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Water transport in parchment and endosperm of coffee bean

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Abstract

This paper aims at contributing to identify the eventual regions where fungus *Aspergillus ochraceus* could grow and produce ochratoxin A (OTA) during drying of coffee beans. Internal structure of coffee bean was analyzed by optical microscopy for endosperm and parchment. From the expression of the dissipation in the grain due to the water transport, we show that a relationship formally analogous to an equation of diffusion governs the water transport. Three structures with mass transfer resistance potential are studied: parchment, silver skin and endosperm. An experimental technique to study the water transfer into the parchment was proposed. In the endosperm, for moisture contents above 65%, a constant transport coefficient controls the drying kinetics of the whole bean. Below this moisture content, water transport coefficient (with and without silver skin) were significantly lesser than those for the whole bean. This is firstly due to the reduction of the pore space occupied by water and second to the increasing bonding energy between solid structure and water as moisture content decreases. The contribution of parchment to the protection of the endosperm is highlighted.

Keywords: Coffee internal structure, drying, sorption isotherms, water transport coefficient, ochratoxin A.

NOMENCLATURE

a	Thermodynamic activity	
C	Volumetric concentration	$kg \cdot m^{-3}$
D	Dissipation	$J \cdot m^{-3} \cdot s^{-1}$
h	Parchment thickness	m

k_c	Mass transfer coefficient	$m \cdot s^{-1}$
K_{eq}	Average water distribution constant between phases	
$K(X)$	Water transport coefficient in a structure	$kg \cdot s \cdot m^{-3}$
l	Characteristic length for diffusion	m
m	Mass	kg
M	Molecular mass	$kg \cdot kgmol^{-1}$
N	Mass flux	$kg \cdot m^{-2} \cdot s^{-1}$
r	Mass transfer resistance	$kg \cdot m^{-2} \cdot s^{-1}$
R	Gas constant (8314.0)	$J \cdot kgmol^{-1} \cdot K^{-1}$
S	Entropy	$J \cdot K^{-1}$
t	time	s
T	Temperature	K or ^{o}C
U	Internal energy	J
v	apparent velocity	$m \cdot s^{-1}$
V	Volume	m^3
X	Moisture content	$kg \cdot (kg\ dm)^{-1}$

Greek symbols

μ	Chemical potential	$J \cdot kg^{-1}$
ρ	Density	$kg \cdot m^{-3}$
Δ_w	Water transport coefficient	$m^2 \cdot s^{-1}$

Subscripts

0	At initial or in one side
1	At the other side
a	For air
av	Averaged

e	At equilibrium
en	In endosperm
pa	In parchment
s	For dry matter
w	For water
α	In a heterogeneous structure

1. INTRODUCTION

Coffee is the second most valuable legal commodity in the world (Pendergrast, 1999; Kouadio *et al*., 2007). According to FAO (2008), coffee is sold in 78 countries around the world and 20 to 25 million families depend on its trade. Coffee cherries are subjected to two different post-harvest treatments where the main objectives are to remove the various layers surrounding coffee beans and to dry them in order to prevent the growth of microorganisms (Paulino De Moraes & Luchese, 2003; Suárez-Quiroz *et al*., 2004). The most usual treatment is called “wet”. In this method, coffee cherries are put in a tank filled with water in order to separate the defective beans and to remove the pulp and mucilage. Then, “washed” coffee beans are dried. An alternative is to use the “dry” method in which coffee cherries are directly dried to get grayish beans known as "coffee coke" or “natural coffee”. After drying, the parchment and the other layers covering the beans are removed mechanically to get the “green” coffee.

Regardless the post-harvest method, drying can be carried out naturally (using sun) and/or artificially (using dryers). Drying has been identified as a step where fungal contamination can develop (Frank, 2000; Paulino de Moraes & Luchese, 2003; Taniwaki *et al*., 2003; Kouadio *et al*., 2007). Particularly, *Aspergillus ochraceus*, a common host fungus, produces a toxin (Ochratoxin A, OTA) which have teratogenic, immunotoxic and possibly neurotoxic and carcinogenic properties. Moreover, this toxin has a high thermal stability up to 250ºC (FAO, 2008). Considering the risk for human health, fungus development should be avoided to prevent OTA production. Among the factors that govern the fungal development, water activity (a_w) has been underlined to be the most important (Suárez-Quiroz *et al*., 2004; Kouadio *et al*., 2007). Actually, temperature influences the production rate while not being a limiting factor (Suárez-Quiroz *et al*., 2004). The optimal conditions for the growing of A. *ochraceus* are given by a water activity of 0.95 and a temperature of 35ºC while its development is inhibited with a water activity lower than 0.80 and a temperature less than 10ºC (Suárez-Quiroz *et al*., 2004). From this research, it results that 0.8 is a critical value for the prevention of OTA production. However, it represents an average value over the whole coffee bean that does not account for the water distribution resulting from moisture diffusion during the drying process. Moreover, *A. ochraceus* develops at the coffee bean surface while fungal spores penetrate

about a few micrometers inside. Then, the development of *Aspergillus ochraceus* in coffee bean may be seen as a competition between its capacity of water supply and a decrease on the water activity in the internal parts of the grain consecutive to drying. When coffee bean has not been damaged (cracks, separation of the parchment) this competition takes place on the surface of the grain, and it is the combination between the water activity and the water transport properties in the parchment and the surface layer of the endosperm. As consequence, it seems essential to analyze precisely the water distribution rather than its average content (Frank, 2000).

During the drying process, water transport coefficient is one of the most important parameters because it governs water distribution in the grain (Geankoplis, 1998). Usually, water transport is evaluated from the fitting of an adequate Fick's law equation to experimental drying kinetic (Mulet, 1994; Maroulis *et al*., 1995; Wang & Brennan, 1995; Bialobrzewski & Markowski, 2004; Efremov & Kudra, 2004; Hernández *et al*., 2008). Sfredo *et al*. (2005) and Correa *et al*. (2006) have determined the water transport coefficient in coffee cherries. Both rely on a Crank's solution of Fick's law valid for sphere (Crank, 1975) since it is a fair approximation of the coffee cherry geometry. The water diffusivity values measured obtained by Sfredo *et al*. (2005) lie in the range [0.1-1x10^{-10}] $m^2 \cdot s^{-1}$ at 45°C and [0.3 - 3x10^{-10}] $m^2 \cdot s^{-1}$ at 60°C, while those found by Correa are 2.91x10^{-10}; 3.57x10^{-10} and 4.96x10^{-10} $m^2 \cdot s^{-1}$ at 40, 50 and 60°C respectively. To improve the geometrical description of coffee cherries, Hernández *et al*. (2008) developed a Fick's law solution considering a non-conventional geometry: prolate spheroid geometry.

In many products with a complex micro-structure such as wood and pasta (Mrani & Bénet, 2005), Agar gel (Mrani *et al*., 1995) and latex (Auria *et al*., 1991), water transfer is controlled by physicochemical and mechanical interactions occurring at the interfaces between phases: capillarity, osmotic effects, surface adsorption, liquid-gas phase change (Bénet *et al*., 2009), water transfer between cells and walls. Therefore, transfer coefficients represent a superposition of different phenomena and depend on moisture content. In particular water transfer coefficients cancel as the moisture content tends towards zero. In this case, the use of diffusion and of Crank's solutions to describe mass transfer may be questionable for media presenting a complex microstructure.

Finally, the objective of this study is to contribute, through microscopic analysis and local mass transfer measurements, the potential regions where fungus could develop and produce OTA during drying processes. Therefore, this paper deals with the four following aspects: 1) Analysis by a thermodynamic approach of the law for water transport in a complex media 2) Microscopic observation of coffee bean in order to identify the different structures of coffee beans and their heterogeneity; 3) Characterization of the relationship between water activity and moisture content and 4) Study of the dependence of transport properties on moisture content.

These physical characteristics will be useful to improve the numerical modeling of the drying process. By simulating various drying scenarios, it should lead to propose different strategies to avoid the development of fungus.

2. Thermodynamic approach to water transport in complex media

Complex media such as food, gel and biological tissues are characterized as having several structures (α at Equation 1) which can be solid, liquid or gas phases, superficial layers, film layers, membranes, cells, and cell walls. In such complex media the use *a priori* of a law similar to Fick's law seems not appropriate. However many experimental results of media as complex as coffee endosperm (wood, gels, food) seem to show that this law is sufficient to describe water transfer at the macroscopic level as it will be demonstrated in the following discussion.

The thermodynamic state of water in a structure α is characterized by the mass chemical potential, given by (Callen, 1985):

$$\mu_{w\alpha} = \left(\frac{\partial U_\alpha}{\partial m_{w\alpha}} \right)_{S_\alpha, V_\alpha, m_{\alpha j} \; j \neq w} \tag{1}$$

Where $\mu_{w\alpha}$ is the water chemical potential at structure α and is defined as the partial derivative of the internal energy contained in a Representative Elementary Volume (REV), with respect to water mass, taking entropy, volume of α in the REV and the mass of the other constituents as constants. The chemical potential characterizes the action of the other media constituents upon the water from the structure α, regardless of the form of the water: liquid, gas, adsorbed by the liquid phases, in films or in superficial layers.

Water transport phenomena in the structure obey the second principle of thermodynamics. Assuming uniform and constant temperature, in the absence of chemical reactions and neglecting the effect of gravity, the dissipation in structure α due to water transport phenomena in all forms can be written as (Müller, 2001; Kuiken, 1994):

$$D_{w\alpha} = -\rho_{w\alpha} v_{w\alpha} \nabla \mu_{w\alpha} \geq 0, \quad \forall \alpha \tag{2}$$

Where $D_{w\alpha}$ is the dissipation in structure α. Considering the Gibbs Duhem relationship (Callen, 1985) applied to each phase, Eq. 2 is retained when water transport is handled by the mechanisms of filtration of the phases and their surface layers (Prigogine & Mazur, 1951; Bénet & Jouanna

1982). The positivity of the dissipation term is ensured if the mass flow of water in structure α is of the following form:

$$\rho_{\alpha w} v_{w\alpha} = -K_{\alpha}(X_{\alpha}) \nabla \mu_{w\alpha}, \quad \forall \alpha \tag{3}$$

Where X_{α} is the moisture content of the structure α. Eq. 3 is the expression of the second principle of thermodynamics. It highlights the fundamental property of the chemical potential (Callen, 1985) i.e. regardless the form in which a constituent is present (water in this case), it moves from high chemical potential values to low chemical potential values. The function $K_{\alpha}(X_{\alpha})$ is positive and represents the water transport coefficient within α. This function depends on the moisture content of α. In agricultural products such as coffee, cocoa and wheat the characteristic dimensions of the structures α are very small if compared with those of the grain. For coffee, as will be shown later, the relationship between cell size and the grain is on the order of 10^{-3}; the ratio for the cell wall is about 10^{-4}. We will assume that the equilibration time between two grain structures α, for example, between the cell and the cell wall is very fast compared to the drying time which can be of the order of one day. We adopt the assumption of local equilibrium at α: the thermodynamic equilibrium of water between the different structures is performed. This hypothesis implies that the chemical potential of water is the same in all structures α and its chemical potential is symbolized by $\mu_w = \mu_{w\alpha} \quad \forall \alpha$.

Then, the global flux of water is obtained by,

$$\rho_w v_w = \sum_{\alpha} \rho_{\alpha w} v_{\alpha w} = -\left(\sum_{\alpha} K_{\alpha}(X_{\alpha}) \right) \nabla \mu_w \tag{4}$$

Each structure is characterized by a desorption isotherm, which represents the monotonic variation of moisture content X_{α} as a function of water activity ($a_{w\alpha}$) in the structure α. We will use the inverse function $a_{w\alpha} = a_{w\alpha}(X_{\alpha})$. The chemical potential of water mass in the structure is given by the relationship (Callen, 1985):

$$\mu_{w\alpha} = \mu_w = \frac{RT}{M_w} \ln a_{w\alpha}(X_{\alpha}), \quad \forall \alpha \tag{5}$$

As μ_w value has being fixed, the moisture contents of each structure X_α adapt to meet the equality of chemical potentials (Eq. 5). The average moisture content of the medium in a REV is defined by,

$$X = \frac{m_w}{m_s} = \sum_\alpha \frac{X_\alpha m_{s\alpha}}{m_s} \tag{6}$$

Where m_w is the total mass of water in the REV, $m_s = \sum_\alpha m_{s\alpha}$ is the total mass of solid in the REV and $m_{s\alpha}$ is the mass of solid in the structure α in the REV. In the absence of dissolution or chemical reactions, the relationships $m_{s\alpha}/m_s$ are constant, knowledge of moisture content in the different structures X_α give the value of X by (Eq.6) and μ_w by (Eq.5). So there is a relationship between X and water activity denoted by $a_w(X)$:

$$\mu_w = \frac{RT}{M_w} \ln a_w(X) \tag{7}$$

Conversely according to Eq.7, knowledge of X lets us know the value of μ_w. With this value, Eq. 6 gives the moisture contents in each structure. There is a relationship of the form $X_\alpha = X_\alpha(X), \forall \alpha$ and therefore the coefficients $K_\alpha(X_\alpha)$ in Eq. (4) can be expressed as a function of X. The global transport coefficient can also be expressed as:

$$K(X) = \sum_\alpha K_\alpha(X_\alpha(X)) \tag{8}$$

Given this relationship, the overall (global) flux of water is expressed by:

$$\rho_w v_w = -K(X) \nabla \mu_w \tag{9}$$

From Eq. (7), Eq. (9) can be written as:

$$\rho_w v_w = -K(X) \frac{RT}{M_w a_w} \frac{\partial a_s}{\partial C_s(X)} \nabla C_s(X) \tag{10}$$

Defining,

$$\Delta_w(X) = K(X)\frac{RT}{M_w a_w}\frac{\partial a_s}{\partial C_s(X)} \tag{11}$$

Eq. (10) becomes,

$$\rho_w v_w = -\Delta_w(X)\nabla C_s(X) \tag{12}$$

Formally Eq. (12) is presented in a similar form to Fick's law. This is valid only to describe the diffusion of a constituent in a unique phase: solid, liquid or gas. The transport coefficient depends on moisture content. With the assumption of local equilibrium, Eq. (12) allows us to describe the water transport in a complex media, formed of juxtaposed structures, in which various mass transport mechanisms are present. This relationship involves the assumption of a thermodynamic equilibrium localized between the different forms of water**.** The formal similarity between Eq. (12) and Fick's law authorizes the use of all the mathematical developments concerning this law. In particular the use of mathematical solutions developed by Crank for particular geometries remains applicable. However, it is improper to call $\Delta_w(X)$ as water diffusivity in media because it combines several transport phenomena; it will be called the water transport coefficient later in this document.

3. MATERIALS AND METHODS

Fermented washed coffee beans (Arabica variety) from crops 2008 and 2009 were used in this study. Both samples were obtained from "Beneficio La Cuchilla" located in Huatusco, Veracruz, Mexico. Moisture content was determined by the method from AOAC (1990) No. 22.013, in which samples are introduced into a vacuum oven and subjected to an absolute pressure of 13.3 kPa and a temperature of 60°C until two consecutive weights differ from less than 10^{-4} g.

3.1 Coffee bean general structure characterization

For the characterization of the general structure, measures of the three principal axes of fermented washed coffee beans were made using an electronic Vernier. Also a computer representation was generated from a real coffee bean. Three cameras where set up surrounding

one coffee bean and shoot at the same time. The obtained pictures served to generate a geometrical model using the software ImageWorks © (2008).

3.2 Preparation of samples for microscopic observation of coffee bean

The cellular distribution of coffee bean was studied from coffee bean slices. The resulting slices were stained by immersion in safranin for 30 min, followed by washings with ethanol of different concentrations, and left in contact with fast green for 10 min, finally they were washed in pure ethanol and observed in an optical microscope Leica DM 500. Pictures of the slices were taken using a camera coupled to the microscope. Also the cell diameter and cellular wall thickness was measured using the software Image J © (2008). To analyze the internal heterogeneity and transport properties, subsamples of coffee beans were prepared. Using a special cylindrical cutting tool (Fig.1.a), coffee beans were separated in 6 different parts (Fig. 1.b). In the following discussion these parts are denominated: parchment (a), silver skin (b), endosperm part 1 (c), endosperm part 2 (d), extremities (e, f). The 2 parts of the endosperm (c, d) are separated by the natural discontinuity observed in Fig. 1.

3.3 Distribution of water activity

In order to check if water content heterogeneities can be observed throughout a coffee bean, sorption isotherms of the different parts were determined. With the subsamples prepared (Fig. 1.b), 5 different sorption isotherms have been determined by considering the whole coffee bean and the 4 internal parts: parchment (a), endosperm part 1 (c), endosperm part 2 (d) and extremities (e, f). The silver skin (b) is too thin and light to get some accurate sorption measurements.

Sorption isotherm points for water activities less than 0.92 were obtained by the standard method using saturated salt solutions at 35°C (AOAC, 1990), while water activities between 0.92 and 0.99 were measured by means of a mechanical method (Ouoba *et al*., 2010). This new method allows to measure high water activity values in a shorter time (about one day) avoiding the risk of fungal development.

3.4 Mass transfer in coffee bean

To identify eventual heterogeneities in water transport, water transport coefficients were evaluated with 4 different samples: the whole bean, the endosperm with silver skin, the endosperm without silver skin and the parchment.

3.4.1 Determination of the water transport coefficient in the endosperm

Analytical solutions of the Fick's equation were established for various configurations (Crank, 1975). In the case of an infinite slab, the asymptotic solution is given by,

$$\frac{X - X_e}{X_0 - X_e} = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 \Delta_{wen}\, t}{4 l^2}\right) \tag{13}$$

This asymptotic solution is valid only for $X - X_e \,/\, X_0 - X_e$ <0.7 (Crank, 1975). To develop this solution, we made the following hypothesis (i) initial moisture content is uniform, (ii) interfacial mass transfer negligible and (iii) a constant transport coefficient over time which implies to consider short times. To approach these conditions, we adopted an incremental method which consists in two stages: (i) equilibrium of a coffee sample with a saturated salt solution to obtain uniform initial moisture content; (ii) change in the saturated salt solution to start the drying process. Ten samples of endosperm, previously separated from coffee beans with and without silver skin, were glued on an aluminum plate. The aluminum plate was disposed in the device described in Fig. 2 in which the samples were equilibrated at 35°C with a saturated salt solution. The equilibrium of the samples was checked by the weight stability over time. The initial salt solution was then replaced by a potassium acetate solution fixing water activity at 0.21. From that point, the plate weight was recorded continuously. At the end of the experiment, the moisture content was determined by standard methods (AOAC, 1990). The water transport coefficient in endosperm (Δ_{wen}) was calculated by fitting Eq. (13) to the weight loss kinetics at times that satisfy $X - X_e \,/\, X_0 - X_e$ <0.7. Like in this case the sample was dehydrated by one side, the characteristic length for diffusion (*l*) is the complete thickness of the sample. This procedure was repeated with different initial salt solutions in order to impose water activities of 0.43, 0.50, 0.62, 0.75 and 0.84.

The experimental device described in above paragraph is such that the endosperm sample were dehydrated by one side under natural convection, therefore in order to verity assumption (ii), the mass Biot number defined by (Córdova *et al.*, 1996) and described in Eq. (14) was estimated.

$$Bi_m = \frac{k_c l}{\Delta_{wen}} \frac{K_{eq} \rho_{sa}}{C_{sen}} \tag{14}$$

Where the mass transfer coefficients (k_c) must be calculated for natural convection. The empirical correlations reported by Geankoplis (1998) were used.

3.4.2 Determination of water transport coefficient on a whole grain with high moisture content

At coffee bean fresh state, it can be admitted that the porous space is saturated with water**.** Water transport may be characterized by an averaged water transport coefficient (Δ_{wav}) which

corresponds at the moisture content of green coffee bean supposed uniform on all the grain. In order to take account of the shape of the grain, Hernandez *et al.*, (2008) show that prolate spheroid geometry fairly approximates the shape of a coffee bean, and the asymptotic solution Fick´s second law in this case is,

$$\frac{X - X_e}{X_0 - X_e} = 0.78 \exp\left(-\frac{12.3 \Delta_{wav} t}{l^2}\right) \tag{15}$$

In this case, the characteristic length for diffusion (l) is the focal distance of prolate spheroid. In order to measure the averaged water transport coefficient in the whole coffee bean, tests were conducted in a pilot plant composed of a fixed bed dryer and an imposed transversal air flow with a 0.0024 m^2 section. The air flow can be regulated up to 2 m s^{-1} and 80°C. Tests were carried at two temperatures: 35 °C and 45°C and the air velocity was imposed at 1.5 $m \cdot s^{-1}$. These conditions are similar to those encountered in solar drying where the risk of OTA development is high (Mburu, 1999). In each test, the drying kinetics is evaluated by recording the weight loss as function of time and moisture content is calculated at the end. Averaged water transport coefficient was calculated by fitting Eq. (15) to the experimental results that satisfied $X - X_e / X_0 - X_e$ <0.7 with semi-log regression. Statistical validation was performed through the 95% confidence interval of the parameter fitted.

3.4.3 Determination of the transfer coefficient in the parchment

Parchment samples look like 6mm diameter and 0.1mm thickness confetti (a in Fig. 1). The thickness of parchment is negligible with respect to endosperm and the methodology described in previous section is not appropriate. Moreover, since the thickness is not uniform, discrepancies are introduced in the estimation of diffusivity. Therefore, we adopt an averaging point of view by relying on a global water transfer resistance. The water flux (N_w) is assumed to be proportional to the water activity difference $a_{w1} - a_{w0}$ imposed on both sides of the parchment,

$$N_w = r \left(a_{w1} - a_{w0} \right) \tag{16}$$

Thus, an experimental method has been developed to determine the water transfer resistance (r) of the parchment. The parchment sample was disposed between two deformable polypropylene tubes (T1, T2) (Fig. 3) and compressed. Then, the compression effort was maintained by needless (E) ensuring perfect airtightness. Each tube is connected to saturated salt solutions imposing 2

different values of water activity, a_{w0} on bottom surface and a_{w1} on top. The entire device was placed in a closed thermo-regulated chamber at 35°C, and the weight of bottom salt solution is recorded continuously. The water activity difference activates a water flux N_w through the parchment sample evaluated by the weight loss or gain of the bottom salt solution. The flux was calculated from the slope obtained by linear regression in the linear zone of weigh vs. time plot. To increase the water vapor flux and therefore decrease measurement discrepancies, five systems (Fig. 3) were set together. Tests have been carried out with 3 and 5 devices and compared to validate the method. The moisture content of the parchment is evaluated from the average of moisture content imposed on both sides by water activities a_{w0} and a_{w1} using the sorption isotherm determined as is described in section 3.3. Experimental conditions are summarized in Table 1. Statistical validation was performed through 95% interval confidence of the slope obtained by linear regression. A comparison between endosperm and parchment water transport coefficients, may be obtained from the Eq. (16) expressed in terms of parchment water transport coefficient (Δ_{wpa}) as follows,

$$N_w = \frac{\Delta_{wpa} C_{spa}}{h} \left(X_1 - X_0 \right) \tag{17}$$

where X_0 and X_1 are the parchment moisture content at water activities a_{w0} and a_{w1} respectively.

4. RESULTS AND DISCUSSION

4.1. Characterization of the structure

4.1.1 Characteristic dimensions

Characteristic dimensions of coffee bean were determined as exposed in section 3.1. The obtained values were for the major axis: 11.6 mm, small axis: 8.1 mm, thickness: 4.6 mm, surface: 1.293×10^{-4} $m^{2,}$ volume: 1.99×10^{-7} m^3, and the focal distance calculated considering a prolate spheroid geometry (Eq. 15) was 4×10^{-3}m.

4.1.2. Internal structure

Cross-sections perpendicular to the coffee major axis were sliced from fermented washed coffee beans. All slices were prepared as described in section 3.2 and images were taken by optical microscopy. The objective is to identify some heterogeneities in the internal structure has already reported (Eira *et al.*, 2006; De Castro & Marraccini, 2006).

Observations reveal a rupture of the tissue in the upper part of the endosperm (Fig. 4). Since it does not have a specific anatomical name, it will be called “natural discontinuity”. Mucilage left-over was found in the natural discontinuity as shown by Sutherland *et al.* (2004).

Heterogeneities in physical properties can result from variations in the cell arrangement and distribution. When focusing at the cell shape, two different geometries are encountered: “rectangular” and “polyhedral” depending on the number of cell edges. On cross-section images, it is generally observed that the natural discontinuity is surrounded by “rectangular” cells while the rest of endosperm is made up of “polyhedral” cells. Therefore, the cells pattern and distribution seems to be oriented by the natural discontinuity. However, even though some differences in the cells arrangement are observed, internal structure dimensions are almost uniform over the whole bean. On a zooming image (Fig. 5), cells dimensions are indicated. Cell diameters were between 30 to 60µm while the wall thickness ranges from 9 to 11µm.

The microstructure of parchment is shown in Fig. 6. One can notice the fibers with a high level of cross-linking in agreement with the description made by Kasser & Kasser (1969). Regarding to the chemical composition, the main compound of endosperm is a polymannan while parchment is principally composed of lignin and pentose. Thus, coffee parchment has a structure that strongly differs from the endosperm and this aspect should result in differences in physical properties.

4.2 Sorption isotherms

Five sorption isotherms were obtained: parchment, internal and external endosperm, extremities and whole bean. The experimental points are plotted in Fig. 7. The continuous lines represent the best fit with GAB model except at high water activities (a_w > 0.84) where the Ferro-Fontan model is used (Ferro-Fontan *et al.*, 1982). No significant differences between the sorption isotherms of the endosperm, extremities and the whole bean were observed. However, the behavior of parchment was found to be different at high water activities (a_w > 0.8). It indicates a lower hygroscopic nature in the parchment which may be attributed to its lignocellulosic composition. This aspect is of particular importance since *Aspergillus ochraceus* develops principally in this region. The sorption behavior difference shown in Fig. 7 implies a moisture content discontinuity at the endosperm/parchment interface, i.e., at equilibrium the moisture of parchment is lower.

4.3. Water transport coefficients

4.3.1. Water transport coefficient in the endosperm

The transport coefficient (Δ_{wen}) of endosperm (c in Fig. 1.b) with and without silver skin (b in Fig. 1.b) was evaluated by the method described in section 3.4.1. The average thickness of samples was 0.9 mm, and the water transport coefficients obtained at different moistures are

plotted in Fig. 8. The moistures associated with water transport were calculated as the mean between the initial and final moisture which are considered for the slope of Eq. (13) log transformation. This figure shows that the water transport coefficient depends on moisture content at moistures < 0.65. This effect confirm the fact that at high moisture contents (>0.65), corresponding to high activity values (a_w>0.95), the water is practically "free", i.e., its mobility is maximal, and therefore it leads a constant value for the water transport coefficient. As the moisture content decreases, two phenomena participate to reduce the water diffusivity which tends to zero. First, the reduction of water volume fraction inside the pore space decreases water flow; second, the increase of water bonding with solid structure since hygroscopic effects become predominant. Moreover, it has already been observed that, during the drying process, the entrance in the hygroscopic domain corresponds to the transition from a water saturated system to a non-saturated system, i.e., a gas phase appears and its volume fraction increases. Therefore, the combination of these two effects account for the decreasing transport coefficient observed experimentally as the moisture content tends to zero. Regarding to the silver skin, Fig. 8 results show that it leads to 10% decrease of the effective diffusivity.

The Biot mass number were calculated with Eq. (14) using the Δ_{wen} values of Fig. 8, with the following values: $l = 0.009\ \mathrm{m}$ (average endosperm thickness), $k_c = 0.007\ \mathrm{m \cdot s^{-1}}$ (Geankoplis 1998 correlation for natural convection), $\rho_{sa} = 1.1\ \mathrm{kg \cdot m^{-3}}$, $C_{sen} = 800\ \mathrm{kg \cdot m^{-3}}$ and $K_{eq} = 0.63$. This last value was calculated as indicate Cordova et al., (1996), and represents the average distribution constant between air and product moistures at low contents in product. The mass Bi number obtained were from 30 to 120. These values confirm the negligible interfacial resistance assumption required in Eq. (13).

4.3.2. Averaged water transport coefficient in the whole grain with a high moisture content

The averaged water transport coefficient at high moisture content can be evaluated from the drying kinetic of the whole bean (Fig. 9) by means of linear regression onto Eq.(15). It can be noticed in Fig. 9 that the curves show a linear behavior between 1 h and 4 h for the test at 45 °C and between 1 h and 8 h for the test at 35 °C. It is in these intervals that are determined the transport coefficients. Average initial moisture of coffee beans (X_0) was 1.054, and the equilibrium moisture (X_e), calculated with sorption isotherms was 0.069. Values obtained at 35°C and 45°C were respectively (2.84±0.125) x 10^{-11} and (9.41±0.494) x 10^{-11} $m^2.s^{-1}$. The error estimation represents the 95% confidence interval. The averaged transport coefficient at 45°C agrees with the water diffusivity reported by Sfredo *et al*. (2005) which ranges between 1.0 x 10^{-11} to 10 x 10^{-11}. The lower and upper limits of averaged water transport coefficient were included in the Fig. 8. One can note that this value agrees with the endosperm one for moisture contents higher than

0.65. Regarding to the whole coffee bean at high moisture content, these results confirm the water transport coefficients obtained for endosperm at high moisture contents. Additionally, the mass Bi number evaluated in the past section was for natural convection, and the averaged water transport coefficient evaluated in this section was under forced convection. Like the interfacial mass transfer is promoted by forced convection, it is evident that the use of Eq. (15), which implies a negligible interfacial mass transfer, is justified.

4.3.3. Water mass transfer resistance in parchment

Fig. 10 shows the weight variation over time of the bottom salt solution for various experiments. After a transitional period required to equilibrate samples with both salt solutions, weight gain varies linearly allowing to identify the water resistance coefficient, *r*, by means of Eq. (16). Results are summarized in Table 1. The errors listed in Table 1 are the result of 95% confidence interval obtained from linear regression of the slope in linear zone of data in Fig. 10. The water transport coefficient in parchment (Δ_{wpa}) can be determined by using Eq. (17). The parchment average thickness was approximated 0.1 mm, and the volumetric concentration of the dry solid was taken 800 kg.m^{-3}. The values obtained are plotted in Fig. 8. Regarding water mass transfer coefficient a unique value of 5x10^{-13} $m^2 \cdot s^{-1}$ has been reported by Nilnont *et al.* (2012). They estimated the water mass transfer in parchment using the water diffusivity which was calculated by fitting the Fick second law solution (Eq. 13) on their drying kinetics results. Water diffusivity is a common name for the water transport coefficient deduced in section 2. Moreover, the reported value is two magnitude order lower than the calculated in this work. However Nilnont *et al.* (2012) values were obtained from drying kinetics performed with 50 g of parchment in a tray drier and they state that parchment is extremely thin but did not report this thickness. The water transport coefficient obtained from Eq. (13) is highly dependent on characteristic length of diffusion. Then, the values of resistance listed in Table 1, and the water transport coefficient in parchment plotted in Fig. 8 have more confidence.

5. CONCLUSIONS

Coffee bean is a system extremely heterogeneous in a macroscopic level (parchment, endosperm, furrow) as well as in a cellular level. Parchment and endosperm present significant differences in their structures. Parchment structure is fibrous, very close to the wood, while that of the endosperm revealed cells of form and orientation fairly uniform. This difference in structure is reflected by the difference of their isotherms for water activities ranging between 0.8 and 1. This difference is particularly important because it is in this interval of water activity that fungus develops. It has been shown that by adopting the water chemical potential as the gradient for transport and the assumption of a local equilibrium inside media, water transport can be described by a law which

combine the different transport mechanisms. The averaged coefficient $\Delta_w X$ depends, for an isothermal case and an undeformable solid phase, on the moisture content of media. Silver skin weakly reduces the water transfer from the endosperm to the parchment. Furthermore, in a fresh state, the silver skin is hydrated and fills the furrow. As drying goes forward, the silver skin gets thinner and a gas phase appears. This could lead to fungal development in the furrow and will be the focus of further investigations. The water transfer resistance of parchment associated with its weak hygroscopic nature can lead to a moisture content discontinuity between external gas phase and the gas phase located at the parchment/endosperm interface. This activity difference can be evaluated through Eq. 17. For instance, with a mass flux corresponding to the drying kinetics at 35°C (Fig. 9), the water activity difference between both sides of parchment is about 0.49. Therefore, parchment reduces the risk of *Aspergillus ochraceus* contamination in the endosperm if compared to a case where it has been destroyed. Finally, the experimental techniques presented should allow a fine analysis of the drying process inside a coffee bean, but description of water transfer at the microscopic scale can only be carried out by numerical simulation. These models will allow the estimation of drying conditions that prevent the fungal development.

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