



## The variable nature of Biot numbers in food drying

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### ABSTRACT

Biot numbers ( $Bi$ ) relate internal and external resistances to mass or heat fluxes and are useful to identify controlling mechanisms. Their variation during drying received little attention despite its importance in model selection. Therefore, variable  $Bi$  were analysed in drying of wheat, a low-moisture product, and in the formation of a low-calorie, dehydrated apple-leather (LCAL), a high moisture product. Wheat drying was predicted with a numerical solution from a m.c. of 0.35 kg water/kg dry matter, to find a variable mass transfer  $Bi$  that shifted the controlling mechanism from internal–external to internal. From a lower m.c. of 0.205 kg water/kg dry matter, the entire process was internally controlled. Drying of shrinking LCAL was solved with the energy balance. The mass transfer  $Bi$  varied from 0.5 to 1600, while the heat transfer  $Bi$ , only from 0.25 to 0.5, and a modified version, from 0.25 to 0.

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### 1. Introduction

The Biot number is a dimensionless group that relates a measure of the rate of internal heat conduction or mass diffusion in solids with a measure of the rate of external convection. It appears in partial differential equations of transport phenomena, when the surface boundary condition relating internal and external fluxes is expressed in dimensionless form.

A typical graph used by many chemical and food engineers was published first by Gurney and Lurie (1923), who analytically solved the unsteady state heat conduction equation with an infinite series, providing the predictions of dimensionless local temperature inside the solids (the dependent variable), as a function of the dimensionless time for several dimensionless positions (the independent variables) and several Biot numbers. An inherent assumption is that the Biot number remains constant during the process. The analytical series eventually converges in one term at long times, allowing straight lines to be plotted in a semilog graph. These graphs were and are still used to solve heat transfer problems for regular geometries as slab, infinite cylinder and sphere, as well as three-dimensional regular geometries (Singh and Heldman, 1993).

The risk of assuming the validity of the heat and mass transfer analogy for using these graphs to solve mass transfer processes as

drying is that the mass transfer Biot number may vary during the process (Giner and Mascheroni, 2001). Another problem that usually appears in drying is that moisture content in solids is not a uniform field across the solid–fluid interface unlike the vapour pressure, so a sorption relationship must be used to transform moisture contents at the solid surface into vapour pressure (Crapiste and Rotstein, 1997).

Adhikari et al. (2005), during a research aimed at predicting stickiness during spray drying of a sugar-rich solution, have predicted the evolution of Biot numbers during the process in a 120  $\mu\text{m}$  initial diameter drop. They found internal control for the mass transfer rate from the start, and a predominantly external control for heat transfer. However, additional contributions are required to study the definition and variation of the heat and mass transfer Biot numbers in larger food particles in order to assess changes in the controlling mechanisms. This feature is in itself relevant, and, besides, provides better background for selection of suitable mathematical models and methods of solution. This is especially important nowadays, where much of the contemporary drying research resorts to empirical kinetic models, which do not explain the drying mechanisms (Akpınar et al., 2003).

Therefore, the objectives of this work were (1) to calculate mass and heat transfer Biot numbers during drying of foods and (2) to analyse their behaviours.

To this end two case studies are presented: wheat drying kinetics, using data from a previous study, and formation of a low-calorie, apple-leather during hot-air dehydration, a novel product.

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**Nomenclature**

$A$	transfer area of food in Eq. (16), $m^{-2}$	$nt$	time index for numerical integration, $t = (nt - 1) \Delta t$
$a_w$	water activity, decimal	$N_{mh}$	parameter in Eq. (3)
$Bi_c$	heat transfer Biot number, dimensionless	$p_s$	saturation vapour pressure of pure water, Pa
$Bi_{cd}$	heat transfer Biot number, defined in Eq. (19), dimensionless	$p_v$	vapour pressure at food surface, Pa
$Bi_m$	mass transfer Biot number, dimensionless	$p_{va}$	partial vapour pressure in the air bulk, Pa
$C_{mh}$	parameter in Eq. (3)	$p_{vad}$	dimensionless vapour pressure at food surface
$C_p$	specific heat of food defined in Eq. (17), $J\ kg^{-1}\ dry\ matter\ K^{-1}$	$p_{vo}$	initial vapour pressure at food surface, Pa
$C_w$	local concentration of water in food in Eq. (13), $kg\ m^{-3}$	$r$	radial coordinate in a wheat grain, m
$C_{w0}$	initial local concentration of water in food, $kg\ m^{-3}$	$R$	equivalent spherical radius in wheat, m
$D_{eff}$	effective diffusion coefficient of water in the food, $m^2\ s^{-1}$	$r_{ad}$	dimensionless radial coordinate in a wheat grain
$D_{eff0}$	effective diffusion coefficient of water in food at $W_0$ defined in Eq. (20), $m^2\ s^{-1}$	$R_g$	gas constant, $J\ mol^{-1}\ K^{-1}$
$D_\infty$	Arrhenius preexponential factor in Eq. (22), $m^2\ s^{-1}$	$t$	time, s
$D_{\infty 1}$	parameter in Eq. (4)	$T$	grain temperature in Eq. (3), $^\circ C$
$D_{\infty 2}$	parameter in Eq. (4)	$T_a$	air temperature, $^\circ C$
$E_a$	activation energy in food drying, $J\ mol^{-1}$	$T_m$	time-dependent average temperature of food in Eq. (16), $^\circ C$
$h_T$	air-food heat transfer coefficient, $W\ m^{-2}\ K^{-1}$	$T_{m0}$	initial food temperature, $^\circ C$
$h_{Td}$	air-food heat transfer coefficient, defined in Eq. (19), $W\ m^{-2}\ K^{-1}$	$x$	coordinate along food thickness in Eq. (13), m
$i$	space index for numerical integration of Eq. (13), $x = (i - 1) \Delta x$	$W$	local moisture content of food, kg water/kg dry matter
$I$	total number of points along $x$ for numerical integration of Eq. (13)	$W_{ad}$	dimensionless moisture content of food
$K_{mh}$	parameter in Eq. (3)	$W_e$	equilibrium moisture content, kg water/kg dry matter
$k_p$	air-food mass transfer coefficient, $kg\ vapour\ m^{-2}\ s^{-1}\ Pa^{-1}$	$W_0$	initial moisture content of food, kg water/kg dry matter
$k_T$	food thermal conductivity, $W\ m^{-1}\ K^{-1}$		
$L$	variable thickness of food during drying, m		
$L_0$	initial food thickness in Eq. (19), m		
$m_s$	food dry mass in Eq. (16), kg		
$m_{wev}$	rate of water evaporation in food in Eq. (16), $kg\ s^{-1}$		
$n$	parameter in Eq. (20)		
		<b>Greek symbols</b>	
		$\Delta H_{ws}$	heat of desorption of water from food in Eq. (16), $J\ kg^{-1}$
		$\Delta x$	distance step for numerical integration of Eq. (13), m
		$\Delta t$	time step for numerical integration of Eq. (13), s
		$\rho$	density of food at moisture content $W$ , $kg\ m^{-3}$
		$\rho_d$	density of food dry matter in Eq. (19), $kg\ m^{-3}$
		$\rho_{d0}$	ratio of the dry matter in the food to its initial volume, $kg\ m^{-3}$
		$\rho_0$	initial density of food, $kg\ m^{-3}$
		$\rho_w$	density of liquid water, $kg\ m^{-3}$

**2. Mathematical modelling****2.1. Model describing wheat drying kinetics**

By assuming the grain as a sphere with an average diffusion coefficient,  $D_{eff}$ , the water transport inside the grain may be represented by the combination of the microscopic mass balance and the first Fick's law of diffusion (Crapiste and Rotstein, 1997):

$$\frac{\partial W}{\partial t} = D_{eff} \left( \frac{\partial^2 W}{\partial r^2} + \frac{2}{r} \frac{\partial W}{\partial r} \right) \quad (1)$$

With the following initial and boundary conditions.

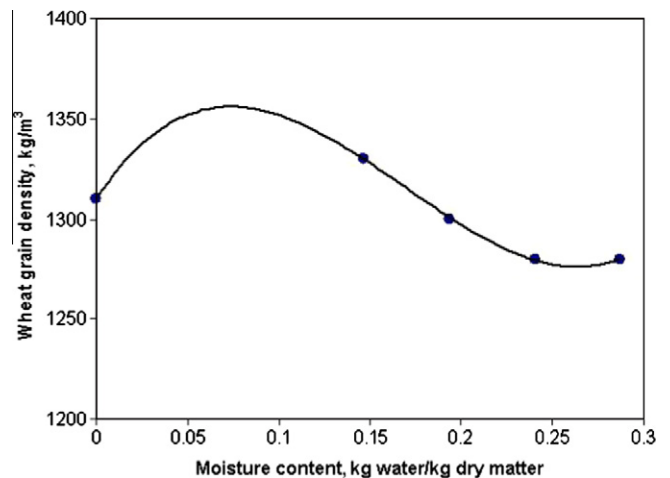
$$t = 0 \quad W = W_0 \quad 0 \leq r \leq R \quad (2.1)$$

$$r = 0 \quad \frac{\partial W}{\partial r} = 0 \quad t > 0 \quad (2.2)$$

$$r = R \quad -\rho_{d0} D_{eff} \frac{\partial W}{\partial r} \Big|_{r=R} = k_p (p_v - p_{va}) \quad t > 0 \quad (2.3)$$

where  $\rho_{d0}$  is the ratio of the dry mass to the grain volume,  $\rho_{d0} = \rho_0 / (1 + W_0)$ ,  $\rho_0$  being the grain particle density at the initial moisture content,  $W_0$ . Wheat density data measured by Giner and Denisienia (1996) was analysed here to develop a third-grade polynomial correlation with moisture content (Fig. 1).

On the other hand, water activity  $a_w = p_v/p_s$  and  $W$ , the local moisture content in the grain (kg water/kg dry matter), are related



**Fig. 1.** Experimental (●) and predicted (—) data of wheat grain density ( $\rho$ ) as a function of moisture content ( $W$ ) in kg water/kg dry matter. The predictive expression used was an empirical third-grade polynomial,  $\rho = 23463.5 W^3 - 11872.3 W^2 + 1370.8 W + 1310.0$ . The coefficient of determination,  $r^2$  was of 0.999. The correlation is valid for moisture contents  $W$  between 0 and 0.3 kg water/kg dry matter.

by the sorption isotherm. Symbol  $p_v$  is the water vapour pressure at the food surface, while  $p_s$  is the saturation vapour pressure of pure water, predicted with a correlation published earlier (Giner and Mascheroni, 2001). The symbol  $p_{va}$  is the partial pressure of water vapour in the air bulk and  $k_p$  is the mass transfer coefficient in kg water vapour/m<sup>2</sup> s Pa. The modified Henderson equation was selected for the  $a_w$ - $W$  relationship, which has been widely used to predict drying processes in grains. Considering that  $a_w = p_v/p_s$ ,

$$W = 0.01 \left[ \frac{-\ln\left(1 - \frac{p_v}{p_s}\right)}{K_{mh}(T + C_{mh})} \right]^{1/N_{mh}} \quad (3)$$

For breadmaking wheat,  $K_{mh}$ ,  $C_{mh}$  and  $N_{mh}$  are  $2.301 \times 10^{-5}$ , 55.815 and 2.2857, respectively (Brooker et al., 1992). Both in wheat (Giner and Mascheroni, 2001) and soybean drying (Gely and Giner, 2007), no quantitative differences were observed in the predicted mean grain moisture content as a function of time, between the isothermal model of Eqs. (1)–(3) and the non-isothermal model that adds heat transfer coupling. The enormous differences between heat and mass transfer rate, the small size of grains and its low-moisture nature were found to be the causes of this nominally isothermal drying. Therefore, only the mass transfer model was solved for wheat. All properties used in wheat were taken from Giner and Mascheroni (2001), except the diffusion coefficient which was developed by the same authors in a subsequent article (Giner and Mascheroni, 2002).

$$D_{eff} = [D_{\infty 1} + D_{\infty 2}(W_0 - 0.1891)] \exp\left(-\frac{E_a}{R_g(T_a + 273.16)}\right) \quad (4)$$

where  $D_{\infty 1} = 5.046 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  and  $D_{\infty 2} = 54.44 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  (kg water/kg dry matter). The value of the activation energy was  $E_a = 27,184 \text{ J mol}^{-1}$ . The symbol  $T_a$  is the drying air temperature, in °C.

### 2.1.1. Calculation of the mass transfer Biot number

To establish an uniform field variable across the grain–air interface, the surface boundary condition Eq. (2.3) was expressed in an equivalent, alternative form, by including the following identity.

$$\frac{\partial W}{\partial r} \equiv \left(\frac{\partial W}{\partial p_v}\right) \left(\frac{\partial p_v}{\partial r}\right) \quad (5)$$

which, once included into the surface boundary condition (Eq. (2.3)), becomes

$$r = R \quad -\rho_{d0} D_{eff} \frac{\partial p_{vs}}{\partial r} = \left(\frac{k_p}{\frac{\partial W}{\partial p_v}}\right) (p_v - p_{va}) \quad t > 0 \quad (6)$$

where  $\rho_{d0}$  is the dry matter divided by the grain volume. To find the mass transfer Biot number, variables must be expressed in dimensionless form

$$W_{ad} = \frac{W - W_e}{W_0 - W_e}; \quad r_{ad} = \frac{r}{R}; \quad p_{vad} = \frac{p_v - p_{va}}{p_{v0} - p_{va}} \quad (7)$$

where  $R$ , is the grain equivalent radius, was taken as  $2.0 \times 10^{-3}$  and  $1.8 \times 10^{-3} \text{ m}$  for initial moisture contents ( $W_0$ ) of 0.35 and 0.205 kg water/kg dry matter, respectively (Giner and Mascheroni, 2002). The symbol  $W_e$  stands for the equilibrium moisture (kg water/kg dry matter), calculated with Eq. (3) for the temperature and relative humidity of the drying air. Knowing that  $p_v$  is the water vapour pressure at the solid surface ( $r = R$ ),  $p_{v0}$  represents its initial value. Vapour pressure drops from  $p_v$  to  $p_{va}$  in the air film surrounding the grain. The derivative of moisture with respect to vapour pressure can be more easily evaluated from the sorption isotherm model if we consider the following identity

$$\left(\frac{\partial W}{\partial p_v}\right) \equiv \frac{1}{p_s} \left(\frac{\partial W}{\partial a_w}\right) \quad (8)$$

The formal definition of the mass transfer Biot becomes,

$$Bi_m = \frac{k_p R}{\frac{1}{p_s} \left[ \left(\frac{\partial W}{\partial a_w}\right)_{r=R} \right] \rho_{d0} D_{eff}} \quad (9)$$

This dimensionless number expresses the ratio of the internal resistance to mass transfer to the external one. The internal is represented by the grain equivalent radius ( $R$ ) and the reciprocal of the diffusion coefficient ( $D_{eff}$ ) while the external, by the reciprocal of the mass transfer coefficient ( $k_p$ ).

By using Eq. (3), the following derivative is found:

$$\left(\frac{\partial W}{\partial a_w}\right) = 0.01 \left(\frac{1}{N_{mh}} - 1\right) \left(\frac{1}{K_{mh}(T + C_{mh})}\right)^{\left(\frac{1}{N_{mh}}\right)} [-\ln(1 - a_w)] \left(-\frac{1}{1 - a_w}\right) \quad (10)$$

By replacing the expressions of Eq. (7)–(9) into Eq. (6), the definition of the mass transfer Biot number,  $Bi_m$  becomes.

$$Bi_m = \frac{k_p R}{\frac{1}{p_s} \left[ 0.01 \left(\frac{1}{N_{mh}} - 1\right) \left(\frac{1}{K_{mh}(T + C_{mh})}\right)^{\left(\frac{1}{N_{mh}}\right)} [-\ln(1 - a_w)] \left(-\frac{1}{1 - a_w}\right) \right]_{r=R} \rho_{d0} D_{eff}} \quad (11)$$

In a previous work, Parti (1993) had defined  $Bi_m$  as  $k_y R/(\rho D_{eff})$ , where  $k_y$  is the mass transfer coefficient for a flux equation that utilises the driving force in air humidity units. While this variable is directly related with the partial pressure of vapour in air, the expression of Parti does not include the conversion between food moisture content and air humidity or vapour pressure at the interface and is therefore incorrect.

On the other hand, if Biot numbers are predicted for non-isothermal systems and/or using moisture-dependent diffusion coefficients, the value of  $D_{eff}$  must be evaluated at the temperature and/or local moisture content prevailing at the surface at any time. Besides, models predicting shrinkage during drying, must update the product characteristic dimension in each time step of the numerical calculation. Therefore, apart from the variable nature of the conversion factor ( $\partial W/\partial a_w$ ), possible variations in  $D_{eff}$  and  $R$  mean that the mass transfer Biot number would change considerably during drying.

### 2.1.2. Conventional heat transfer Biot number

The heat transfer Biot number.

$$Bi_c = \frac{h_T R}{k_T} \quad (12)$$

was calculated at the same conditions as for the mass transfer counterpart. As  $h_T$ , the interfacial heat transfer coefficient (Giner and Mascheroni, 2001) have a weak temperature dependence, and as  $k_T$  is a smooth function of moisture content (Sokhansanj and Bruce, 1987),  $Bi_c$  is not expected to vary considerably during drying.

## 2.2. Drying model for the formation of a low-calorie apple-leather (LCAL)

### 2.2.1. Product characteristics

The LCAL was formulated to experience gelation during drying by the saccharide-acid-high methoxyl pectin mechanism. A previous formulation (Leiva Díaz et al., 2009) composed of peeled apple puree, sucrose and citric acid, was modified by replacing sucrose by polydextrose which is a polysaccharide and thickener that provides only a quarter of the energy intake of sucrose (Cicuttin and Giner, 2006). The initial formulation had the following composition (% w/w): water, 80 (or 4 kg water/kg dry mater); carbohydrates, 8.86; proteins, 0.27; lipids, 0.087; citric acid, 0.17; polydextrose, 10; sucralose, 0.02. It was dried in a forced convection oven with



**Fig. 2.** Photograph of the dehydrated low-calorie, apple pectic gel, with a moisture content of 0.50 kg water/kg dry matter and a water activity of 0.86. When removed, it occupied the whole base of a  $0.13 \times 0.18$  m tray. Product thickness was of about 2.5 mm.

an air velocity of 0.2 m/s from its initial moisture content up to a final value of 0.5 kg water/kg dry matter, corresponding to a water activity of 0.86, which prevents growth of pathogenic bacteria (Beuchat, 1981, 1983). A photograph of the product, is given in Fig. 2. It must be indicated that the LCAL provides 667.1 kJ/100 g of finished product (Cicuttin and Giner, 2006), 42% less than the sucrose-added apple-leather developed by Leiva Díaz et al. (2009).

### 2.2.2. Diffusion equation

The diffusion equation with variable diffusion coefficient, considering product shrinkage involves a coupled model of heat and mass transfer in a plane sheet, formed by the microscopic mass balance considering product shrinkage plus the macroscopic energy balance. This was solved by a combination of the explicit finite-difference and the fourth-order Runge Kutta methods, respectively. The diffusion equation is as follows:

$$\frac{\partial c_w}{\partial t} = D_{\text{eff}} \frac{\partial^2 c_w}{\partial x^2} + \frac{\partial D_{\text{eff}}}{\partial c_w} \left( \frac{\partial c_w}{\partial x} \right)^2 \quad (13)$$

The initial and boundary conditions, are:

$$t = 0 \quad c_w = c_{w0} \quad 0 \leq x \leq L \quad (14.1)$$

$$x = 0 \quad \frac{\partial c_w}{\partial x} = 0 \quad t > 0 \quad (14.2)$$

$$x = L \quad -D_{\text{eff}} \frac{\partial c_w}{\partial x} = k_p \cdot (p_v - p_{va}) \quad t > 0 \quad (14.3)$$

where  $L$  is the variable thickness of the LCAL,  $D_{\text{eff}}$  is the diffusion coefficient of water in the forming gel ( $\text{m}^2 \text{s}^{-1}$ ), dependent on the local water concentration,  $c_w$  in kg water/ $\text{m}^3$  product, and temperature,  $T$  in °C. The symbol  $x$  stands for the coordinate in the thickness direction (m). The relationship between local water concentration and local moisture content in kg water/kg dry matter is:

$$W = \frac{c_w}{\rho - c_w} \quad (15)$$

where  $\rho$  stands for product density.

### 2.2.3. Macroscopic energy balance

Preliminary numerical solutions using a microscopic heat balance coupled with the mass balance showed that the temperature profiles are almost uniform, so that the problem of describing product temperature as a function of time can be tackled with a macroscopic energy balance.

$$m_s C_p \frac{dT_m}{dt} = h_T A (T_a - T_m) - \Delta H_{ws} m_{\text{wev}} \quad (16)$$

where  $T_m$  is the average product temperature and °C,  $T_a$  the drying air temperature. The value of  $\Delta H_{ws}$ , the heat of desorption of water from the food, was considered the same as that for pure water in the moisture range considered, as observed in sugar-rich products by Kaymak-Ertekin and Gedik (2004). In turn,  $C_p$  is the variable specific heat based on the product dry mass, ( $\text{J kg}^{-1}$  dry matter °C), whose expression was developed by rearranging the well-known Siebel correlation for high moisture foods (Mohsenin, 1980)

$$C_p = 837.4 + 4187 W \quad (17)$$

The symbol  $m_{\text{wev}}$  is the rate of water evaporation i.e., kg water vapour/s, which for using in Eq. (16) can be calculated by the interfacial mass transfer equation:

$$m_{\text{wev}} = k_p A (p_v - p_{va}) \quad (18)$$

The initial condition to solve Eq. (16) was  $t = 0$ ;  $T_m = T_{m0}$ , the initial product temperature.

### 2.2.4. Product properties

**2.2.4.1. Shrinkage relationship.** Volume of product decreases linearly with the decrease in moisture content, in agreement with previous reports (Leiva Díaz et al., 2009). Shrinkage was one-dimensional, being the thickness the only shrinking dimension in agreement with observations for gels by Kechaou et al. (1987). Therefore, the volumetric ratio  $V/V_0$  becomes the thickness ratio  $L/L_0$ . Shrinkage was considered equivalent to the volume of water evaporated, so the following relationship was utilised for this LCAL, based on a similar model previously developed for sucrose-added, apple-leather (Leiva Díaz et al., 2009).

$$\frac{V}{V_0} = \frac{L}{L_0} = 1 - \frac{W_0}{\rho_w \left( \frac{1}{\rho_d} + \frac{W_0}{\rho_w} \right)} + \frac{1}{\rho_w \left( \frac{1}{\rho_d} + \frac{W_0}{\rho_w} \right)} W \quad (19)$$

where  $W_0 = 4$  kg water/kg dry matter. The value of the dry matter density,  $\rho_d$  was considered equal to that for sucrose-added, apple leathers, i.e.,  $1382 \text{ kg m}^{-3}$ . The symbol  $\rho_w$  stands for the density of liquid water.

**2.2.4.2. Diffusion coefficient.** This transport parameter,  $D_{\text{eff}}$ , was correlated with the volumetric water concentration by Cicuttin and Giner (2006). They have observed that analytical solutions for diffusion for plane sheets (Crank, 1975; Leiva Díaz et al., 2009), considering constant volume and diffusion coefficient, predicts the drying curve of apple leathers reasonably well. Analytical solutions include the dimensionless time or Fourier number  $D_{\text{eff}} t/L^2$  and, as gels evidently shrink, it was considered that the ratio of  $D_{\text{eff}}$  to  $L^2$  must remain reasonably constant on an average basis so  $D_{\text{eff}}$  must also decrease during drying. To extend this concept to a local basis, it can be proposed that the ratio of the local diffusion coefficient,  $D_{\text{eff}}$  to the instantaneous total thickness  $L$  is such that  $D_{\text{eff}}/L^n$  is a constant. Then, the relationship used to determine  $n$  was as follows.

$$\frac{D_{\text{eff}0}}{L_0^n} = \frac{D_{\text{eff}}}{L^n} \quad (20)$$

Using kinetic data at short times, where shrinkage was neglected, the initial diffusion coefficients  $D_{\text{eff}0}$  were fitted with an analytical solution for  $\text{Bi} = 2$  (Leiva Díaz et al., 2009). These coefficients were considered only a function of temperature obeying the Arrhenius law. Then, data at long times were predicted with an analytical series for internal control. Using the final moisture content and sheet thickness,  $L$ , the final diffusion coefficient  $D_{\text{eff}}$  was

estimated. Then the power  $n$  was calculated by Eq. (20) to be 1.58. Therefore, the diffusion coefficient relationship was now the following.

$$D_{\text{eff}} = D_{\text{eff0}} \left( \frac{L}{L_0} \right)^{1.58} \quad (21)$$

where  $D_{\text{eff0}}$ , as indicated earlier, was an Arrhenius function of temperature, only. Using Eq. (19) in Eq. (21) and rearranging, the final expression of the local diffusion coefficient in the presence of shrinkage was obtained.

$$D_{\text{eff}} = \left[ D_{\infty} \exp \left( \frac{-E_a}{R_g(T_m + 273.16)} \right) \right] \cdot \left\{ \frac{0.28067}{1 - 0.71933 \cdot \frac{c_w(1+W_0)}{\rho_0 W_0}} \right\}^{1.58} \quad (22)$$

where  $D_{\infty} = 7.547 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  is the preexponential factor, while  $E_a$ , the activation energy, was found to be  $19,715 \text{ J mol}^{-1}$ . The factor enclosed by square brackets is  $D_{\text{eff0}}$ , while the multiplier written in curly brackets, represents the ratio of  $L/L_0$ . The effective diffusion coefficient increases for increasing water concentration  $c_w$  and product temperature,  $T_m$ . The correlation of Eq. (22) was developed by Cicuttin and Giner (2006) and follows structural collapse concepts of a products in the rubbery state (Aguilera, 2005). Symbol  $\rho_0$  stands for the initial product density =  $1058.5 \text{ kg m}^{-3}$ . To convert from moisture content on dry matter basis to water concentration in  $\text{kg m}^{-3}$ , Eq. (15) was used in the form

$$c_w = \rho \left( \frac{W}{1+W} \right) \quad (23)$$

Concerning the dependence of total product density with moisture content, the model developed earlier by Leiva Díaz et al. (2009) was utilised, which is related with the shrinkage model of Eq. (19). The density model predicts:

$$\rho = \frac{\rho_d(1+W)}{1 + \frac{\rho_d}{\rho_w} W} \quad (24)$$

**2.2.4.3. Air-product heat and mass transfer coefficients.** These were measured in previous experiments (Cicuttin and Giner, 2006) of steady-state water evaporation carried out in the same mechanical-convection oven at an air velocity of  $0.2 \text{ m/s}$ . The average heat transfer and mass transfer coefficient were found to be  $h_T = 21.9 \text{ W m}^{-2} \text{ K}^{-1}$  and  $k_p = 1.51 \times 10^{-7} \text{ kg water vapour/(m}^2 \text{ s Pa)}$ . Existing correlations differ considerably in the low air velocity zone (Welti-Chanes et al., 2003; Marinos-Kouris and Maroulis, 1995), thus the need of the experimental determinations.

**2.2.4.4. Variable thickness.** The domain of Eq. (14), i.e.,  $x$  from 0 to  $L$  was discretised in  $I$  nodes, so  $I - 1$  distance intervals  $\Delta x$  were created, with  $x = (i - 1) \Delta x$ . Then, the space index “ $i$ ” varies from 1 to  $I$  for nodes and from 1 to  $I - 1$  for intervals. The time, in turn, was discretised as  $t = (nt - 1) \Delta t$ . Therefore the leather thickness at any time during drying was calculated by:

$$L = \sum_{i=1}^{I-1} \Delta x_{i,nt} \quad (25)$$

Each space interval is reduced after each time interval using the shrinkage expression (Eq. (19)).

### 2.2.5. Calculation of the heat transfer Biot number during drying

Given the absence of published data for this type of leather, the thermal conductivity for apples in  $\text{J m}^{-1} \text{ K}^{-1}$  was utilised (Mohsenin, 1980).

$$k = 0.148 + 0.493 \frac{W}{1+W} \quad (26)$$

Therefore, the expression used to calculate the time-varying heat transfer Biot number is

$$\text{Bi}_c = \frac{h_T L}{k} = \frac{h_T \sum_{i=1}^{I-1} \Delta x_{i,nt}}{0.148 + 0.493 \frac{W_{i,nt}}{1+W_{i,nt}}} \quad (27)$$

The peak observed in Fig. 6 reflects the interplay occurring in Eq. (26) as a function of time between a decreasing thickness in the numerator and a decreasing thermal conductivity in the denominator. Both parameters diminish as a consequence of the reduction in the surface moisture content. Nevertheless, the order of magnitude keeps unaltered, since the values range from 0.25 at the beginning, to 0.55 at the peak and then reduce back to almost 0.30 at the end of the drying process.

### 2.2.6. Calculation of the mass transfer Biot number

By using the formal definition established in Eq. (11) and adapting it to this case study where variable diffusion coefficient, and variable leather thickness are predicted as a function of time, a specific definition of the mass transfer Biot number for shrinking materials was reached using Eqs. (14.3), (23) and (24), which was computed as follows:

$$\text{Bi}_m = \frac{k_p \sum_{i=1}^{I-1} \Delta x_{i,nt}}{\left\{ \frac{1}{\rho_s} \left( \frac{\partial W_{i,nt}}{\partial a_w} \right) \rho_d \frac{D_{i,nt}}{\left( 1 + \frac{\rho_d}{\rho_w} W \right)^2} \right\}} \quad (28)$$

The derivative of moisture content at the surface with respect to water activity was calculated in this LCAL with a Halsey equation, whose parameters were previously fitted to experimental data measured by an Aqualab 3TE water activity meter (Cicuttin and Giner, 2006). No net effect of temperature was found, in agreement with Leiva Díaz et al. (2009). Moisture contents were measured in atmospheric oven at  $105 \text{ }^\circ\text{C}$  until constant weight (Greensmith, 1998). In this high initial moisture product, the water activity interval was divided in two, leading to high and low-moisture Halsey models (see Appendix).

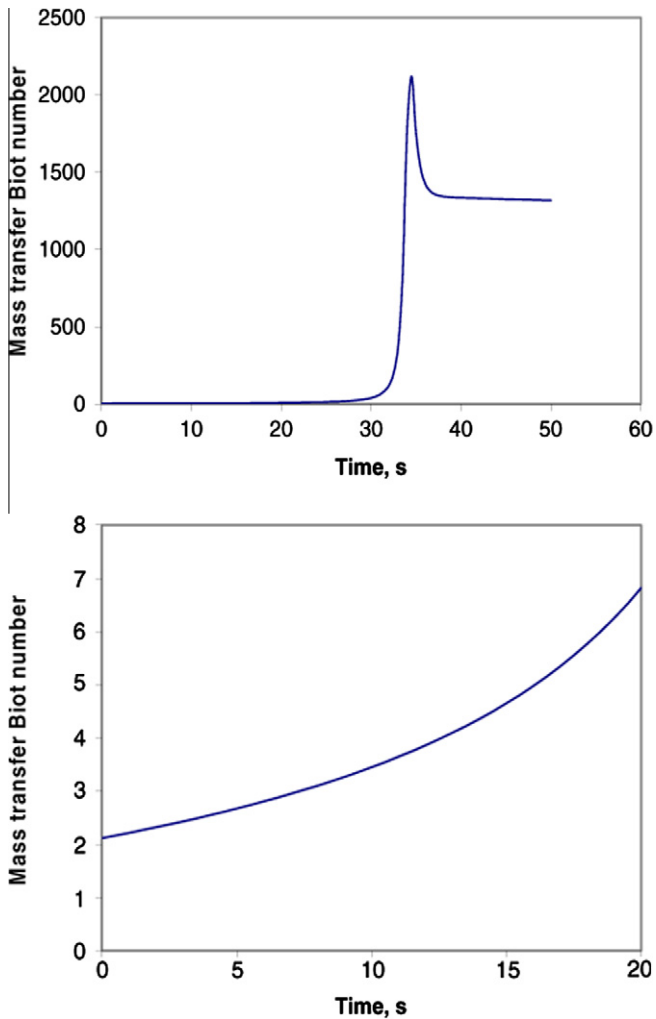
## 3. Results and discussion

### 3.1. Wheat drying

#### 3.1.1. Variation of the mass transfer Biot number for high moisture contents

The exact analytical solution for Eq.(1), with initial and boundary conditions (2.1), (2.2), (2.3) (Crank, 1975), assumes that the Biot number is constant, i.e., not time-dependent. Few if any contributions were provided by the literature to depict the variation of the mass transfer Biot number during drying. For this purpose, the diffusion equation mentioned above was numerically solved by an implicit finite-difference scheme. The radius domain was discretised in 31 nodes, using a time step of 1 s. A Matlab program was written for this purpose, being the predictions completely stable. The mass transfer Biot number was studied as a function of time for wheat drying, firstly from an initial moisture content of  $0.35 \text{ kg water/kg dry matter}$ . This unusually high water content for wheat was selected in order to clarify the predicted behaviour plotted in Fig. 3.

Being the mass transfer coefficient, sphere radius, dry matter density relationship and effective diffusion coefficient assumed constant, the only variable factor is the derivative of moisture content with respect to water activity (hereafter slope). This slope is placed in the denominator of Eq. (10), so the mass transfer Biot depends reciprocally on it. The behaviour of  $\partial W/\partial a_w$  is typical of a

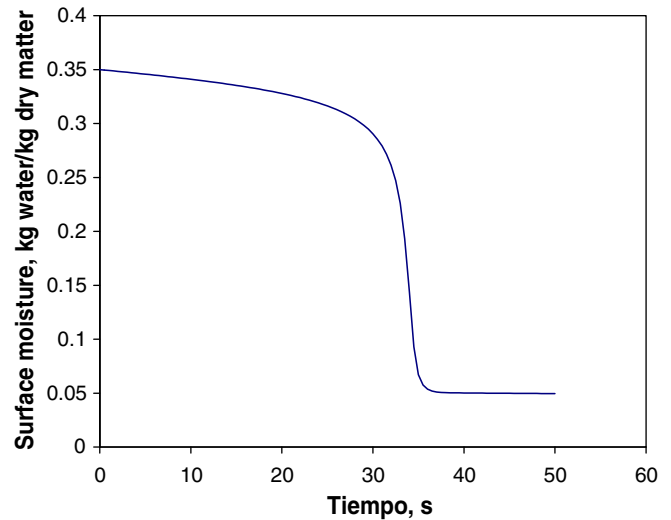


**Fig. 3.** Mass transfer Biot number as a function of time during drying of a wheat seed initial moisture content: 0.35 kg water/kg dry matter. (Top) General behaviour and (bottom) initial behaviour, magnified. The Biot number over the first seconds of drying suggests internal–external control. Operating conditions: initial moisture content of wheat, 0.35 kg water/kg dry matter (25.93% w/w); air temperature, 60 °C; air relative humidity, 0.08; air mass flow rate, 0.30 kg m<sup>-2</sup> s<sup>-1</sup>; and grain equivalent radius, 2.0 × 10<sup>-3</sup> m.

well-founded sorption relationship for starch-based foods: it tends to  $\infty$  for both  $a_w \rightarrow 0$  and  $a_w \rightarrow 1$ . Thus, according to Eq. (10),  $Bi_m$  will be very low initially, will then increase and decrease again. However, the decrease is mechanistically unimportant, since it occurs well inside the zone of strict internal control. The variation of the derivative would explain the predicted peak in the graph of the mass transfer Biot in Fig. 3 (top) as a function of time. The initial predicted value of this Biot number under these conditions was 2.1, suggesting that control of the mass transfer rate is initially shared between the internal and the external resistances. However, this state of affairs lasts less than 20 s (Fig. 3 bottom) as internal control takes over from then on, i.e., the mass Biot increases dramatically with time. Another evidence of the sudden increase of the internal resistance to mass transfer within the first 30 s is provided by Fig. 4, where the surface moisture content is predicted to drop very sharply from the initial moisture content, towards the equilibrium value with the drying air conditions.

### 3.1.2. Variation of the mass transfer Biot number at lower, practical moisture contents

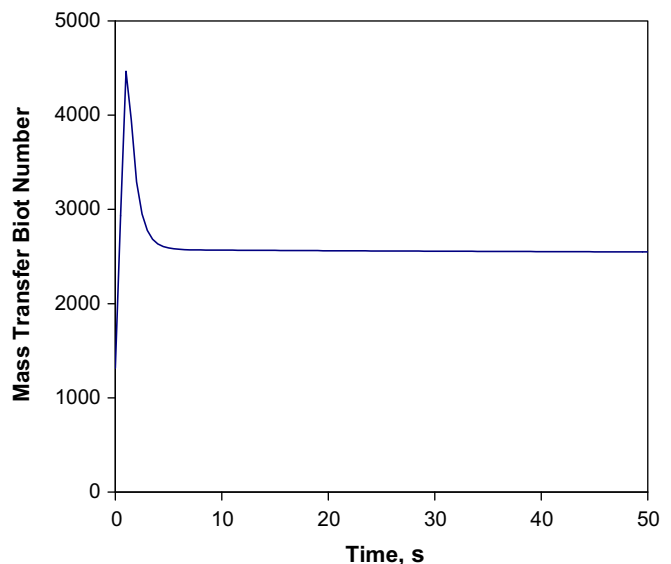
At an initial moisture content  $W_0$  of about 0.205 (17% w/w), which is a typical water content of freshly harvested wheat fed



**Fig. 4.** Predicted surface moisture content as a function of time during drying, for the conditions of Fig. 3. Surface equilibrium would be approached in some 35 s, and strict internal control to the mass transfer rate would prevail from then on.

to commercial dryers, the behaviour of the mass transfer Biot number as a function of time is shown in Fig. 5.

Though comparable with the variation observed for high moisture contents in Fig. 3, the mass transfer Biot number in Fig. 5 starts with a value of about 1200, which denotes a strict internal control, in agreement with previous literature on grain drying (Bruce, 1985; Gastón et al., 2004). Therefore, the range of variation in the mass transfer Biot number during drying seems to be related with the difference between initial and equilibrium moisture contents. Unlike in the results for high moisture content (Fig. 3), all the variation shown in Fig. 5 including the peak is mechanistically irrelevant, since it occurs entirely in the region where definite internal control prevails. The lack of variation after about 15 s indicates that equilibrium was reached at the surface very rapidly.



**Fig. 5.** Mass transfer Biot number as a function of time during drying of a wheat grain. Operating conditions: initial moisture content of wheat, 0.205 kg water/kg dry matter (17% w/w); air temperature, 60 °C; air relative humidity, 0.08; air mass flow rate, 0.30 kg m<sup>-2</sup> s<sup>-1</sup>; and grain equivalent radius, 1.8.0 × 10<sup>-3</sup> m.

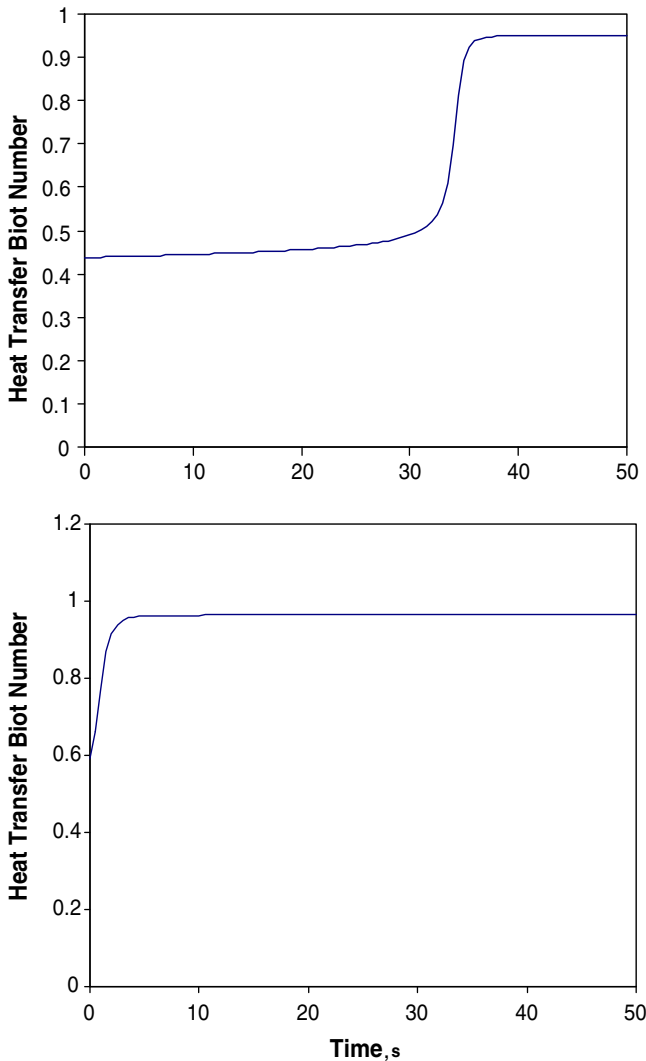


Fig. 6. Conventional heat transfer Biot number for wheat drying at 60 °C. Initial moisture content = 0.35 kg water/kg dry matter (top) and 0.205 (bottom). Relatively small changes occur during drying, and all within the same apparent controlling mechanism: internal–external.

3.1.3. Evolution of the heat transfer Biot number in wheat drying

For an initial moisture content of 0.35 kg water/kg dry matter, the variation in the heat transfer Biot number (Fig. 6 top) is governed by the variation of the surface thermal conductivity. The lower the surface moisture content, the lower the thermal conductivity and the higher the Biot number (see Eq. (12)): in the first seconds, the surface moisture content in Fig. 4 decreases only slightly and then the heat transfer Biot number remains substantially constant. However, then the surface moisture drops sharply to reach a constant value, and, simultaneously, the Biot increases suddenly to reach a value of about 0.95 after some 30 s.

Concerning wheat drying from an initial moisture content of 0.205 kg water/kg dry matter, the evolution of the heat transfer Biot number is simpler. From an initial value of 0.6, it increases to 0.95, to remain then constant due to attainment of equilibrium conditions. The final value is the same for both drying conditions, since it depends, through the thermal conductivity, on the surface moisture content, which tends to a value in equilibrium with the same air conditions.

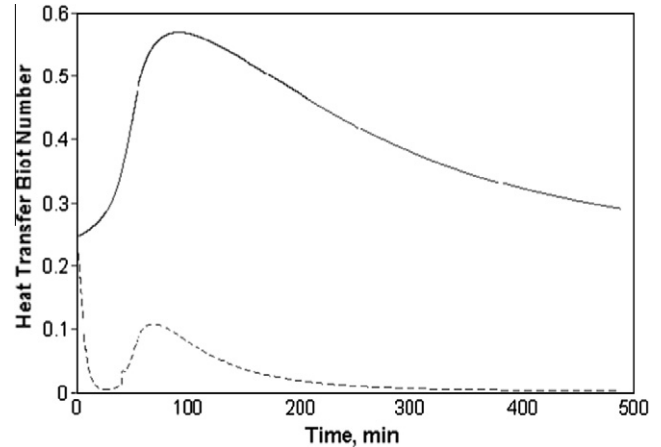


Fig. 7. Conventional (–) and modified (---) heat transfer Biot number predicted as a function of time during the drying of low-calorie, apple leathers. The modified number suggests a more externally controlled heat transfer rate during drying than that predicted by the conventional definition. This emphasizes the mass transfer-controlled nature of food drying.

3.2. Formation of a low-calorie apple-leather by hot-air dehydration

3.2.1. Analysis of the conventional and a modified heat transfer Biot number

As the original definition of the heat transfer Biot number for this product (Eq. (26)) is strictly valid in the absence of mass transfer, it may not be suitable for drying processes. In this regard, Chen and Peng (2005) have proposed a modified heat transfer Biot number, which can be termed “heat transfer Biot number for drying” ( $Bi_{cd}$ ).

$$Bi_{cd} = \frac{h_{Td}L}{k_T} = \frac{\left[ \frac{h_T - \Delta H_{vs} k_p (p_v - p_{va})}{(T_a - T_m)} \right] L}{k_T} \quad (29)$$

where  $h_{Td}$  is the “net” heat transfer coefficient in a drying operation, giving its reciprocal a measure of the effective external resistance to the heat flux entering the product. As part of the heat is employed for surface water evaporation, the net heat influx is lower than in a

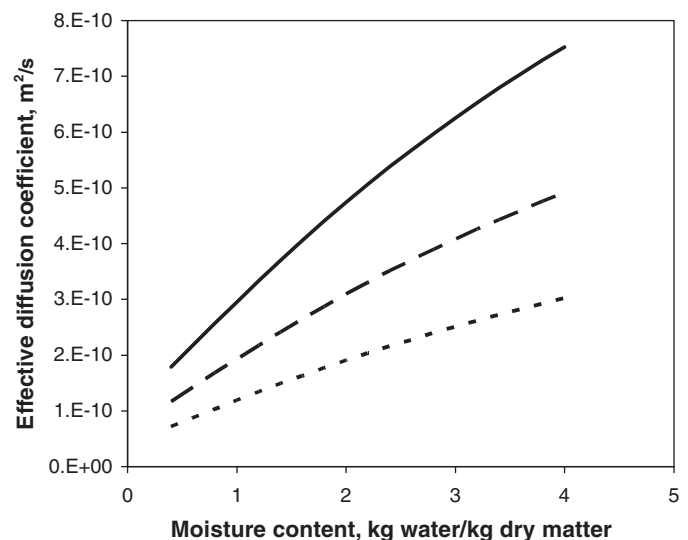
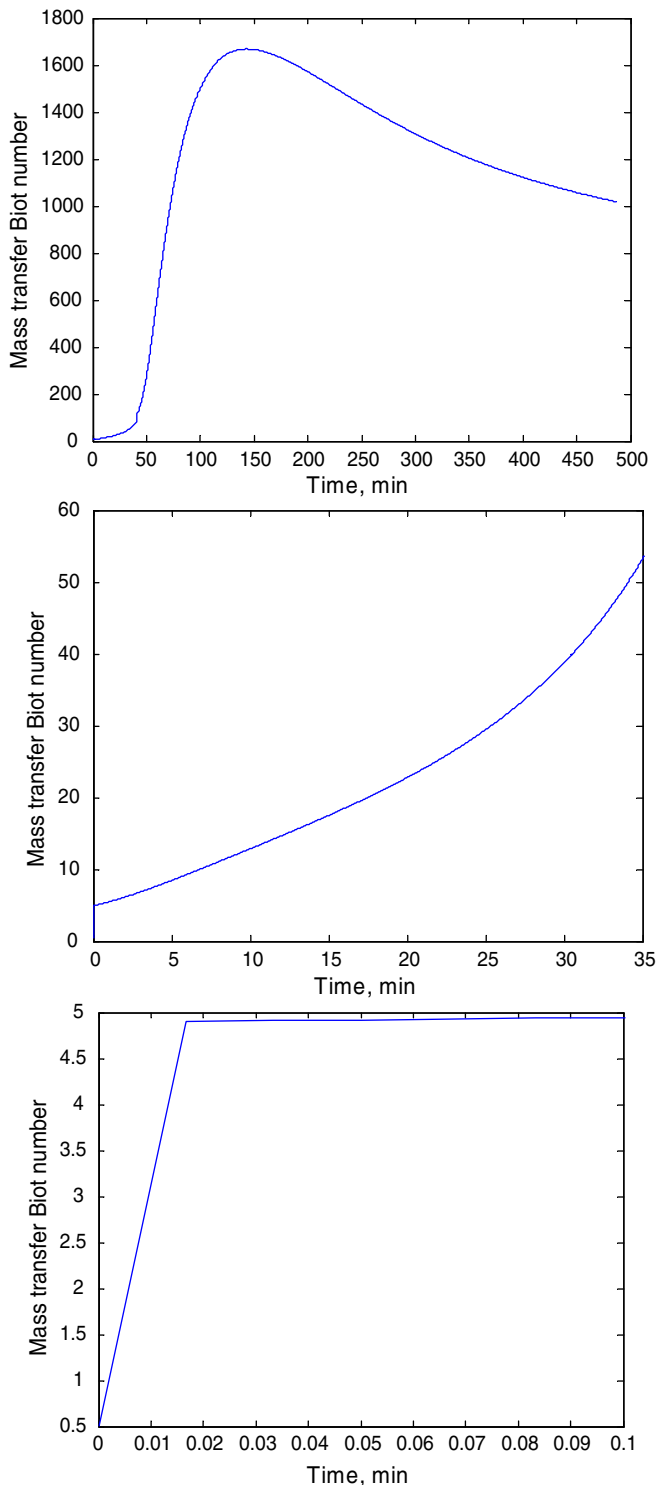


Fig. 8. Diffusion coefficient for low-calorie apple leathers as a function of moisture content for product temperatures of 30 (···), 50 (–) and 70 °C (–) as predicted with the correlation developed for this shrinking food.



**Fig. 9.** Mass transfer Biot number as a function of time during drying of low-calorie, apple-leather. (Top) Entire drying process; (middle), first 35 min; (bottom) first 6 s. The predicted Biot number at the start of drying is about 0.5.

situation with no drying. Therefore, from the viewpoint of the Biot number analysis, the situation is equivalent to a decrease in the heat transfer coefficient, and, therefore, to an increase of the external resistance to heat transfer.

The behaviours of both conventional and modified heat transfer Biot numbers are presented in Fig. 7 for the low-calorie apple-leather: while the conventional Biot keeps within a zone of internal–external control, the modified Biot reaches very low

values, almost zero, denoting an external control. This is congruent with predictions of uniform temperature profile inside the leather (though not constant with time). The increase and decrease of both heat transfer Biot numbers along the course of drying reflects the combined influences of decreasing thermal conductivity at the surface and decreasing thickness. As surface conductivity decreases faster than thickness, both Biots first increase. Then, as conductivity remains almost constant and thickness keeps decreasing, both Biots tend to diminish.

The variable diffusion coefficient of the reduced-calorie apple-leather (Eq. (22)) was plotted as a function of moisture content for temperatures of 30, 50 and 70 °C in Fig. 8. The plots indicate that both independent variables contribute considerably to the variation of the effective diffusion coefficient during drying.

The evolution of the mass transfer Biot number in Fig. 9 (top) shows low initial values, increasing to a situation of strong internal control with time. The predicted maximum reflects the simultaneous effects of a decreasing diffusion coefficient and decreasing factor  $(1 + (\rho_d/\rho_w)W)^2$  both evaluated at the surface (the factor appears as a consequence of adimensionalization of boundary condition (14.3)), a variable slope of the sorption relationship  $(\partial W/\partial a_w)$  and a decreasing thickness. Mechanistically, the relevant changes occur in the first 30–40 min, being the succeeding variations unimportant, as they occur within the zone of strict internal control. However, in order to observe the initial behaviour, Fig. 9 (middle) shows the state of affairs for the first 35 min of drying, where the Biot number changes from low values to about 50, almost in the zone of pure internal control. Hence the duration of the zone of internal–external control is about 35 min. However it would be important to detect the nature of controlling mechanism at the start of drying, i.e., if internal–external or external. In this regard, Fig. 9 (bottom) indicates that the initial control to the mass transfer rate is internal–external, starting with a mass transfer Biot of 0.5 and rapidly evolving to a value of about 5. Therefore, no convective, external control is predicted to prevail in any interval of the drying of low-calorie apple leathers. This is in agreement with an analysis carried out with analytical, Biot-dependent solutions, in a previous article (Giner, 2009).

On the basis of the predictions described above, the highly variable nature of the mass transfer Biot number suggests that analytical solutions using constant Biot number are not a realistic representation of the mass transfer process because, at most, it can only be valid for a limited period. These analytical solutions, however, are suitable for heat transfer problems involving neither mass transfer nor considerable variation of product volume or structural characteristics.

#### 4. Conclusions

In wheat drying, variation of the Biot number during drying is relevant at high initial moisture contents, e.g., 0.35 kg water/kg dry matter. In the first minute, drying rate control shifts from internal–external to internal, keeping as such from then on.

In wheat drying at practical initial moisture contents, e.g., 0.205 kg water/kg dry matter, the mass Biot number is very high from the beginning of the drying process, drying rate control is internal throughout and variations are irrelevant.

In view of both behaviours in wheat drying, analytical solutions may be used for low initial moisture content grain. In the case of high moisture contents, the shifting drying rate control and the possibility of shrinkage suggests the use of numerical solutions.

In a high moisture product as a low-calorie apple-leather, the mass transfer Biot number varies during drying in a complex manner, starting and keeping internal–external control of the drying rate for a period as long as 35 min at an air temperature of 60 °C. Mass transfer rate is internally controlled from then on. Therefore,



an analytical solution of a diffusion equation with internal control would be defective for the initial 35 min of drying and is therefore not recommended.

The heat transfer Biot number both in wheat and low-calorie apple-leather keeps within the internal–external control region during the drying process.

A modified version of the heat transfer Biot for drying tends asymptotically to zero during the process because the heat influx to the product is lower than in pure heat transfer due to the fraction of heat demanded for water evaporation at the surface.

This is congruent with the predictions of practically flat internal temperature profile during drying of foods. The modified heat transfer Biot during drying.

As a consequence of the above conclusions, numerical solutions considering shrinkage and variable diffusion coefficient are suggested for drying kinetic studies in high moisture foods.

## Appendix.

The Halsey equations are as follows:

$$W = \left( \frac{-\text{Exp}(-2.502)}{\text{Ln}a_w} \right)^{\frac{1}{0.9017}} \quad (\text{A1})$$

fitted with  $r^2 = 0.996$ , and valid for  $0.855 \leq a_w \leq 0.999$  while

$$W = \left( \frac{-\text{Exp}(-2.367)}{\text{Ln}a_w} \right)^{\frac{1}{1.100}} \quad (\text{A2})$$

fitted with  $r^2 = 0.998$  and valid for  $0.1 \leq a_w < 0.855$ .

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