constant relative humidity (64% ≤ RH ≤ 93%) and constant temperature (25 °C) (298 K) that might be extended to the temperature range of 5–35 °C (278–308 K).

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Author contribution

José A. Barreiro: Conceived and designed the analysis, Collected the data, Contributed data or analysis tools, Performed the analysis, Wrote the paper. Aleida J. Sandoval: Conceived and designed the analysis, Collected the data, Contributed data or analysis tools, Performed the analysis, Wrote the paper.

Declaration of competing interest

None.

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