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Sorption Isotherms and Drying Characteristic Curve of Fermented Cocoa

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ABSTRACT

An experimental study has been carried out on fermented coca beans. First, the desorption isotherms have been experimentally determined at 40 and 55°C. Second, an experimental study of the convective drying of fermented cocoa has been achieved under different operative conditions: drying air speed: 0.25, 0.5 and 1.0 m.s^{-1}; drying temperature: 40 and 55°C; thickness of cocoa layer: 2, 3 and 4 cm. After testing several sorption isotherm models, it was shown that the Modified-Oswin's equation enables a good reconstitution of experimental results with a Root Mean Square Deviation of 0.0071 $kg_w.kg_{db}^{-1}$ between the experimental and the modelled values of the cocoa water content (varying from 0.02 to 0.12 $kg_w.kg_{db}^{-1}$). Another result is that the drying curves may be satisfactorily represented by the Drying Characterisitc Curve (DCC) model. It was also found that the cocoa beans characteristic curve does not depend strongly on the product layer thickness and may be represented by a power function which exponent has been determined.

Keywords: *cocoa, desorption isotherm, drying characteristic curve, kinetics*

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1. INTRODUCTION

The economy of developing countries is often based on the culture of tropical products. Particularly in sub Saharan Africa, cocoa plays an important role in the national economy of several countries. On the world market, because of the lack of quality of cocoa from this zone, a discount sometimes reaching 40% (case of the Cameroon) has been recorded.

A very important and rapid improvement can be obtained by optimising the drying conditions [1]. In fact, convective drying is an essential operation for the improvement of the quality of the product since drying enables a good conservation of the product by stopping enzymatic reactions and limiting the development of micro-organisms. Therefore all efforts made to produce cocoa of good quality are inefficient, if the drying which follows fermentation is not controlled.

Present knowledge in this domain enables a description of the phenomena occurring during drying [2,3]. However, it is impossible to foresee the drying curve of a product using a calculation that takes into account the influence of all these phenomena. The only way of knowing the drying kinetics is thus the experimental determination [4].

Numerous authors recommend drying cocoa at a moderate temperature (less than 80°C) [5, 6,7], because a higher temperature will favour the retention of acidity in the cotyledons [8]. Some authors recommend the use of a moderate drying air speed (less than or equal to 1 $m.s^{-1}$) to avoid the phenomena of crusting [9].

To our knowledge, a very few studies concerning the kinetics of drying cocoa with moderate air speeds and the identification of fermented cocoa drying curve characteristics have been published. Some experimental drying curves are however given in the literature [9, 10, 11]. A previous work was limited to an air speed of 0.2 $m.s^{-1}$ [12], a more recent study was limited to a layer of 1 cm thickness and a very low air speed (0.01 $m.s^{-1}$) [13].

The first objective of this study is to determine experimentally the sorption isotherms of fermented cocoa at 40°C and 55°C that are usual drying temperatures. The second objective is to determine experimentally the drying characteristic curve of cocoa for three thicknesses of product layer (2, 3 and 4 cm).

2. MATERIALS & METHODS

2.1 Desorption isotherms

Sorption or desorption isotherms indicate the water content at the equilibrium (X_{eq}) of a product placed in a given environment to a given temperature. A sorption or desorption isotherm is expressed theoretically by the relations:

$$X_{eq} = f\,(RH)_{Ta}$$

Where:

X_{eq}: water content at the equilibrium of the product in ($kg_w.kg_{db}^{-1}$)

RH: relative humidity of the surrounding air (%)

T_a: temperature of surrounding air (°C).

The sorption isotherm is obtained with determination of the adsorption of water on a product sample, initially dry, exposed to an environment with an imposed relative humidity.

Desorption curve is obtained by placing a product, initially humid, in environment at decreasing relative humidity.

Several experimental methods enable one to determine the sorption or desorption

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isotherms.

In this work, the gravimetric method described elsewhere [14] was used to establish the desorption isotherms.

After breaking the cocoa pod, the beans were placed in a plastic cup of 1 liter in volume. They were covered with banana leaves as done by the producers. After the fermentation process that lasts for several days (4-6 days), the beans were placed in three small dishes which masses were previously measured.

The three small dishes and their contents were then weighed and introduced into a regulated oven whose temperature and humidity are maintained constant and equal to set values. The dishes with the cocoa samples were weighed regularly each day. When the weight remained constant, the measurement of the final weight gave the equilibrium mass content m_{eq}. The measurements were then repeated for new air conditions. For a given temperature, the first point was obtained for a relative humidity of 90%. The variation of relative humidity from 90% to 20% with 10% step lead to the determination of the equilibrium mass m_{eq} of each of the three samples for eight relative humidities and two temperatures.

The tested samples were then placed in an oven at 103 °C. Weighing was carried out with an electronic scale every 12 hours. After 72 hours the mass of the samples no longer varied and this mass was thus considered as the dry mass m_s of the sample.

The dry mass was used to calculate the equilibrium water content X_{eq} of each sample for each condition fixed beforehand using the following relation:

$$X_{eq} = \frac{m_{eq} - m_s}{m_s}$$

The experiment was carried out for two temperatures: 40 °C and 55 °C. The initial mass m_0 introduced in the climatic enclosure was the same for each sample: m_0 = 168.0g and the dried mass was m_s = 84.8g. The mean initial water content was 0.95 $kg_w.kg_{db}^{-1}$. The balance precision for mass measurement was dm = 0.1g. The uncertainty on X_{eq} calculated by relation (3) was found to be very low.

$$dX_{eq} = X_{eq}\left(\frac{2}{m_{eq} - m_s} + \frac{1}{m_s}\right)dm \qquad (3)$$

The uncertainty on the imposed relative humidity in the oven was dRH = 2%.

The validation of the sorption isotherm model has been done by calculating the Root Mean Square Error (RMSE) between experimental and calculated points.

2.2 Drying kinetics

The influence of the different parameters (drying air temperature and speed, thickness of the product layer) on the drying kinetics has been studied by experimental measurement under various conditions presented in Table 1.

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Table 1: Parameters values for the different drying experiments

Test number	T (°C)	v(m.s^{-1})	e (mm)	Loading density (kg.m^{-2})	Test number	T (°C)	v(m.s^{-1})	e (mm)	Loading density (kg.m^{-2})
1	40°C	0.25	20	14.2	10	55°C	0.25	20	14.2
2		0.5			11		0.5		
3		1.0			12		1.0		
4		0.25	30	24.0	13		0.25	30	24.0
5		0.5			14		0.5		
6		1.0			15		1.0		
7		0.25	40	32.0	16		0.25	40	32.0
8		0.5			17		0.5		
9		1.0			18		1.0		

For each product layer thickness, the experimental curves have also been used to determine the parameters of the drying characteristic curves of the fermented cocoa.

Sample conditioning was the same as previously described for sorption isotherm determination. The beans were placed on a tray of dimension 10.5 cm x 10.5 cm and of height 4, 3 or 2 cm. The tray was then introduced in a channel in a parallel airflow which temperature, humidity and speed were maintained constant during a test. This drying channel previously used [15] is represented in figure 1.

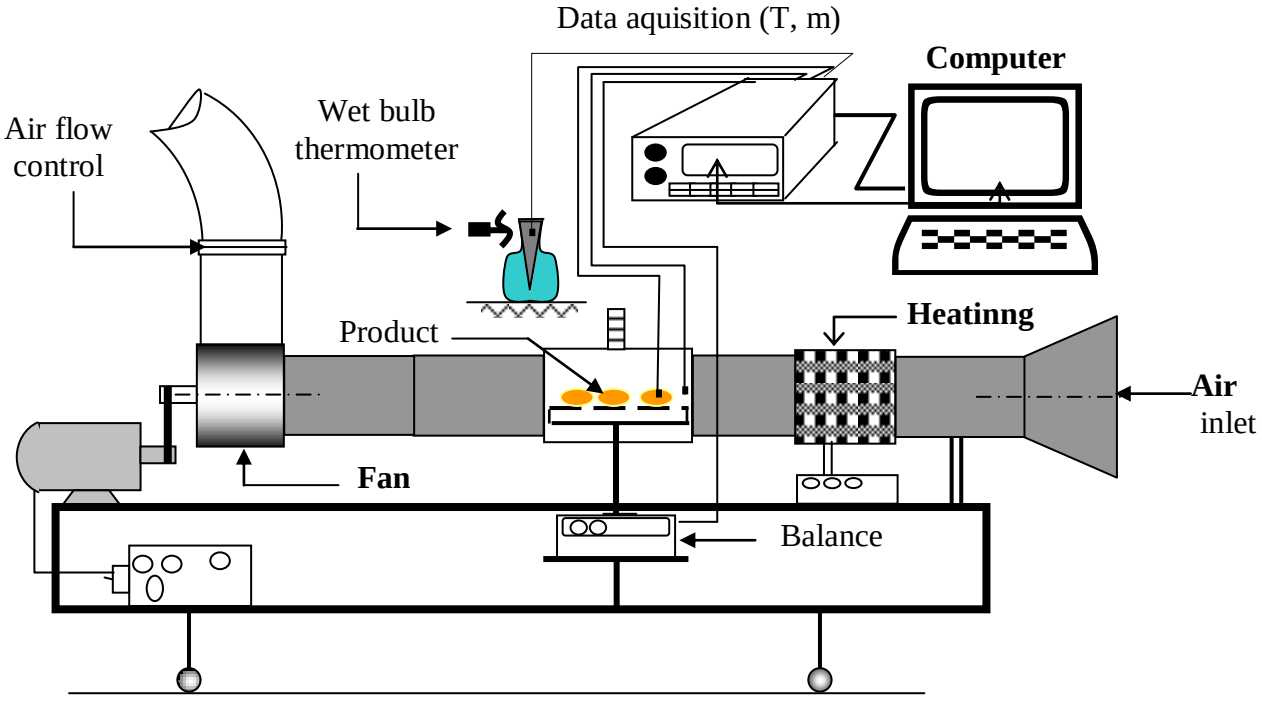

Figure 1: Schematic view of the drying tunnel

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The mass of the empty tray was determined before filling it with cocoa. The mass of the tray loaded with product, the relative humidity and the temperature of the drying air were recorded at regular time interval (15 minutes at the beginning of the test and 30 to 45 minutes at the end of the test).

At each measuring time, these mass measurement enabled the determination of the product mass m(t) and of the product water content by:

$$X = \frac{m(1+X_0)}{m_0} - 1 \qquad (4)$$

During the tests, drying air temperature was measured by means of an electronic thermometer with platinum probe. Speed control was achieved using a hot wire anemometer.

3. RESULTS AND DISCUSSION

3.1 Sorption isotherms

The experimental results are presented in Table 2.

Table 2: Experimental results for cocoa sorption isotherms

Temperature : 40°C		Temperature : 55°C	
RH	X_{eq}	RH	X_{eq}
0.9	0.122	0.9	0.131
0.8	0.084	0.8	0.087
0.7	0.068	0.7	0.064
0.6	0.056	0.6	0.055
0.5	0.048	0.5	0.042
0.4	0.040	0.4	0.037
0.3	0.032	0.3	0.028
0.2	0.031	0.2	0.020

Several empirical and semi-empirical models: GAB [16,17,18], BET [19], Harkins, Henderson [20], Oswin [21, 22], Chung [23] may be used to represent the desorption isotherms obtained experimentally.

In this study, three temperature dependent models (Henderson, Modified-Oswin and Chung) were tested to reproduce the desorption isotherms of cocoa. The constant values of the models were determined from the experimental results through minimization of the sum of the quadratic errors between the experimental points and the theoretical model using the Levenberg-Marquart algorithm [24]. Figure 2 shows that the Modified-Oswin's equation is the one that allowed the best description of the desorption isotherm of cocoa.

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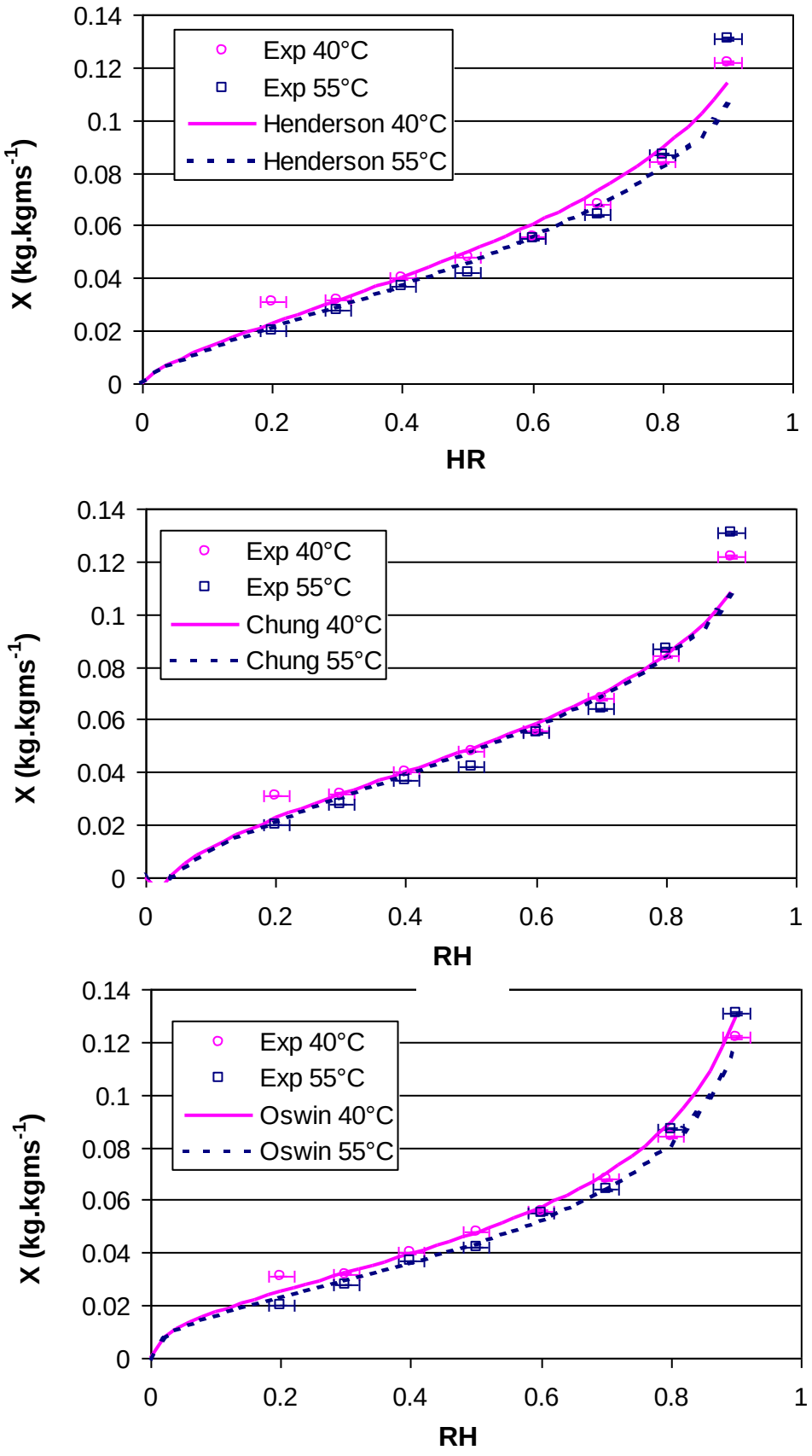

Figure 2: Experimental (40°C and 50°C) and modelled sorption isotherms of cocoa

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The estimation method leads to the following expression:

$$RH = 100 \times \left[1 + \left(\frac{0.1379 - 2.89 \times 10^{-4} T}{X} \right)^{2.187} \right]$$

Where T: Temperature (K)

The Root Mean Square Error (RMSE) between the experimental points and the model is 0.0071 $kg_w.kg_{db}^{-1}$ for a cocoa water content varying from 0.02 to 0.12 $kg_w.kg_{db}^{-1}$ and the average relative difference is 6.2 %. One generally considers that a value lower than 10% gives an acceptable representation of experimental results [25, 26]. Equilibrium water content decreases when temperature decreases. Nevertheless the difference in equilibrium water content remains low for isotherms at 40°C and 55°C (mean deviation of 5% between RH = 90% and RH = 30%). This result is in perfect agreement with previous works concluding that temperature has a weak influence on food products desorption isotherms between 25°C and 60°C [26, 27].

3.2 Drying kinetics

The transfer of moisture between air and the product is represented by a curve describing the change of water content with respect to time or the evolution of drying speed with respect to water content. The drying curves are determined from the measurements of the variation of the weight of the samples over time. They represent either the variations of the average water content X with respect to time, or the drying rate $-\frac{dX}{dt}$ with respect to X. To determine the curve $-\frac{dX}{dt} = f(X)$ is obtained by calculating the derived equation directly from the experimental points using the following expressions:

$$\left(\frac{dX}{dt}\right)_{t_i} = \frac{1}{2}\left[\frac{X_{i+1} - X_i}{t_{i+1} - t_i} + \frac{X_i - X_{i-1}}{t_i - t_{i-1}}\right] \quad i \neq 0, n$$

$$\left(\frac{dX}{dt}\right)_{t=0} = \frac{(X_0 - X_2)t_1^2 - (X_0 - X_1)t_2^2}{t_1 t_2 (t_2 - t_1)}$$

and $$\left(\frac{dX}{dt}\right)_{t_n} = \frac{X_n - X_{n-1}}{t_n - t_{n-1}}$$

Where n is the number of experimental points and t_n the drying experiment duration.

Error calculations on the values of the water content X, of the drying rate $V = \frac{dX}{dt}$ and of the reduced drying rate V_r has been done using the classical relations presented elsewhere [28]. Since the mean initial mass product was m_0 = 350.0g for a mean dried mass of 180.0g and a balance precision of 0.1g, the calculated uncertainties were very low (less than 0.006 $kg_w.kg_{db}^{-1}$ on X for example) and thus have not been represented on the figures.

Drying kinetics model

Several theories and models have been derived to predict the drying kinetics and to describe the physical processes controlling the heat and mass transfers. The complexity of the transfer mechanisms and the variable character of products

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(nature, form, physical properties) prevent establishing a unique model to be able to represent all the situations. The method of the characteristic curve of drying (CCD) is used in representing the reduced drying rate:

$$V_r = \frac{V}{V_0} = f(\phi)$$

Where:

$$\phi = \frac{X - X_{eq}}{X_0 - X_{eq}}$$

With:

V_r reduced drying rate

V_0 initial drying rate ($kg_w.kg_{db}^{-1}.s^{-1}$)

X_{eq} equilibrium water content ($kg_w.kg_{db}^{-1}$)

X average water content of product ($kg_w.kg_{db}^{-1}$)

X_0 initial water content ($kg_w.kg_{db}^{-1}$)

V_0 is calculated from the equation (7).

The whole reduced drying rates $V_r = f(\phi)$ obtained for different drying air conditions can often be represented with an acceptable precision by a unique curve called the drying characteristic curve of drying (DCC).

The direct method that supposes that the initial product water content is lower than the critical humidity was used to determine the value of V_0 from the experimental drying curve $-\frac{dX}{dt} = f(X)$.

The function f(ϕ) is a priori supposed to be the characteristic of the product studied. The mathematical expression of the function is chosen arbitrarily [29]. For the treatment of our data we choose to represent the drying characteristic curves by the commonly used power function:

$$f(\phi) = \phi^{\alpha}$$

Equations (9), (10), and (11) lead to the expression:

$$V_r = \frac{V}{V_0} = f\left[\frac{X - X_{eq}}{X_0 - X_{eq}}\right] = \left[\frac{X - X_{eq}}{X_0 - X_{eq}}\right]^{\alpha}$$

Where α is positive or null

The following process has been used to determine α: the points (X, V) and the values X_0, V_0 and X_{eq} are known for each test and enable the calculation of V_r and α for each measurement time t. One deduces for each experimental point an instantaneous value α_t such that

$$\alpha_t = \left[\frac{\ln(V_r)}{\ln(\phi)}\right]$$

For each test carried out with a given product thickness and known air drying conditions, the average value α_i is calculated by the expression:

$$\alpha_i = \frac{1}{n}\sum_{i=1}^{n}\alpha_t$$

Where n is the number of measurement points. The average value retained for the parameter α is calculated from the expression:

$$\alpha = \frac{1}{K}\sum_{i=1}^{K}\alpha_i$$

Where K is the number of drying tests carried out for each product thickness. The values of X_{eq} at 40°C and 55°C are determined by the isotherms of desorption at 40 and 55°C. The estimated values of the exponent α are reported in Table 3.

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Table 3: Value of α, characteristic parameter of the cocoa drying characteristic curve

n° exp.	α	n° exp.	α
1	1.77	10	1.28
2	1.58	11	1.51
3	1.55	12	1.25
4	1.45	13	1.41
5	1.64	14	1.45
6	1.71	15	1.53
7	1.72	16	1.82
8	1.23	17	1.49
9	1.52	18	1.48

The α value characterizes the drying rate decreasing from its initial value to the null asymptotic value. The mean α values estimated for each product thickness are finally: α_{20mm} = 1.61 ; α_{30mm} = 1.47 ; α_{40mm} = 1.48. These three mean values are very closed: the deviation of the estimated values for each product thickness from the mean value α = 1.52 is lower than 5.5%. So, one may considered that α does not depend strongly on the product thickness within the range 20-40mm and Considering the mean value of α, the modeled curves are closed to the experimental results as shown by figure 3 representing the experimental and simulated curves corresponding to tests number 8.

we further consider the mean value for all the experiments.

The model presented by expression (11) is used to describe the evolution of the reduced speed with respect to reduced water content. Its integration leads to the following expression of the product water content:

$$X = X_{eq} + \left[\left[X_0 - X_{eq} \right]^{1-\alpha} - \frac{V_0 \, (1-\alpha) \, t}{\left(X_0 - X_{eq} \right)^{\alpha}} \right]^{\frac{1}{1-\alpha}}$$

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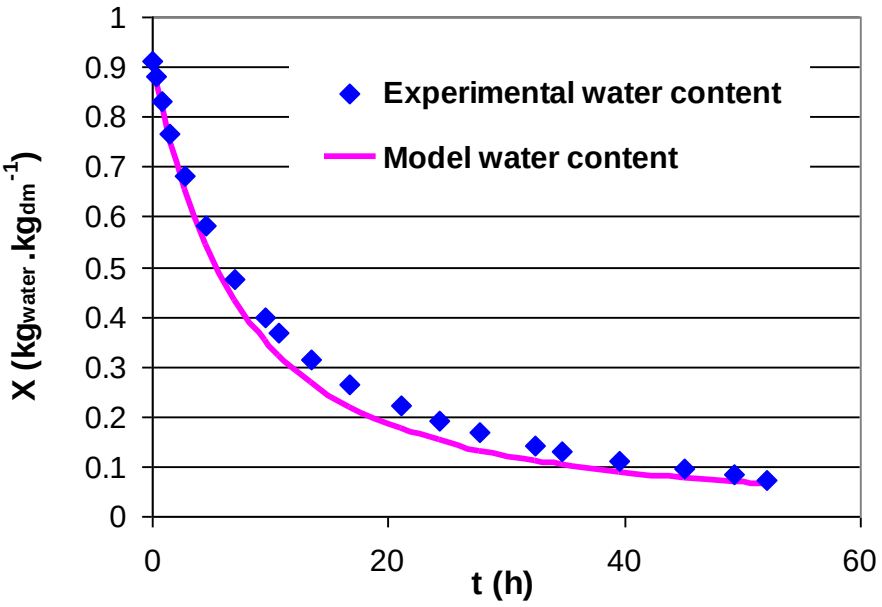

Figure 3: Experimental and model water content for test number 8: T = 40°C, ν= 0,5 m.s^{-1}, layer thickness = 4 cm, loading density = 32 kg.m^{-2}

The Root Mean Square Error (RMSE) between the whole experimental points and the model is 0.0346 $kg_w.kg_{db}^{-1}$ for a cocoa water content varying from 0.95 to 0.12 $kg_w.kg_{db}^{-1}$.

4. CONCLUSION

The desorption isotherms of fermented cocoa have been determined experimentally using the dynamic gravimetric method. A satisfactory mathematical representation has been obtained using the Modified-Oswin's model.

A series of drying curves for different operating conditions (air speed, air temperature, thickness of cocoa layer) were also obtained experimentally. An analysis of these curves enables the determination of the drying characteristic curve for cocoa beans. It was found that the drying characteristic curve does not depend on the product layer thickness since the main mass transfer resistance is located inside the bean and not between them.

The correlations obtained lead to a good theoretical reconstitution of the experimental results. One can thus calculate the duration of drying, an important parameter for driers conception, with respect to the conditions of drying air adopted and to the thickness of the product layer.

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NOMENCLATURE

dm	mass measurement uncertainty	kg
e	thickness of the layer of product	m
m_o	initial weight of product	kg
m	product mass	kg
m_{eq}	equilibrium product mass	kg
m_s	dry product mass	kg
RH	relative humidity	%
T_a	temperature of surrounding air	°C
T	temperature	°C
V	drying rate	$kg_w.kg_{db}^{-1}.s^{-1}$
V_r	reduced drying rate	
V_0	initial drying rate	$kg_w.kg_{db}^{-1}.s^{-1}$
X_{eq}	equilibrium water content	$kg_w.kg_{db}^{-1}$
X	average water content	$kg_w.kg_{db}^{-1}$
X_0	initial water content	$kg_w.kg_{db}^{-1}$
α	exponent of the function representing the drying characteristic curve	
ϕ	reduced water content	
ν	speed of drying air	$m.s^{-1}$

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