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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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A B S T R A C T

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. 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 °C was analysed by applying equations derived from nonlinear irreversible thermodynamics to experimental data. According to the results obtained, vacuum impregnation with isotonic sucrose solution before drying at 30 °C 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.

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 and 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

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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 and 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, around 75 mm outer diameter apples (var. Granny Smith) were washed, cut into 10 mm thick slices in the direction perpendicular to the longitudinal axis and cored with a 22 mm in diameter cylindrical steel punch. Given that apple cutin moisture diffusion coefficient is more than 100 times lower than that of parenchymatic apple tissue (Veraverbeke et al., 2003), mass transfer trough the lateral outer surface of unpeeled apple rings was assumed to be negligible. Also taking into account that the lateral inner surface accounted for less than 5% of the total surface of the ring, contribution of mass transfer trough it was assumed to have no relevant effect on compositional changes undergone by apple samples during the drying step. According to this, apple rings were considered to behave like an infinite plane sheet during further modelling of experimental data.

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.

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

Solution	[Sucrose] in g/L	[Calcium lactate] in g/L[a]	%RDA[b]
Suc	215.68	0	0
Suc+20%Ca	112.29	44.22	20
Suc+40%Ca	74.79	97.17	40

[a] Calculated as described in Barrera et al. (2009).

[b] % of the Recommended Dietary Allowance for calcium in 200 g of vacuum impregnated apple.

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 °C (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). 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).

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

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}).

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

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