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Calcium and temperature effect on structural damage of hot air dried apple slices: nonlinear irreversible thermodynamic approach and rehydration analysis

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Abstract

Mathematical models traditionally employed in fitting convective drying data do not use to report information about chemical and other physical changes different from the simple decrease in moisture content. <u>In the present study, structural damage undergone by fresh and vacuum impregnated apple slices with different calcium lactate concentrations during convective drying at 30, 40 and 50 ºC was analysed by applying equations derived from nonlinear irreversible thermodynamics to experimental data.</u> According to the results obtained, vacuum impregnation with isotonic sucrose solution before drying at 30 ºC provided maximum protection to cellular structure by promoting reversible deformations against irreversible breakages. On the contrary, cell walls strengthen with calcium had severe damaged during drying. Regarding air temperature, it was directly related both to the molar energy employed in deforming structures and the drying rate. These results were confirmed by analysing dried samples behaviour during further rehydration.

Keywords: apple, calcium, vacuum impregnation, hot air drying, rehydration, nonlinear irreversible thermodynamics

1. Introduction

Hot air drying involves the transfer of water from a solid or solution to a surrounding gaseous phase. Since drying conditions have considerable effect on the cost and length of the process and the properties of the final product, research in this unit operation at academic, government and private industries is increasing every year.

Drying of food materials is an extremely complex process in which heat, mass and momentum transfer in unsteady state take place simultaneously and coupled to physical and chemical changes (Sabarez, 2015). In hot air drying, heat is usually transferred by convection to the food surface and by conduction inside the food. Mechanisms involved in mass transport are somewhat more complex, especially in the case of those foods with an organized cellular structure. Moisture that evaporates inside the solid diffuses out as vapour due to a pressure gradient. Liquid water is usually transferred by diffusion due to water activity gradients. Unbound moisture in porous or granular solids also moves through capillaries and interstices by a mechanism involving surface tension. Across the two sides of a permselective membrane, such as plasma membrane, the transport of water takes place by an osmotic pressure gradient promoted mechanism. Additionally, since cell water loss involves considerable volume reduction (Chiralt & Fito, 2003; Seguí et al., 2012), pressure gradients also appear coupled to chemical potential ones in mass transfer phenomena. Deformation of the structure inherent to the drying process usually involves irreversible breakages of plasma membranes, the bindings between adjacent cells and/or, in the particular case of plant tissue, the bindings between the protoplast and the cell wall. These breakages may also be given as a result of the crystallization of those solutes that appeared originally dissolved in the liquid phase of the product. The incidence of such breakages would be affected by the degree of stiffness of the structure, so that this impact will be greater in rigid structures than in flexible ones. Despite everything mentioned above, mathematical models traditionally employed in the kinetic study of mass transport through plant tissues tend to simplify the complexity and heterogeneity inherent to biological materials (Fito et al., 2008). Furthermore, thermodynamic and kinetic models that describe the diffusional mechanism in liquids or ideal gaseous systems when are closed to equilibrium are often applied to foods with colloidal or cellular structure that are far from thermodynamic equilibrium (Bird et al., 2002). In spite of their limitations, the resulting equations are easy to use and have been proven to predict with reasonable accuracy changes over time in the moisture content of several foods submitted to convective drying, as well as to evaluate the effect of different processing variables (Dinani et al., 2014; Guo et al., 2014; Mwithiga & Olwal, 2005; Shi et al., 2013; Vega et al., 2007). It is even common to find equations that incorporate shrinkage in an approximate way via, for instance, the characteristic dimension as a function of water content (Clemente et al., 2011; Garcia et al., 2007). While useful from a kinetic point of view, none of these equations is able to quantify structural and physicochemical modifications taking place during convective drying, which are closely related to the quality of the final product. To overcome this situation, analysing dried samples behaviour during rehydration would be an option. In parallel, approaches based on the thermodynamics of irreversible processes have been developed to simultaneously control both transport phenomena and phase and structural changes inherent to food processing and therefore, to predict real changes in the quality of food products in line with the process progression. Analysis by non-linear irreversible thermodynamics have been successfully applied in predicting compositional and structural changes occurred during air drying of vacuum impregnated apple (Betoret et al., 2015) and pork loins (Traffano-Schiffo et al., 2014), in modelling the osmotic dehydration process of isolated apple cells (Seguí et al., 2012) and kiwifruit half slices (Castro-Giráldez et al., 2011; Tylewicz et al., 2011), in describing the salting cheese process (Velázquez-Varela et al., 2014) and the internal water flux taking place in meat freezing process (Castro-Giráldez et al., 2014). Generally, experimental data acquisition in these cases is somewhat more complex and requires continuous measurements of changes in volume, temperature, water activity, composition, etc., undergone by whole samples and the different phases that make them up.

According to what is discussed above, this study aims to evaluate through non-linear irreversible thermodynamics analysis and trough the analysis of samples behaviour during their rehydration, the extent of structural damage undergone by apple slices (var. Granny Smith) submitted to hot air drying at different temperatures as affected by vacuum impregnation and the incorporation of calcium to the cellular tissue.

2. Materials and methods

2.1. Raw material

In all the experiments, apples (var. Granny Smith) purchased from a local market were washed and cut into 10 mm thick slices in the direction perpendicular to the longitudinal axis. In order to restrict mass transfer through the side surface and ensure a unidirectional flow of matter, the peel was kept in the samples. Moreover, seeds were removed by using a cylindrical steel punch, 22 mm in diameter.

2.2. Vacuum impregnation (VI)

Vacuum impregnation experiments were carried out with sucrose aqueous solutions ($a_w \approx 0.986$) including different amounts of food grade 5-hydrate calcium lactate (PANREAC QUÍMICA S.L.U., Barcelona, Spain) on its composition, as detailed in Table 1.

In all vacuum impregnation treatments, apple slices immersed in the corresponding impregnating solution (at least 1:20 fruit to solution mass ratio) were subjected to a subatmospheric pressure of 50 mbar for 10 min, after which it was restored atmospheric pressure for 10 min more.

2.3. Air drying

Air drying of fresh and vacuum impregnated apple slices took place in specially designed equipment (Contreras et al., 2008), where air temperature and velocity could be controlled. Besides this, the dryer was provided with sensors for measuring ambient air temperature and relative humidity, as well as an electronic balance connected to a computer for continuous recording of the samples weight.

For this study, apple slices were place inside the drying chamber in a direction perpendicular to the air flow and air conditions were set so that its temperature was 30, 40 or 50 ºC (to prevent thermal damage) and its velocity was 3.5 m/s (to ensure internal control of the process). Each drying treatment was carried out in triplicate until the moisture content of the samples reached 10% (wet basis), ~~so it was necessary to determine the water content of fresh and vacuum impregnated apple slices, apart from recording the samples weight along the process~~. Mass change was recorded along the process and employed to calculate the molar flow of water (J_w, in mol water/m^2·s) according to Eq. (1).

$$J_w = -\frac{M_{n-1} - M_n}{S \cdot MW_w \cdot (t_n - t_{n-1})} \quad (1)$$

M_{n-1} being the weight of the sample at time t_{n-1} in g, M_n being the weight of the sample at time t_n in g, S being the surface of the section perpendicular to the flow direction in m^2 and MW_w being the molecular weight of water (18 g/mol).

Moreover, experimental measurements of ambient air temperature and relative humidity (T_{amb} and φ_{amb}, respectively) were used to estimate by Eq. (2) the relative humidity of the drying air (φ_{dry}) at each of the different drying temperatures employed (T_{dry}).

$$\frac{\varphi_{amb} \cdot P_{Samb}}{P - \varphi_{amb} \cdot P_{Samb}} = \frac{\varphi_{dry} \cdot P_{Sdry}}{P - \varphi_{dry} \cdot P_{Sdry}} \quad (2)$$

P being the atmospheric pressure in atm and P_{Samb} and P_{Sdry} being respectively the air saturation pressures at T_{amb} and T_{dry}.

2.4. Drying models

In a first approximation, the analytical solution to Fick's second law given by Crank (1975) for infinite plane sheet geometry and long term treatments was applied to calculate the effective diffusion coefficients of water (D_e) for each of the conditions tested. It should be noted that the application of this equation implied assuming not only that the initial moisture was uniformly distributed in the samples, but also that the samples dehydrated at the same rate on either side of the symmetry axis and that both the water diffusivity and the slice thickness remained constant throughout the drying process. It is worth noting that the diffusional approach was applied to the whole drying process, thus assuming that the water flow was controlled by the food resistance to the internal transport of water. Since the constant drying rate is in fact very short or even inexistent in such foods with an organized cellular structure, this assumption should not increase the difference between experimental data and data predicted by the diffusional approach.

From a thermodynamic point of view (Eq. (3), the water flow occurring during the convective drying of a food (J_w) is related to the chemical potential gradient of water between the food and the air stream ($\Delta\mu_w$) by the phenomenological coefficient of water through the system (L_w).

$$J_w = -L_w \cdot \Delta\mu_w \tag{3}$$

In the case of spontaneous transport of water under constant conditions of pressure and temperature, free energy consumed for water transport (J/mol) would be calculated from the water activity gradient between the food and the external phase in contact with it (Eq. (4)):

$$\Delta\mu_w = RTLn\left(\frac{a_w}{\varphi}\right) \tag{4}$$

R being the universal gas constant (8.31 J/mol·K), T being the system absolute temperature (K), φ being the drying air relative humidity expressed as a fraction and a_w being the water activity of the food submitted to the drying process.

When also considering pressure differences between the different phases making up the system (as in the case of existing cell turgor), partial molar free energy available for spontaneous transport of water between two points of the system (J/mol) would be calculated according to Eq. (5).

$$\Delta\mu_w = RTLn\left(\frac{a_w}{\varphi}\right) + \overline{V_w} \cdot (P_{int} - P_{ext}) \tag{5}$$

$\overline{V_w}$ being the partial molar volume of water.

If finally, as in most cases, the free energy available to water transport (J/mol) is conditioned by the need to modify or generate structures, Eq. (5) would become Eq. (6):

$$\Delta\mu_w = RTLn\left(\frac{a_w}{\varphi}\right) + \overline{V_w}\cdot(P_{int} - P_{ext}) - \overline{V_w}\cdot(\Delta P_{DE} + \Delta P_R) \quad (6)$$

$\overline{V_w}\cdot\Delta P_{DE}$ being the energy dissipated in breakages and/or irreversible deformations and $\overline{V_w}\cdot\Delta P_R$ standing for the molar energy used in elastic and reversible deformation and, therefore, involved in the transport of water through hydrodynamic mechanisms.

Calculating the chemical potential gradient from the experimental data obtained in this study involved assuming negligible the contribution of pressure gradients as in Eq. (4). As explained by Betoret et al. (2015), values of the phenomenological coefficient calculated taking into account only the difference between the water activity of the food and the air in contact with it (L_w^{cal}) (Eq. (7)) will be higher or lower than the real ones (L_w) (Eq. (8)) depending on the contribution of cell turgor and deformation/relaxation phenomena to water transport.

$$L_w^{cal} = \frac{-J_w}{RTLn\left(\frac{a_w}{\varphi_{dry}}\right)} \quad (7)$$

$$L_w = \frac{-J_w}{RTLn\left(\frac{a_w}{\varphi_{dry}}\right) + \overline{V_w}\cdot(P_{int} - P_{ext}) - \overline{V_w}\cdot(\Delta P_{DE} + \Delta P_R)} \quad (8)$$

Once L_w^{cal} and L_w values have been calculated, it is possible to estimate the molar energy employed by samples in deforming and/or relaxing structures during hot air drying (Eq. (9)).

$$\frac{1}{L_w} - \frac{1}{L_w^{cal}} = \frac{-\overline{V_w}\cdot(P_{int} - P_{ext}) + \overline{V_w}\cdot(\Delta P_{DE} + \Delta P_R)}{J_w} \quad (9)$$

Considering only the period from which the cells have completely lost their turgor, one can consider that pressure gradient between the different stages that make up the system are negligible ($\overline{V_w}\cdot(P_{int} - P_{ext}) = 0$). Thus, Eq. (9) would be turn into Eq. (10).

$$\overline{V_w} \cdot (\Delta P_{DE} + \Delta P_R) = J_w \cdot \left(\frac{1}{L_w} - \frac{1}{L_w^{cal}}\right) \quad (10)$$

2.5. Rehydration

After drying, apple slices were rehydrated by immersion in distilled water (dried sample to rehydration media mass ratio of 1:70 at the beginning of the process) at 30 ºC for 9 hours. At different immersion times (0 10, 20, 30, 40, 50, 60, 120, 180, 24, 300, 360, 420, 480 and 540 minutes), samples were taken out of the rehydration media, gently dried with tissue paper and weighed. Once the process was completed, rehydrated samples were analysed in triplicate in terms of apparent density, moisture and soluble solids content. From these measurements it was possible to calculate the three indices proposed by Lewicki (1998) to describe the behaviour of foods submitted to rehydration (Eqs. (11) to (13)): water absorption capacity (WAC), dry matter holding capacity (DHC) and rehydration ability (RA).

$$WAC = \frac{M_R \cdot x_R^w - M_D \cdot x_D^w}{M_0 - M_D} \quad (11)$$

$$DHC = \frac{M_R \cdot (1 - x_R^w)}{M_D \cdot (1 - x_D^w)} \quad (12)$$

$$RA = WAC \cdot DHC \quad (13)$$

M being the total mass in g and x^i being the mass fraction of component i in g/g. Subscripts 0, D and R refer to the product just before drying, the completely dried product and the rehydrated one, respectively. Superscript i refer to water (w) or soluble solids (ss).

Additionally, it has been measured the water holding capacity (WHC) of the rehydrated structure from the soluble solids content of its liquid phase (z_R^{ss}) and the amount of liquid removed (M_{CF}) by centrifuging it at 4000 rpm for 10 minutes (Eq. (14)).

$$WHC = \frac{M_R \cdot x_R^w - M_{CF} \cdot (1 - z_R^{ss})}{M_R \cdot x_R^w} \quad (14)$$

2.6. Analytical determinations

The moisture content was in most cases estimated gravimetrically from the water evaporated in a vacuum oven (2-3 days at 133 mbar and 63 ºC) by a known amount of sample. Along the drying process, the moisture content of apple slices was calculated at every moment (x_t^w in g water/ g total mass) from the recorded mass change and the initial moisture content (x_0^w in g water/ g total mass), by applying a dry matter balance (Eq. (15)).

$$M_t \cdot (1 - x_t^w) = M_0 \cdot (1 - x_0^w) \quad (15)$$

When it was required, the soluble solids content of samples (x^{ss}, in g solutes/ g total mass) was calculated from their moisture content and the soluble solids content of their liquid phase (z^{ss}, in g solutes/ g liquid phase) measured at 20 ºC with an Abbe thermostated refractometer (ATAGO, mod. 3-t), as shown in Eq. (16).

$$x^{ss} = \frac{z^{ss} \cdot x^w}{(1 - z^{ss})} \quad (16)$$

The calcium content of fresh and vacuum impregnated samples was determined by chemical suppression and dialysis in an ion exchange liquid chromatograph (Metrohm Ltd. mod. MIC-7 Compact). Metrosep C2-150 separation column (150 mm length and 7 mm internal diameter) filled with 7 µm carboxylated silica gel particles was used as stationary phase. Mobile phase consisted of an aqueous solution of tartaric acid (4 mmol/L) and dipicolinic acid (0.75 mmol/L) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) flowing at 1.5 mL/min. Sample preparation for calcium determination involved its carbonization on a heating plate at 450 ºC and subsequent incineration in a muffle furnace at 550 ºC until white ashes were obtained. Then, the ashes were collected with extra pure nitric acid (65% w/v) and dissolved in bidistilled water until concentrations were in the measuring range of the equipment (0-50 ppm).

As described above for the moisture content, both the soluble solids content and the calcium content at any particular moment of the drying process were calculated from the component mass balance posed between starting (x_0^i, in g component i/ g total mass) and instantaneous conditions (x_t^i, in g component i/ g total mass) (Eq. (17)).

$$M_t \cdot x_t^i = M_0 \cdot x_0^i \quad (17)$$

Compositional data at every processing time allowed predicting the instantaneous water activity of the samples until the saturation of their liquid phase was reached. For this purpose, the equation proposed by Ross (1975) for ternary solutions of electrolytes and non-electrolytes was employed (Eq. (18)).

$$a_w = (a_w)_1 \cdot (a_w)_2 \quad (18)$$

$(a_w)_1$ being the water activity of the aqueous solution of sucrose, fructose and glucose calculated according to the generalized Norrish equation (1966) and $(a_w)_2$ being the water activity of the aqueous solution of calcium lactate calculated as a function of its molality, its osmotic coefficient (deduced from the results published by Apelblat et al., 2005) and the amount of ionic species per mole of solute in solution (Bromley, 1973). Since the liquid phase of the samples get saturated till the end of the drying process, water activity of apple slices was deduced from the corresponding desorption isotherm. Desorption isotherms at different temperatures were obtained by the gravimetric method of the saturated salt solutions in the range of water activity values between 0.11 and 0.9. The fitting of experimental data to the model proposed by Caurie (1970) showed practically no effect of the temperature and provided the mathematical expression (Eq. (19)) which related the water activity and the moisture content in dry basis for long processing times.

$$\mathrm{Ln}\left(\frac{1}{X_t^w}\right) = -4.110 \cdot a_w + 3.974 \quad (19)$$

2.7. Statistical analysis

The statistical significance of the results obtained was analysed with the 5.1 version of the Statgraphics Plus software package. Since each response variable was affected by more than one independent factor, multifactor analysis of variance (ANOVA) with 95% confidence level (p-value < 0.05) was the type of analysis chosen.

3. Results and discussion

3.1. Diffusional approach to the analysis of the drying operation

Values of coefficient D_e (Table 2), which were obtained by applying a non-linear procedure to get the best fit between experimental data and values predicted after adding the first seven terms of the sum, resulted of the same order as those obtained by other authors for the same product and similar processing conditions (Atarés et al., 2009; Contreras et al., 2008; Fito et al., 2001; Kaya et al., 2007; Ramírez et al., 2011; Sacilik & Elicin, 2006). As expected, D_e values increased with the drying temperature, which led to an increase in the driving force responsible for the water transport between the air stream and the samples. It should be note that, when calcium was added by vacuum impregnation to the solid matrix of the product, the effect of air temperature on D_e values was less evident when passing from 30 to 40 ºC than when passing from 40 to 50 ºC. This fact could be explained in terms of the increase in the pectin esterase activity with the drying temperature. As stated in Luna-Guzmán et al. (1999) and Luna-Guzmán & Barret (2000), pectin esterase activation is known to occur in the temperature range of 55-70℃. According to this, drying with air at 50 ºC w as closer than drying at either of the other two temperatures to the optimum temperature for this enzyme activation. Therefore, calcium added by vacuum impregnation was expected to be set in a greater extent in the middle lamella and the cell wall of apple samples to form stiffer and subsequently more fragile structures (Gras et al., 2003) which required less energy to be deformed.

Regarding the effect of the vacuum impregnation step applied to the samples previously to their convective drying, it significantly reduced D_e values. This slowdown in the drying process makes sense if one considers the replacement of the gas occluded in the food porous structure by the impregnating solution as a result of vacuum impregnation, thus increasing the fruit density and limiting the vapour diffusion in the pores (Fito et al., 2001; Martínez-Monzó et al., 2000). Worth noting that, despite the different composition of vacuum impregnated samples at the beginning of the drying process displayed in Table 2 ($\mathbf{x_0^w}$, $\mathbf{x_0^{ss}}$ and $\mathbf{x_0^{Ca}}$), multifactor analysis of variance showed no effect of the impregnating solution tested on D_e values.

As regards the accuracy of Fick's diffusion model (Fig. 1), significant difference was observed for all the treatments tested between the driving force values (Y_t) calculated from the experimental data and the predicted ones. It must be taken into account that, although its implementation in modelling mass transport phenomena occurring in food systems is a very common practice and usually provides satisfactory fits, Fick's general diffusion equation was developed for ideal gaseous systems or liquid systems that are close to equilibrium (Bird et al., 2002), which is not fulfilled in the case of convective drying of a cellular structured food. In fact, these differences between experimental and predicted values, particularly large when adding calcium to the samples porous structure, show the contribution of other mechanisms, apart from diffusional ones, in transporting water during the drying process. In this context, using irreversible thermodynamics has been demonstrated to be a useful tool to model mass transport and its coupling to deformation-relaxation phenomena during different cellular systems dehydration (Betoret et al., 2015; Fito et al., 2007; Seguí et al., 2006; Seguí et al., 2010; Seguí et al., 2012).

3.2. Thermodynamic approach to the analysis of the drying operation

Changes in the calculated phenomenological coefficient along the processing time are shown in Fig. 2. As it can be observed, L_w^{cal} values remained almost constant at the beginning of the convective drying, when the deformation/relaxation phenomena hardly affects the water transport (Oliver et al., 2012), but decreased as time progressed. L_w^{cal} values obtained at short processing times are supposed to be close to real values of the phenomenological coefficient (L_w), which remained constant throughout the entire process (Table 3). Although the thermodynamics of irreversible processes is being increasingly used as a tool to predict compositional and structural changes occurring during food processing, it is still difficult to find in the scientific literature values for the real phenomenological coefficient comparable to those obtained in the present study. In general, L_w values shown in Table 3 are in the same order as those reported by other authors for water transport through the protoplast membrane in fruits

(Ferrando & Spiess, 2002 & 2003). In a microscopic approach, the application of irreversible thermodynamics to the osmotic dehydration of apple isolated protoplasts (var. Fuji) at different temperatures and different water–sucrose solutions provided L_w values on the order of 4.5 ± 0.3 x10^{-5} $mol^2/J{\cdot}s{\cdot}m^2$ for experiments at 30 ºC, 6.5 ± 0.4 x10^{-5} $mol^2/J{\cdot}s{\cdot}m^2$ for experiments at 40 ºC and 9.9 ± 0.6 x10^{-5} $mol^2/J{\cdot}s{\cdot}m^2$ for experiments at 50 ºC (Seguí et al., 2006). This increase in the kinetic coefficient L_w with the osmotic solution temperature, which was attributed in that research to an increase in the plasmalemma permeability, is not in line with the significant decrease (p-value < 0.05) in L_w values reported in the present study as drying temperature increases from 30 to either 40 or 50 ºC. This finding would confirm that not only the water activity gradient between the food and the air in contact with it, but also the energy used in deform and break the structure, increase with the drying temperature. As a result, the increase in the water flow with increasing the drying temperature was not as high as that undergone by the driving force. Also in connection to the mechanical properties of the structure, phenomenological coefficient values obtained for 5 mm thick halves of apple slices (var. Granny Smith) submitted to vacuum impregnation with isotonic solutions previous to convective drying at 40 ºC for 15 hours were reported to increase when adding trehalose and/or calcium to the impregnating solution (Betoret et al., 2015). Similar behavior is shown in Table 3, so that the samples including calcium in their structure had, regardless of the mineral concentration, L_w values slightly higher than those just impregnated with a sucrose solution but considerably higher than those samples dried without previous impregnation. By the same reasoning as set forth above, calcium enriched structures would be the stiffest and therefore the most susceptible to undergo irreversible breakage during convective drying.

Mean values of the molar energy used both in reversible and/or irreversible deformations of the structure along the drying process are graphed in Fig. 3. As deduced from the shape of the curves, the amount of energy employed by the system in deforming the structure increased as the drying progressed and decreased more or less sharply after reaching a maximum value. Regarding the vacuum impregnation of the samples, it significantly reduced the molar energy employed by the system in deforming structures. The major contact existing between the liquid fraction and cellular structures in vacuum impregnated samples has been reported to promote the higher solubilization and/or hydrolysis of pectin substances in the cell wall and the middle lamella (Contreras et al., 2005), thus reducing the energy required to generate structural deformation and/or breakage efforts in such kind of samples. Just as expected, the addition of calcium to the food matrix resulted in a notable decrease in the molar energy used both in reversible and/or irreversible deformations of the structure. Previous studies about the impact of this mineral on viscoelastic properties of apple tissue (Anino et al., 2006; González-Fésler et al., 2008; Salvatori et al., 2011) evidence that while calcium allows maintaining middle lamellae and/or pectin network integrity by promoting cross-linking of pectin polymers, it also favors the general inner disruption of cells (plasmolysis, membrane breakage and severe folding of walls). As a result, calcium-containing tissues have a mechanical resistance very much reduced than that of calcium free ones.

Regarding the effect of the temperature, it markedly increased the molar energy employed by the system in deforming structures, as it did with the drying rate. In this way, the analysis of experimental data by using the thermodynamics of irreversible processes highlights the close relationship existing between the water flow and the energy available for the cellular tissue deformation.

3.3. Analysis of the rehydration operation

Rehydration is often applied to simply assess the damage occurring in the cellular structure during drying and the previous conditioning treatments.

To quantitatively evaluate the effect of different drying conditions on samples behavior during the rehydration process, the empirical model proposed by Peleg for the description of moisture sorption curves (Peleg, 1988) was applied (Eq. (20)):

$$\frac{t}{M_t - M_0} = k_1 + k_2 \cdot t \qquad (20)$$

M_0 being the weight of the dried apple slice in g, M_t being the weight of the apple slice rehydrated for a time t in g and k_1 (min/g) and k_2 (g^{-1}) being the kinetic constants of the process. In particular, the intercept (k_1) is inversely related to the total mass transfer rate (including water and solutes) and the slope (k_2) is inversely related to the maximum gain of total mass along the rehydration process.

Kinetic constants obtained from the linear fit of experimental data to this mathematical model proposed by Peleg are collected in Table 4. With a confidence level of 95%, multifactor analysis of variance revealed that ~~the total mass transfer rate ($1/k_1$) was mainly affected by the drying temperature and that the effect of such factor on $1/k_1$ values was dependent on the previous impregnation of the samples with different impregnating solutions. On the contrary,~~ k_2 values were only affected by the treatment applied to the samples previous to their convective drying. To be more precise, the maximum gain of total mass along the rehydration process ($1/k_2$), which is closely related to the degree of relaxation of the structure, reached significantly higher values in vacuum impregnated samples. As expected, the addition of calcium to the impregnating solution resulted, with independence on the concentration, in a notably increase in k_2 values. Similar results were observed when analyzing the mass recovery data that is, the ratio between the weight reached by rehydrated samples at equilibrium and that of samples at the beginning of the drying process (M_∞/M_0). In this way, it becomes evident once again the protective effect that the vacuum impregnation exerts on the structure of cellular tissues submitted to convective drying, which decreases with the addition of a strengthen structure agent such as calcium to the impregnating solution. Said in other words, deformations of vacuum impregnated structures during the drying step seemed to be the most reversible ones. On the contrary, increasing the concentration of calcium in the food matrix significantly enhanced the irreversible breakage of the structure.

In order to have complete information about the amount of water absorbed or the amount of solutes removed during the rehydration process, the three indices proposed by Lewicki (1998) together with the water holding capacity were also calculated (Table 5). As it can be deduced from the significantly higher values of both the water absorption capacity and the dry matter holding capacity, the vacuum impregnation with an isotonic sucrose solution previous to the drying process provided, at any of the temperatures assayed, samples with higher ability to be submitted to a rehydration process. As expected by the increase in rigidity resulting from the addition of calcium to the apple structure, samples enriched with this mineral showed rehydration indices more close to those of non-impregnated ones. Since both the water absorption capacity and the dry matter holding capacity are inversely related to the damage suffered by the cellular tissue along its dehydration, the vacuum impregnation with an isotonic sucrose solution was proven to be a useful treatment to preserve the structure of dehydrated fruits and vegetables. This statement was corroborated by higher water holding capacity values reached by VI suc samples.

4. Conclusions

In accordance with the above discussed results it can be concluded that both the application of equations derived from nonlinear irreversible thermodynamics and the analysis of dried samples behaviour during their further rehydration provided relevant information about the level of structural damage undergone by apple slices submitted to hot air drying, which is a key determinant of dried products quality. Among the different process variables tested, vacuum impregnation with an isotonic sucrose solution previous to air drying at 30 ºC was found to exert a protective effect on the cellular structure, so that deformations under these conditions were the most reversible ones. However, increasing the stiffness of the tissue by means of the addition of calcium to the impregnating solution increased the incidence of irreversible breakages. Although the energy employed in deforming the structure, as well as the drying rate, increased with the drying temperature, this not always led to more damaged cellular tissues. In no way, the amount of energy employed in deforming structures and also the type of deformation (reversible or irreversible) experienced by the structure could have been estimated by applying regular equations derived from the Fick's second law of diffusion.

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Table 1. Composition of the different solutions employed in the vacuum impregnation step.

SOLUTION	[sucrose] in g/L	[calcium lactate] in g/L*	%RDA**
suc	215.68	0	0
suc+20%Ca	112.29	44.22	20
suc+40%Ca	74.79	97.17	40

* calculated as described in Barrera et al. (2009).

** % of the Recommended Dietary Allowance for calcium in 200 g of vacuum impregnated apple.

Table 2. Composition of samples at the beginning of the drying process and effective diffusion coefficients of water (D_e) obtained by fitting experimental data to the Fick's diffusion model.

TREATMENT	x_0^w (g/g)	x_0^{ss} (g/g)	x_0^{Ca} (mg/g)	T (ºC)	D_e x 10^{10} (m^2/s)	SSE
no VI	0.856 (0.008)[b]	0.115 (0.006)[a]	0.028 (0.008)[a]	30	3.3 (0.2)	0.388
				40	6.6 (0.4)	0.205
				50	8.0 (0.4)	0.231
VI suc	0.837 (0.013)[a]	0.138 (0.009)[c]	0.027 (0.007)[a]	30	2.5 (0.3)	0.301
				40	3.97 (0.04)	0.263
				50	5.0 (1.4)	0.336
VI suc+20%Ca	0.856 (0.003)[b]	0.120 (0.002)[ab]	1.19 (0.08)[b]	30	2.2 (0.3)	0.330
				40	4.1 (0.3)	0.560
				50	5.9 (0.7)	0.486
VI suc+40%Ca	0.855 (0.010)[b]	0.122 (0.005)[b]	2.7 (0.3)[c]	30	2.05 (0.14)	0.934
				40	4.005 (0.007)	0.566
				50	6.7 (0.6)	0.440

Mean values and standard deviation in brackets. SSE is the sum of squared errors of prediction. x_0^w, x_0^{ss} and x_0^{Ca} respectively stand for the water, soluble solids and calcium content of the samples at the start of drying.

Table 3. Real values of the phenomenological coefficient (L_w, in $mol^2/J·m^2·s$, x10^6) obtained by the thermodynamics of irreversible processes model.

T (ºC)	no VI	VI suc	VI suc+20%Ca	VI suc+40% Ca
30	2.49 (0.13)	3.86 (0.13)	4.25 (0.07)	3.4 (0.4)
40	2.09 (0.08)	2.9 (0.3)	3.0 (0.6)	2.9 (0.2)
50	2.1 (0.3)	1.95 (0.08)	3.1 (0.6)	2.8 (0.8)

Mean values and standard deviation in brackets.

Table 4. Kinetic constants of the Peleg model for the different conditions tested.

TREATMENT	T (ºC)	k_1 (min/g)	k_2 (g^{-1})	SSE	M_∞/M_0
no VI	30	4.7 (0.5)	0.066 (0.005)	0.054	0.684 (0.009)
	40	4.5 (0.2)	0.060 (0.002)	0.127	0.70 (0.02)
	50	4.0 (0.2)	0.067 (0.005)	0.138	0.650 (0.014)
VI suc	30	4.7 (0.8)	0.038 (0.002)	0.366	0.78 (0.02)
	40	4.6 (0.2)	0.044 (0.002)	0.169	0.71 (0.02)
	50	4.1 (0.3)	0.040 (0.004)	0.196	0.745 (0.007)
VI suc+20%Ca	30	5.6 (0.2)	0.052 (0.003)	0.276	0.66 (0.02)
	40	3.87 (0.08)	0.050 (0.009)	0.302	0.645 (0.013)
	50	5.0 (0.3)	0.049 (0.003)	0.291	0.655 (0.002)
VI suc+40% Ca	30	5.42 (0.14)	0.058 (0.004)	0.537	0.62 (0.02)
	40	4.3 (0.2)	0.056 (0.002)	0.081	0.603 (0.003)
	50	4.238 (0.009)	0.048 (0.008)	0.388	0.602 (0.008)

Mean values and standard deviation in brackets. SSE is the sum of squared errors of prediction.

Table 5. Rehydration indices for the different process conditions tested.

TREATMENT	T (ºC)	WAC	DHC	RA	WHC
no VI	30	0.627 (0.003)	0.200 (0.003)	0.125 (0.002)	0.59 (0.02)
	40	0.67 (0.03)	0.21 (0.02)	0.142 (0.012)	0.612 (0.002)
	50	0.67 (0.02)	0.196 (0.003)	0.132 (0.005)	0.51 (0.06)
VI suc	30	0.71 (0.03)	0.253 (0.003)	0.180 (0.009)	0.67 (0.09)
	40	0.72 (0.02)	0.24 (0.03)	0.17 (0.02)	0.76 (0.06)
	50	0.74 (0.02)	0.22 (0.02)	0.16 (0.02)	0.72 (0.03)
VI suc+20%Ca	30	0.69 (0.02)	0.213 (0.014)	0.147 (0.006)	0.654 (0.009)
	40	0.60 (0.04)	0.22 (0.02)	0.13 (0.02)	0.54 (0.06)
	50	0.64 (0.02)	0.22 (0.02)	0.143 (0.013)	0.61 (0.05)
VI suc+40% Ca	30	0.614 (0.014)	0.191 (0.002)	0.117 (0.003)	0.58 (0.13)
	40	0.646 (0.013)	0.221 (0.008)	0.143 (0.003)	0.502 (0.002)
	50	0.63 (0.02)	0.23 (0.02)	0.144 (0.012)	0.47 (0.03)

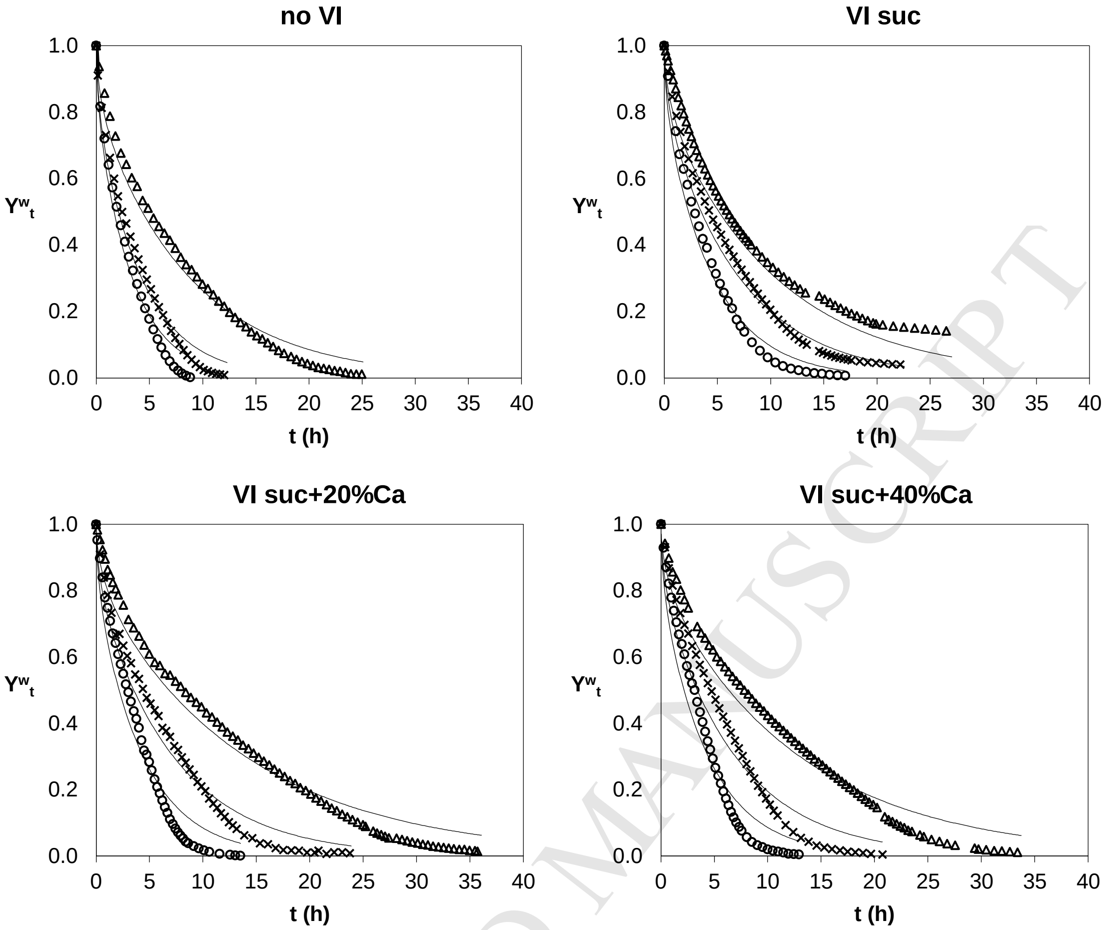
Mean values and standard deviation in brackets.

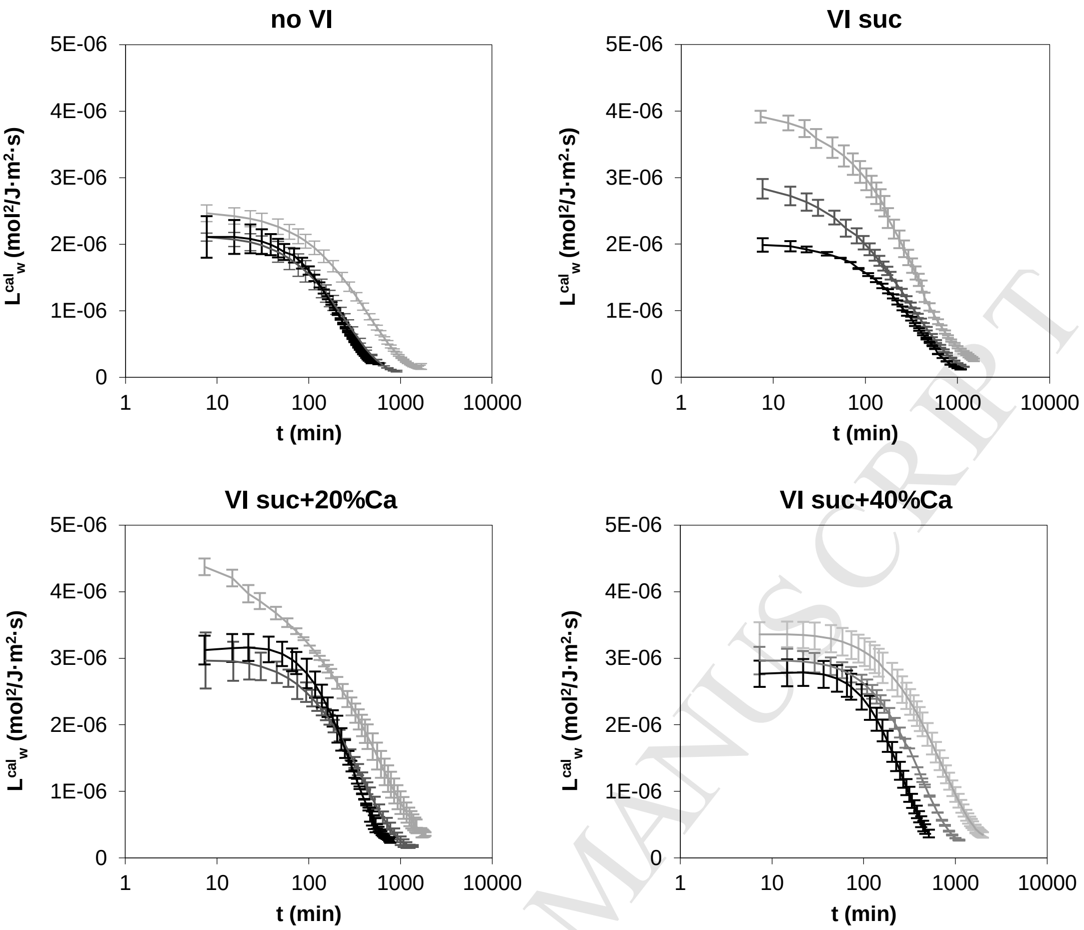
Figure captions

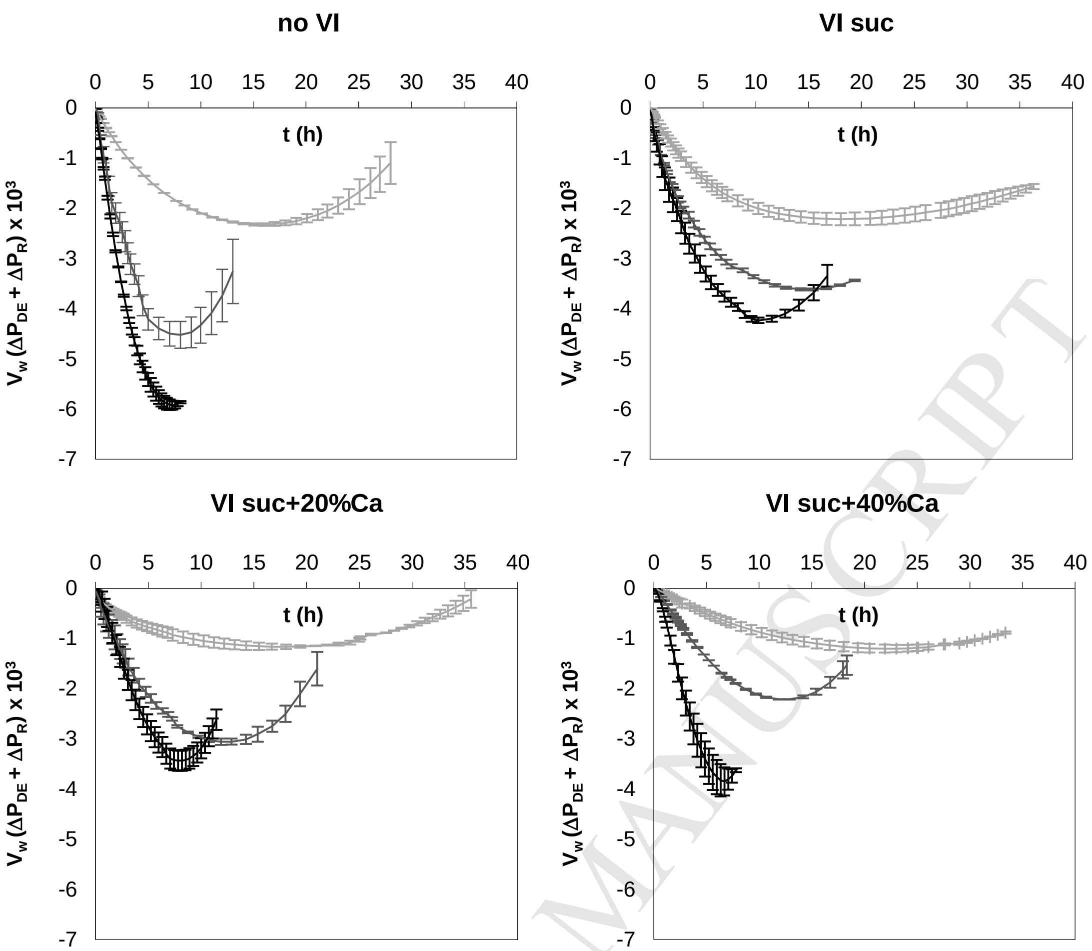
Fig. 1. Changes in the driving force (Y^{w}_{t}) with the time for the different pretreatments tested and the three drying temperatures: 30 ºC (Δ), 40 ºC (x) and 50 ºC (o). Mean values of experimental data (points) and fitted diffusional model (lines).

Fig. 2. Changes in the calculated phenomenological coefficient (L^{cal}_{w}) with the time for the different pretreatments tested and the three drying temperatures: 30 ºC (the lightest grey line), 40 ºC (grey line) and 50 ºC (black line). Mean values of experimental data and standard deviation (error bars).

Fig. 3. Changes in the free energy to generate structural deformation and/or breakages efforts (V_w (ΔP_{DE}+ΔP_R), in J/mol) with the time for the different pretreatments tested and the three drying temperatures: 30 ºC (the lightest grey line), 40 ºC (grey line) and 50 ºC (black line). Mean values of experimental data and standard deviation (error bars).


no VI
VI suc
VI suc+20%Ca
VI suc+40%Ca
Y^w_t
t (h)
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
40


no VI
VI suc
VI suc+20%Ca
VI suc+40%Ca
L^cal_w (mol²/J·m²·s)
t (min)
5E-06
4E-06
3E-06
2E-06
1E-06
0
1
10
100
1000
10000


no VI
VI suc
VI suc+20%Ca
VI suc+40%Ca
t (h)
0 5 10 15 20 25 30 35 40
0 -1 -2 -3 -4 -5 -6 -7
$V_w (\Delta P_{DE} + \Delta P_R) \times 10^3$

Highlights

- Mechanical changes in convective drying are hardly assessed by diffusional models.
- Energy used in deformations is estimated by nonlinear irreversible thermodynamics.
- Data confirm the coupling between diffusional and deformation-relaxation phenomena.
- Samples behaviour during rehydration confirms the extent of structural damage.
- Apples including calcium were the stiffest and the most damaged during air drying.