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Effect of temperature on hot-air drying rate and on retention of antioxidant capacity in apple leathers

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ABSTRACT

Fruit leathers are pectic gels, eaten as snack or dessert, obtained by dehydrating fruit purees. In this work, apple leathers were prepared by a hot-air drying process which allows the formation of a gel, following the "saccharide–acid–high methoxyl pectin" gelation mechanism. Leathers were produced at 50, 60 and 70 °C, from two formulations: control and added with potassium metabisulphite (KM) as antioxidant. The drying process was studied applying a diffusive model, while antioxidant capacity (AC) losses were represented by a first-order model. Activation energy for drying (20.6 kJ/mol) was lower than those estimated for AC losses in control (31.5 kJ/mol) and KM-added (37.9 kJ/mol) leathers. Therefore, the drying time reduction achieved by increasing air temperature is not sufficient to decrease AC losses in the range covered. AC retention decreased in both formulations at increasing air temperature. KM-added samples showed higher AC retention than the controls, except for those dried at 70 °C. Kinetic constants were lower for KM-added samples, suggesting a protective effect of the additive, especially at moderate air temperatures. In the most favorable situation, AC retention was of only 16%. Therefore, the functional character of these products may not be preserved if dried with hot air and the research on economically viable, less-severe drying technologies should be intensified.

Keywords: Fruit leather; Apple; Hot-air drying; Antioxidant

1. Introduction

Dehydration extends the shelf life of a great variety of products, by inhibiting microbial growth and significantly reducing weight and volume for easier transportation and handling of large amounts of food. The water removal step may not only be used to preserve the raw material but also to form a restructured food matrix. Fruit leathers are dehydrated fruit-based products that are eaten as candy or snacks, usually presented as flexible stripes or sheets. They receive this name because of its shiny appearance and texture. Due to its attractive structure, and for being products that do not require refrigeration to avoid microbial growth, leathers constitute a practical way to incorporate fruit solids. Their consumption adds variety to the diet and allows the intake of dietary fiber, vitamins and minerals, while providing a substantial energy input. In the United States, home preparation of these products is usual, to preserve and consume ripe and even slightly overripe fruit. In recent years their popularity has increased, transforming fruit leathers from a homemade preparation into an industrial product.

In early publications (Bains et al., 1989; Chan and Cavaletto, 1978; Moyls, 1981), physicochemical properties and sensory attributes of fruit leathers were studied. Subsequent research added data about quality and stability during storage (Vijayanand et al., 2000; Wandi and Che Man, 1996). Recent work encompassed various subjects, as combined preservation technologies and drying kinetic studies (Fiorentini

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et al., 2008;Gujral and Khanna, 2002; Jaturonglumlert and Kiatsiriroat, 2010). An important issue, insufficiently studied yet, is the effect of processing conditions on quality of the final product (Sablani, 2006). This is the subject matter of the present research, in which hot-air drying was applied to obtain apple leathers by the "saccharide–acid–high methoxyl pectin" gelation mechanism. Apples are particularly suitable as raw material, since their parenchyma contains a high proportion of pectins (0.15–0.25 kg/kg dry matter) (Rinaudo, 1996). In addition, apples provide a great variety of polyphenols with antioxidant activity (Brewer, 2011; Oszmiański et al., 2008) as well as moderate amounts of potassium, phosphorus and vitamin C (USDA, 2010). The formulation included a low-calorie polysaccharide, polydextrose, which provides soluble fiber and yields only 1 kcal/g, i.e., a quarter of the energy input of sugars (Achour et al., 1994). Polydextrose is non-cariogenic, acts as prebiotic and is adequate for diabetics (Zhong Jie et al., 2000). This newly formulated leather can be consumed as a convenience food or snack, contributing to increase fruit solids intake with a reduced caloric contribution. It may also be used as yogurt topping, in cereal bars, desserts, ice creams, etc. (Leiva Díaz et al., 2009).

It is well known that fresh fruits and vegetables are excellent source of minerals, vitamins, bioactive compounds (as phenolics and carotenoids) and fiber. However, the drying process usually leads to undesirable changes in some quality parameters as, for instance, nutritional losses (Ratti, 2001), and these changes were not yet sufficiently studied to make them available to processing industry and consumers. Therefore, the aim of this work was to describe the effect of air temperature on drying kinetics and on retention of antioxidant capacity of apple leathers, formulated with and without potassium metabisulphite (KM). This additive was used because of its high sulphur dioxide yield, and is expected to improve retention of apple polyphenols by restraining oxidative losses during drying.

2. Materials and methods

2.1. Fruit sample

Apples (*Malus Domestica* Borkh. cv. Granny Smith), purchased on a local market in La Plata, Argentina, were stored at 4 °C for no longer than 10 days before using. A flow sheet describing the preparation of apple leathers is shown in Fig. 1.

2.2. Pre-treatment

Apples were washed, peeled manually and cut into 1 cm side cubes, discarding the core. Then, 250 g of these were placed in a steamer at 99.1 °C (Moulinex, France) fed with distilled water, and processed for 10 min to inactivate the polyphenol oxidase (PPO) in the whole volume of pieces to avoid enzymatic browning of apple pulp in subsequent stages. Cubes were removed from the steamer to be immediately placed in a container cooled by an ice/water bath.

2.3. Guaiacol test

The thermal resistance of peroxidase (POD) is slightly higher than that of PPO, so the guaiacol test, a qualitative assay detecting POD activity, can be utilized to confirm inactivation of PPO (Yemenicioğlu et al., 1998). After applying the thermal pretreatment for various times, apple cubes were processed into a homogenous purée. Approximately 1 g of the purée was added with 0.15 ml of H_2O_2 3% (w/v) and 0.15 ml of guaiacol 1% (v/v). Guaiacol is oxidized by H_2O_2 in the presence of peroxidase to produce brown pigments. As no brown color was observed in the sample after 1 min of contact with the reactants, POD and, subsequently, PPO were considered inactivated.

2.4. Formulation

The pretreated material was processed using a blender (Philips, Holland), until obtaining a homogenous purée. This was mixed with the rest of the ingredients to the following proportions (%, w/w): apple purée, 78.98; sucrose, 9.00; polydextrose powder (Winway I), 9.00; citric acid solution, 3.00; sucralose micronised powder (Tate and Lyle), 0.02. The concentration of citric acid solution was 0.302 M, equivalent to that in lemon juice. This formulation was similar to that reported by Leiva Díaz et al. (2009), with the exception that 9 g out of the 18 g of sucrose added by these authors were replaced by polydextrose to reduce the energy intake. A similar formulation was also prepared here, but added with potassium metabisulphite (KM) to reach 6.3×10^{-3}% (w/w), corresponding to 100 ppm of SO_2 in the final product.

2.5. Hot-air drying conditions

Control and KM-added formulations were placed in 0.20 m side stainless steel trays, with an initial thickness of 6 mm, and dehydrated in a purpose-developed laboratory tray dryer with an in situ weighing system (Fiorentini et al., 2008), at 50, 60 and 70 °C with an air velocity of 2 m/s. These operating conditions are typical in industry (Greensmith, 1998; Velić et al., 2004). Samples were dried until reaching a moisture content of about 0.3 kg water/kg dry matter, which corresponds to a water activity of 0.70, sufficiently low in acid medium to inhibit mold growth at room temperature (Chirife, 1993). A mass balance was solved assuming constant dry matter in the product during drying (Eq. (1)) to calculate the product mass corresponding to the drying endpoint.

$$m_t = \left(\frac{1 + W_t}{1 + W_0}\right) m_0 \quad (1)$$

where W_t and m_t are the moisture content (kg water/kg dry matter) and the product mass respectively, at time t, whereas W_0 and m_0 are the corresponding initial values.

2.6. Drying kinetics

The drying experiments at each temperature were conducted in triplicate. To construct the drying curves, experimental moisture contents were determined by weighing the sample at several times during drying and solving Eq. (1) for W_t. Data of room temperature and ambient relative humidity was recorded using a Testo 608-H2 thermohygrometer. Both parameters were supplied to a psychometric chart software (Akton Associates Inc., USA) to determine the relative humidity (h_d) at the corresponding drying air temperature. The equilibrium moisture content at the drying conditions, W_e, was calculated with a correlation proposed by Leiva Díaz et al. (2009)

$$W_e = 0.0994 \exp\left(3.584\, a_w^{3.307}\right) \quad (2)$$

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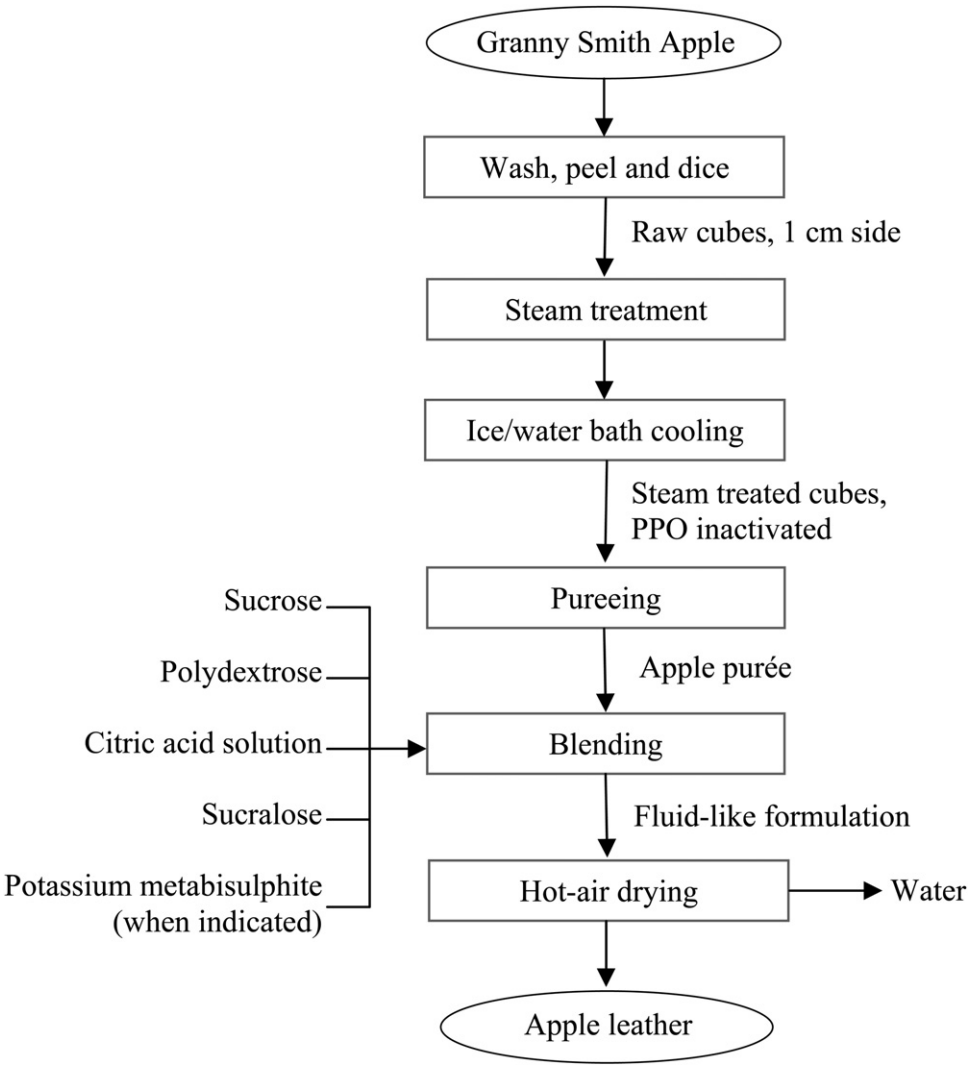

Fig. 1 – Flow sheet for the preparation of apple leathers.

where a_w, the water activity of the product, is assumed to be equal to h_d at equilibrium conditions. In general, fresh apple isotherms show a slight dependence whit temperature that gradually disappears as water activity decreases, so at a_w values below 0.15 the effect of temperature is negligible (Djendoubi Mrad et al., 2012). Moreover, when saccharides are added to the fruit as in fruit leathers preparation, isotherms are not affected by temperature at a_w below 0.80 (Kaya and Kahyaoglu, 2005). This consideration allows the calculation of W_e by Eq. (2) for all drying temperatures, as the relative humidity of the drying air (h_d), and so the product a_w at equilibrium, were never higher than 0.080 in the experimental conditions of this work. Drying curves were modeled by applying a diffusional model for isothermal drying (Crank, 1975), which accurately predicted the drying of apple leathers (Leiva Díaz et al., 2009) and tomato leathers (Fiorentini et al., 2008). The model solution of the unsteady-state, local mass balance for internal–external control to the mass transfer rate, integrated over a plane sheet, is as follows:

$$W_{ad} = \frac{W_t - W_e}{W_0 - W_e} = \sum_{n=1}^{\infty} \frac{2Bi^2 \ \exp((-\beta_\eta^2 Dt)/d^2)}{\beta_\eta^2(\beta_\eta^2 + Bi^2 + Bi)} \quad (3)$$

where W_{ad} is the dimensionless moisture content, Bi is the mass transfer Biot number, d stands for the initial product thickness in m, t is the time in s and D is the effective diffusion coefficient in m^2/s. In turn, β_n is the nth root of the transcendental equation

$$\beta_n tg\beta_n - Bi = 0 \quad (4)$$

The model is proposed for describing drying of apple leathers which proceeds in a tray with air flow parallel to the evaporative surface. A plane sheet geometry was adopted to represent the food. Being length and width of the product more than 30 times higher than the thickness, water diffusion was taken as one-dimensional in the thickness direction.

2.7. *Initial and final moisture content*

Samples of approximately 5 g of formulation (for initial moisture content) and apple leather (for final moisture content) were placed in a Mettler LP 16 Moisture Analyser set at 105 °C, until reaching constant weight, according to the AOAC method 984.25 (AOAC, 1998). Moisture contents were expressed in kg water/kg dry matter, as the average ± standard deviation of

the six samples corresponding to every formulation and air temperature used.

2.8. Water activity

The water activity (a_w) of apple leathers was measured at 25 °C by the AOAC hygrometric method 978.18 (AOAC, 1998), using a temperature-controlled AquaLab 3TE meter (Decagon Devices, Inc.). Results were averaged as described in Section 2.7.

2.9. pH

Apple leather samples of about 5 g were conditioned according to AOAC method 981.12 (AOAC, 1998) by freezing in liquid N_2 and grinding in a laboratory mill. Then, 1 g of the ground material was dispersed in 10 ml distilled water. The pH was measured in the dispersion using an Alpha PW-40 electrode connected to an Altronix TPA-V pHmeter with digital display. Results were averaged as described in Section 2.7.

2.10. Antioxidant capacity

The procedure carried out to determine antioxidant capacity (AC) in formulations (AC_0) and apple leathers (AC_f) was that proposed by Brand Williams et al. (1995), and is based on inhibition of the free radical 2,2-diphenyl-1-picrilhydrazil (DPPH•) in ethanolic extracts of the samples. A modified version was applied here following recommendations by Molyneux (2004). Fig. 2 shows a diagram of the extraction and quantification procedure. In order to evaluate AC_0, a 2 g sample of each formulation was suspended in 10 ml ethanol 96° (Anedra) under stirring for 40 min at 4 °C. The extract was then centrifuged for 10 min at 10,000 × g at 4 °C to retain the supernatant. Concerning AC_f, ethanolic extracts from the corresponding leathers were prepared, using 4 g of the frozen leather, ground in a laboratory mill. Extractions were conducted in duplicate and the extracts were kept at −18 °C until performing the DPPH• test. Extract volumes ranging from 0 to 500 μl were mixed in test tubes, with 1 ml of an ethanolic solution of DPPH• (Sigma–Aldrich) 40 ppm, prepared on the same day. Ethanol 96° was added to reach a constant final volume of 1.5 ml. The reaction evolved at 25 °C for 60 min in the dark, after which absorbance at 517 nm was read using a Hitachi U-1900 spectrophotometer. The percentage inhibition of DPPH• was calculated for every extract volume as follows:

$$\%\text{DPPH}^{\bullet}\ \text{inhibition} = 100 \times \left(\frac{A_0 - A_{\text{sample}}}{A_0}\right) \quad (5)$$

where A_0 is the reference value of absorbance, measured in a reaction mixture without sample, and A_{sample} is the absorbance of each reaction mixture containing different volumes of ethanolic extract. Then, the sample mass required to cause 50% DPPH• inhibition (EC_{50}) was determined and antioxidant capacity was expressed as the reciprocal of EC_{50}, i.e., $AC = 1/EC_{50}$ (1/g dry matter). AC retention was calculated for every formulation and drying temperature studied, as the ratio of AC_f to AC_0.

2.11. Statistical analysis

A two-way analysis of variance (ANOVA) was carried out ($P < 0.05$) to analyze the effect of air temperature and potassium metabisulphite (KM) on AC retention. The effects on kinetic constants for AC losses were also studied. Average values of AC retention and kinetic constants were compared by the Least Significant Difference (LSD) Fisher test ($P < 0.05$).

3. Results and discussion

3.1. Process and product characteristics

According to the results of the guaiacol test, inactivation of polyphenol oxidase (PPO) in 1 cm side apple cubes occurs after a steam treatment of 3 min. However, after careful observation of the effect of steam treatments of 3, 5, 10 and 15 min on the handling of apple leathers, a time of 10 min was chosen to increase their mechanical resistance (possibly as a consequence of an improved gelation capacity of pectins).

The fluid-like formulation (initial moisture content, 2.46 ± 0.08 kg water/kg dry matter) was transformed during hot-air drying into a gel-like structure by the "saccharide–acid–high methoxyl pectin" gelation, promoted by solids concentration and low pH (Rinaudo, 1996). For pH above 3.5, the carboxyl groups in pectins are dissociated, their protons being released to the medium and generating a negatively charged, highly hydrated pectic polymer. As pH becomes lower than 3.5, the carboxyl groups now retain their protons, and the pectic polymer remains uncharged and only slightly hydrated. As the matrix is dried to reach a soluble solid content above 60% (w/w), saccharides compete with pectins for binding the remaining water molecules (Damodaran et al., 2007). This behavior decreases the hydration level of pectins, which thus stabilize linking each other by hydrogen bonds and hydrophobic interactions (Oakenfull, 1991). So, a three-dimensional network of pectic polymers entrapping a sugar solution (pectic gel) is formed during drying as moisture content reaches about 0.67 kg water/kg dry matter. Then dehydration is continued until reaching the final moisture of 0.3 kg water/kg dry matter, so the formed gel maintains its structure while losing moisture. Hence the finished apple leather can be described as a partially dehydrated pectic gel. Fig. 3 exhibits photographs of the formulation and the finished product.

The amount of potassium metabisulphite (KM) used here represents only one tenth of the admissible level of SO_2 appearing in the Codex Alimentarius for dehydrated fruits (FAO/WHO, 2011). As expected by its extremely low mass proportion, KM had no effect on drying kinetics of leathers, nor on physicochemical properties. For both formulations, hot-air drying at 50, 60 and 70 °C demanded 7.25, 6.17 and 4.37 h, respectively (Table 1). Comparable drying times have been reported for hot-air dried fruit leathers (Azeredo et al., 2006; Gujral and Khanna, 2002; Lee and Hsieh, 2008). Final product characteristics were as follows: moisture content, 0.280 ± 0.01 kg water/kg dry matter; a_w, 0.699 ± 0.009 and pH, 3.41 ± 0.07. The proportion of apple solids in the leather was calculated as 24.4% (w/w), which is 1.83 times the value contained in a fresh peeled apple (USDA, 2010). This product is microbially stable at room temperature due to limited water activity, low pH and high soluble solid content.

3.2. Drying kinetics

Operating conditions for the drying runs are shown in Table 1 (first to fourth column from left to right). In turn, Fig. 4 illustrates the experimental drying curves, in which the dimensionless moisture content (W_{ad}) was plotted as a function of time, for the three drying temperatures. In order to

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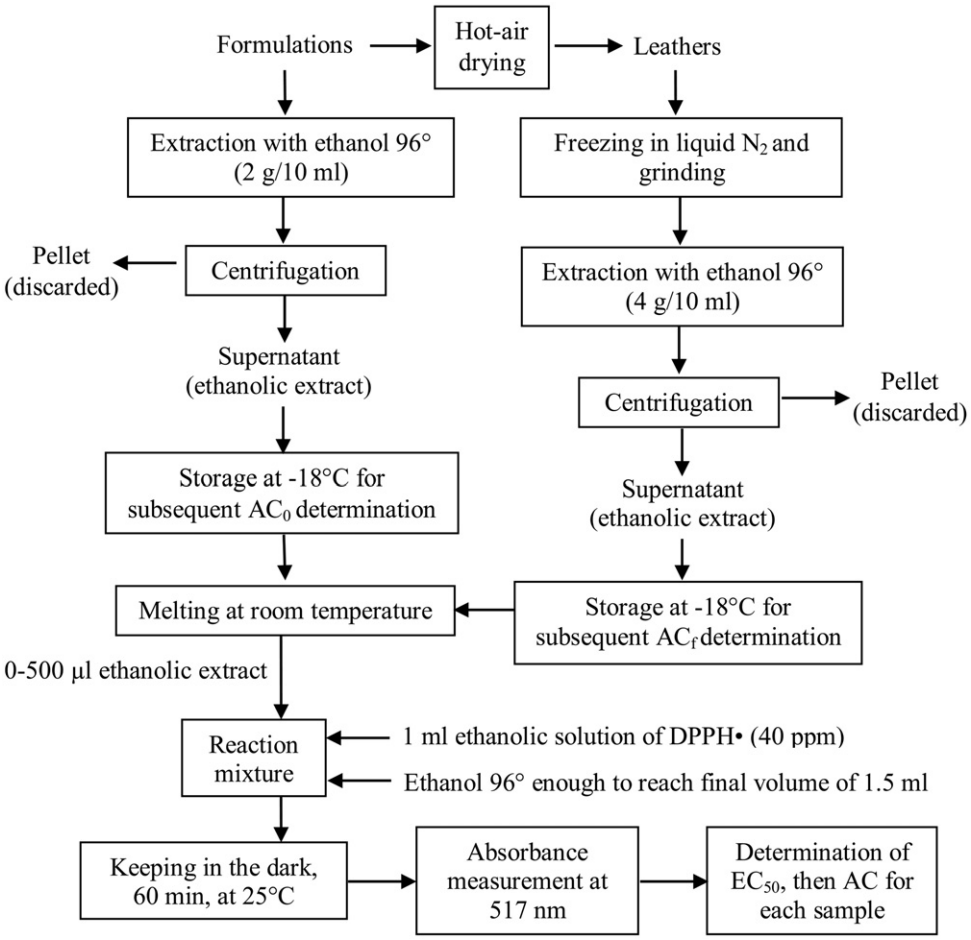

Fig. 2 – Operations followed for extraction and measurement of antioxidant capacity (AC) of the two formulations, hot-air dried at 50, 60 and 70 °C, before (AC_0) and after (AC_f) drying.

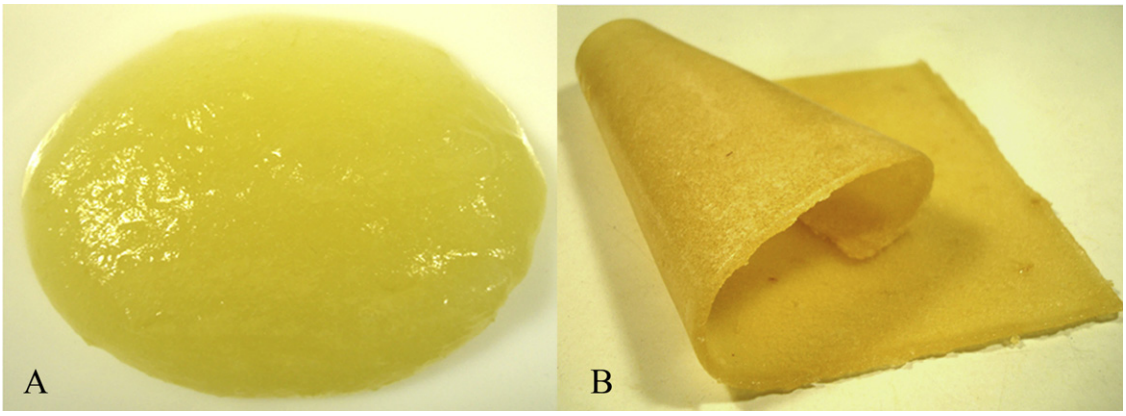

Fig. 3 – Photograph of fluid-like formulation (A) and apple leather (B).

Table 1 – Operating conditions for the drying experiments.

T (°C)	t_f (h)	h_d (dec.)	W_e (dec. d.b.)	Bi	D (m^2/s)	r^2
50 ± 0.5	7.25 ± 0.31	0.080 ± 0.004	0.0995	0.966	4.753×10^{-9}	0.999
60 ± 0.5	6.17 ± 0.28	0.075 ± 0.003	0.0995	0.966	5.583×10^{-9}	0.999
70 ± 0.5	4.37 ± 0.27	0.035 ± 0.005	0.0994	0.966	7.442×10^{-9}	0.998

T: drying air temperature; t_f: total drying time; h_d: relative humidity of the drying air; W_e: equilibrium moisture content; Bi: mass transfer Biot number; D: effective diffusion coefficient; r^2: coefficient of determination for Eq. (3).

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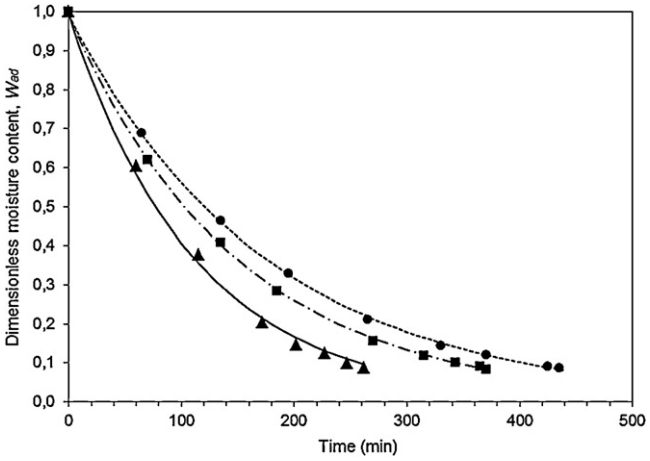

Fig. 4 – Experimental dimensionless moisture content (W_{ad}) as a function of time, at 50 °C (●), 60 °C (■) and 70 °C (▲). The lines represent the corresponding diffusive model predictions.

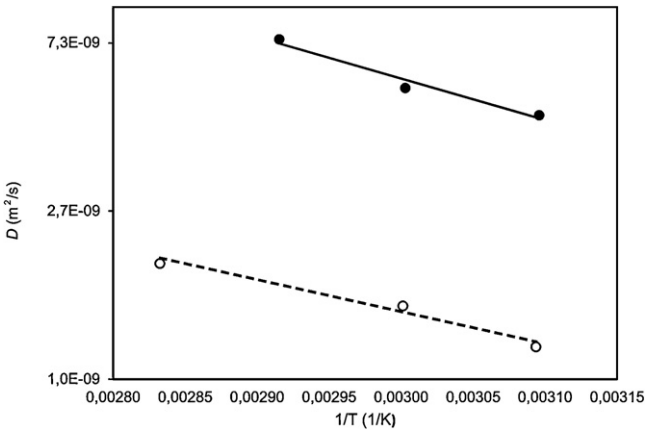

Fig. 5 – Effective diffusion coefficient (logarithmic scale, base *e*) as a function of the reciprocal of the absolute drying air temperature. Experimental data from this work (●) and from Leiva Díaz et al. (2009) (○) is compared. The lines represent the corresponding Arrhenius model predictions.

apply Eq. (3), a preliminary study was carries out: the optimum value of D was calculated for various Biot numbers, using 1, 2, 3 and 6 terms of the series. In a range encompassing almost external ($Bi \to 0$) to almost internal control to the mass transfer rate ($Bi \to \infty$), the use of more than one term did not bring a practical improvement of accuracy. So, only the first term was considered to find the fitting parameters mentioned above, for this polydextrose-added leather for which kinetic studies were not done in a laboratory tray dryer before. The built-in function *nlinfit* of the Matlab 7.0 programming environment was employed to carry out nonlinear fitting by the least-squares method in a purpose-developed program. The value of β_1 was also calculated in the same Matlab program, using the correlation proposed by Leiva Díaz et al. (2009):

$$\beta_1 = 1.494(1 - \exp(-0.855\,\mathrm{Bi}^{0.564})) \quad (6)$$

The initial thickness of the plane sheet (6×10^{-3} m) was used as datum. Fitting parameters were Bi and D. Results of the fitting are provided in Table 1 with, on the basis of the coefficients of determination reported, an excellent agreement of predictions and data, as also demonstrated in Fig. 4. The mass transfer Biot number was the same, almost unity, for the three drying temperatures, indicating that internal and external resistances to the mass transfer rate are equivalent. This model is functionally effective, because it is based on the assumption that the water diffusion coefficient and the product thickness are constant during drying. However, a considerable one-dimensional shrinkage in the thickness direction was observed for apple leathers in this work, as measured by Leiva Díaz et al. (2009) and described by Kechaou et al. (1987). In view of that, the accurate predictions exhibited by Eq. (3) may suggest that, in fact, it is the ratio D/d^2 which remains constant in practice, which is mathematically equivalent to the assumption valid for Eq. (3), where both D and d are unaltered. Therefore, as the initial thickness was used, the diffusion coefficient and Biot numbers fitted by the program should correspond to the conditions prevailing initially during each drying experiment. This might explain why the fitted Bi was essentially the same for the three drying temperatures, leaving the temperature effect to be self-contained within the diffusion coefficient. The increase of D with temperature, observed in Table 1, followed an Arrhenius behavior (Fig. 5), so the model

$$D = D_\infty \ \exp\left(\frac{-E_a}{RT_K}\right) \quad (7)$$

was fitted to the corresponding data, being $R = 8.314$ J/K mol the ideal gas constant and T_K the drying temperature in K. The fitted Arrhenius preexponential factor (D_∞) was 9.932×10^{-6} m^2/s, with an activation energy (E_a) of 20.6 kJ/mol, ($r^2 = 0.968$). Many studies (Fiorentini et al., 2008; Gastón et al., 2004) have determined E_a for food drying between 20 and 30 kJ/mol. Comparing the present results with those obtained by Leiva Díaz et al. (2009) in Fig. 5, it can be said that the replacement of part of the sugar in the formulation by polydextrose, leads to higher values of D in the range of temperature from 50 to 80 °C, usually applied for food hot-air drying. Besides, E_a is also higher for the formulation containing polydextrose: 20.6 kJ/mol against 15.2 kJ/mol for the conventional product.

3.3. *Antioxidant capacity*

Table 2 lists the antioxidant capacity before (AC_0) and after (AC_f) hot-air drying, while Fig. 6 compares AC retention for

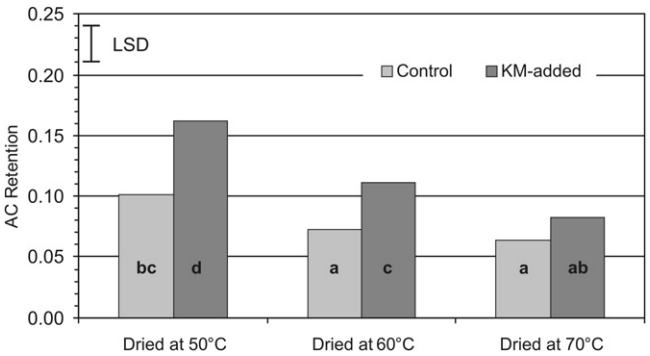

Fig. 6 – Retention of antioxidant capacity (AC) in apple leathers dried at 50, 60 and 70 °C, from control and potassium metabisulphite (KM)-added formulations. Different letters in the bars represent significantly different values ($P < 0.05$).

Table 2 – Experimental values for antioxidant capacity of samples, and first-order kinetic constants (k) for antioxidant capacity loss.

Formulation	Drying air temperature (°C)	AC_0 (1/g dry matter)[a]	AC_f (1/g dry matter)[a]	k (1/h)[a,b]
Control	50	124.15 ± 4.57	12.50 ± 1.67	0.317 ± 0.013d
Control	60	124.15 ± 4.57	9.02 ± 0.02	0.425 ± 0006c
Control	70	124.15 ± 4.57	7.94 ± 0.95	0.630 ± 0.019a
KM-added	50	151.87 ± 1.79	24.65 ± 2.28	0.251 ± 0.011e
KM-added	60	151.87 ± 1.79	16.87 ± 1.95	0.357 ± 0.017d
KM-added	70	151.87 ± 1.79	12.47 ± 1.75	0.573 ± 0.029b

KM: potassium metabisulphite; AC_0 and AC_f: antioxidant capacities before and after hot-air drying, respectively.
[a] Expressed as average ± standard deviation.
[b] Different letters stand for significantly different values ($P < 0.05$).

each formulation and drying temperature tested. AC retention in apple leathers varied from 6.4% in the control formulation, dried at 70 °C, to 16.2% in the KM-added formulation, dried at 50 °C. Goula and Adamopoulos (2006) have found a comparably low nutritional retention on a different dehydrated food matrix as halved tomatoes, measuring ascorbic acid losses of 90% during 7 h of drying at 80 °C. Similarly, Mejia-Meza et al. (2008) have reported an antioxidant activity retention of only 10% in blueberries after hot-air drying at 76.6 °C during 4.5 h.

In general, AC retention decreased in both formulations for higher air temperatures. However, in the control sample, differences of AC retention during drying at 60 and 70 °C were not significant. Effect of temperature appears to be nonlinear: it is stronger between 50 and 60 °C than between 60 and 70 °C. This may be possibly caused by time–temperature interaction: higher temperatures imply shorter exposure times. In hot-air dehydration, and in agreement with the results obtained in the present work, Rovedo and Viollaz (1998) observed stronger nutrient losses for higher temperature, as well as Inyang and Ike (1998) and Mohamed and Hussein (1994), who observed lower retention of ascorbic acid and carotenoids at higher temperatures.

KM-added formulations exhibited higher AC retention than the controls after drying at 50 and 60 °C, but not at 70 °C. In view of the differences of AC retention (Fig. 6), KM seems to exert a strongest protective action at 50 °C. This trend was also observed by Ahmed et al. (2010) in sweet potato flour obtained from sulphite-treated sweet potatoes. In order to analyze whether this higher AC retention is solely caused by the antioxidant capacity of KM itself or else by a preservative action of KM on sample antioxidants, the AC ratios of KM-added to control samples were compared before and after drying, using the values in Table 2. As, the ratio was 1.22 before drying, it is assumed that KM increased AC by 22% in the formulation and this can be considered the baseline effect of the additive on total AC. After drying, ratios increased to 1.97, 1.87 and 1.57 at 50, 60 and 70 °C respectively, well above the baseline value, which can be understood as an authentic preservative action of KM on natural antioxidants of leathers. Nevertheless, further work must be conducted with various KM proportions and using other analytical techniques, as HPLC, in order to discriminate between AC provided by natural compounds and additive.

Given that plant antioxidants are considered important nutrients for preventive medicine (Ramarathnam et al., 1995) and in view of the substantial losses of AC caused by hot-air drying observed in this and previous research, it is considered here that alternative dehydration technologies (vacuum and microwave-vacuum) should be used in industry for products that are to be commercialized as functional foods.

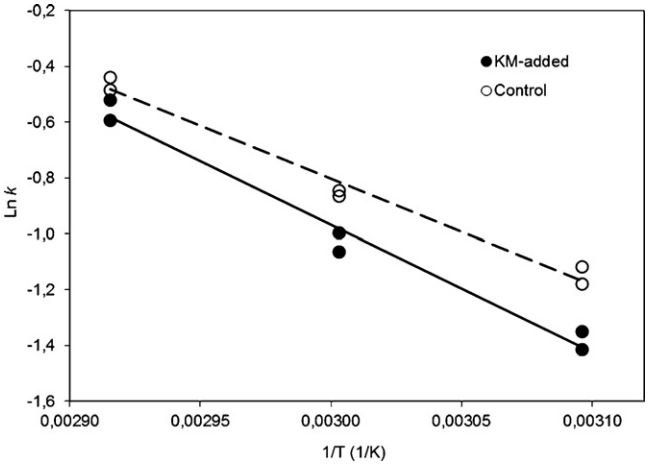

Fig. 7 – Experimental values of the natural logarithm of the first order kinetic constant (ln k) as a function of the reciprocal of the absolute drying air temperature (1/T), for both formulations. The lines represent the corresponding Arrhenius model predictions.

3.4. *Estimation of kinetic parameters for the loss of antioxidant capacity*

In order to carry out a mathematical assessment of the effect of temperature and presence of KM, a first-order kinetic model was assumed for the loss of AC. With this model, the experimental kinetic constant (k) was determined as follows

$$k = \frac{\ln(AC_0/AC_f)}{t_f} \quad (8)$$

for drying experiments carried out at 50, 60 and 70 °C with control and KM-added samples. The symbol t_f stands for the drying time in h. AC_0 and AC_f represent the antioxidant capacity of samples before and after drying, respectively. Table 2 includes the values of the kinetic constants. By plotting the natural logarithm of these constants as a function of the reciprocal of the absolute temperature in Fig. 7, the kinetic parameters are observed to follow an Arrhenius-type behavior (see Table 3) with r^2 of 0.984 for the control sample

Table 3 – Arrhenius parameters of the kinetic constants (k) for antioxidant capacity loss, in both formulations.

Formulation	Equation of linear regression[a]	r^2	E_a (kJ/mol)
Control	$y = -3793.8x + 10.577$	0.984	31.5
KM-added	$y = -4563.1x + 12.721$	0.980	37.9

KM: potassium metabisulphite; r^2: coefficient of determination; E_a: activation energy.
[a] y: ln k; x: reciprocal of the absolute temperature (1/K).

and of 0.980 for the KM-added sample. The corresponding E_a for antioxidant losses in apple leather during drying were 31.5 and 37.9 kJ/mol. Being these values higher than the activation energy for drying, the effect of temperature on antioxidant losses results considerably stronger than on drying rate. The ratio of E_a for AC losses to E_a for drying gives a numerical expression of the relative effect of temperature on velocity of the studied processes. For the results obtained here, the relative thermal effects are 1.53 for control formulation and 1.84 for KM-added product, both higher than unity. Thus the time–temperature interaction is such that the use of higher temperatures decreases quality more than it reduces the drying time, so it may increase production at the expense of a reduction in quality. Table 2 also shows that kinetic constants for KM-added samples are lower than for the controls. This is expected, since the additive should hinder antioxidant losses. However, as observed in Fig. 7, the effect of temperature on the kinetic constants was slightly stronger in KM-added samples than in the controls, suggesting that the protective action is more effective at moderate drying temperatures.

4. Conclusions

Apple leathers were obtained from a reduced-calorie formulation by hot-air drying at 50, 60 and 70 °C. The experimental drying kinetics was accurately predicted by a one-term diffusive analytical solution for plane sheets considering internal–external control to the mass transfer. The mass transfer Biot number resulted almost unity and the Arrhenius dependency of the effective diffusion coefficient with temperature provided an activation energy for drying of 20.6 kJ/mol.

Retention of antioxidant capacity (AC) of apple leathers was low (6–16%) and decreased for increasing air temperatures even when the resulting drying times were shorter. In mathematical terms, this effect is explained by the higher activation energy for AC losses (above 31 kJ/mol), compared with that for drying.

Potassium metabisulphite (KM), added in low proportion (100 ppm SO_2 in the final product) protects to some extent the natural AC of the matrix. The first-order kinetic constants determined for the loss of AC in both formulations were accurately predicted by the Arrhenius model. KM-added samples exhibited lower kinetic constants and higher activation energy for the loss of AC. Hence, the protective effect of KM was more manifest at lower drying temperatures.

The hot-air drying method, still the conventional technology in industry, was corroborated here to produce strong antioxidant losses. Therefore, economically feasible alternative technologies, drying conditions and additives should be tested, in order to find a suitable procedure for developing fruit leathers while preserving their nutritional value.

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