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1 **Vacuum drying of rosehip leathers: Modelling of coupled moisture content and**
 2 **temperature curves as a function of time with simultaneous time-varying ascorbic**
 3 **acid retention**

4
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19
 20 **Abstract**

21
 22 Vacuum drying kinetics, thermal histories and quality kinetics of two rosehip leather
 23 formulations were determined, at tray temperatures between 40 and 70°C. Data was
 24 simultaneously modelled as an ordinary differential equations system encompassing a
 25 transient water balance, a transient energy balance, and a variable-order quality kinetics
 26 equation, coupled to heat and mass transfer. A set of parameters was fitted for each
 27 formulation and satisfactory representations of the experimental data were obtained.
 28 Differences in drying rate compensated for the effect of the tray temperature on quality
 29 loss, so vacuum drying at 70 °C was recommended for rosehip leathers due to the
 30 shorter drying time required. In particular, the reaction order for ascorbic acid
 31 degradation was found to be dependent on the tray temperature.

32
 33 **Keywords:** rosehip leather; vacuum drying; quality; mathematical modelling.

34
 35 **Nomenclature**

AA	ascorbic acid
a_w	water activity
C_p	product specific heat (J/kg dry matter °C)
D	water diffusion coefficient (m ² /s)
D_0	pre-exponential factor in Eq. (4) (m ² /s)
e_0	initial product thickness (m)
E_a	activation energy for drying (J/mol)
E_{aq}	activation energy for quality loss (J/mol)
F	statistic value from Snedecor distribution

h_{eff}	effective heat transfer coefficient (W/ m ² °C)
k	kinetic constant for quality loss (s ⁻¹)
k_0	pre-exponential factor in Eq. (6.1) (s ⁻¹)
k_1, k_2	coefficients in Eq. (6.2)
L_w	heat of desorption of water (J/kg)
n	kinetic reaction order
n_1, n_2	coefficients in Eq. (6.1)
PAF	polydextrose-added formulation
Q	ascorbic acid content (mg/g dry matter)
Q_0	initial ascorbic acid content (mg/g dry matter)
R	ideal gas constant (J /K mol)
r^2	coefficient of determination
SAF	sucrose-added formulation
SSR	sum of squared residuals
T	product temperature (°C)
T_0	initial product temperature (°C)
T_b	tray temperature (°C)
t	time (s)
t_0	initial time (s)
t_f	final time (s)
t_{pP}	time required to reach the intended W for polydextrose leathers (s)
t_{pS}	time required to reach the intended W for sucrose leathers (s)
W	moisture content (kg water/kg dry matter)
W_0	initial moisture content (kg water/kg dry matter)
W_d	dimensionless moisture content
W_e	equilibrium moisture content (kg water/kg dry matter)
ρ_{d0}	dry mass of product referred to the initial volume (kg/m ³)
ρ_F	density of fresh formulation (kg/m ³)

36

37 **1. Introduction**

38

39 In the food industry, fruits and vegetables are generally processed by drying (Lusas &
40 Rooney, 2001). Today, the suitability of drying methods is quality-driven, so vacuum
41 drying, which presumably reduces processing times and allows exposure to oxygen to
42 be reduced, may represent an adequate technique for developing vitamin-rich snack
43 products with high content of natural fruit solids. In this work, vacuum drying was
44 applied to obtain rosehip leathers, which are healthy snacks and even functional
45 products, with a high content of ascorbic acid (AA) naturally present in rosehip fruits.
46 Food dehydration involves simultaneous heat and mass transfer phenomena, occurring
47 along with physical and chemical changes in complex food matrices that depend on
48 structure and composition. In this regard, mathematical modelling of experimental data
49 obtained during the process is important to understand, predict and compare such
50 phenomena for different matrices and drying conditions. The aim of this work was to
51 carry out a detailed study of the vacuum drying of two rosehip leather formulations,
52 simultaneously determining and modelling drying kinetics, thermal histories and AA

53 degradation kinetics (as quality index) in each formulation. The effect of tray
54 temperatures between 40 and 70 °C was also evaluated.

55 Unlike low moisture foods such as oilseeds or cereals, in which heat transfer is
56 considerably faster than mass transfer, fruits and vegetables or other high moisture
57 products based on them demand the sample thermal history to be determined, since its
58 temperature is well below the asymptotic, i.e., tray temperature during much of the
59 process, especially under partial vacuum conditions which limit the heat transfer rate.
60 Concerning moisture content, the use of theoretical models with physical background
61 provides useful information to describe drying mechanisms, as well as more applied
62 issues such as the prediction of process times, which is related to dryers design (Ratti,
63 2001; Crapiste & Rotstein, 1997). However, these models do not always provide good
64 predictions in vacuum drying (Richter Reis, 2014), so many authors use them to
65 determine mass transfer parameters, though then apply empirical models to predict the
66 moisture content as a function of time (Amellal & Benamara, 2008; Ashraf et al., 2012;
67 Jena & Das, 2007; Lee & Kim, 2009). Regarding the AA degradation under vacuum
68 conditions, first and second order kinetics equations are usually applied (Lin &
69 Agalloco, 1979; Santos & Silva, 2008; Singh et al., 1976). In the case of drying
70 processes, where both the moisture content and the product temperature vary with time,
71 the complexity of determining quality kinetic parameters is much higher than in
72 isothermal and constant moisture content conditions. On these grounds, the challenge of
73 this work was to use heat and mass transfer models along with a quality prediction
74 model that will depend on each other (coupled equations), to describe the phenomena
75 occurring during vacuum drying of rosehip leather formulations. Modelling AA
76 degradation kinetics considering the simultaneous variations of moisture content and
77 temperature would be a valuable tool to explain experimental results and to predict
78 quality variations at different drying conditions.

79

80 **2. Materials and Methods**

81

82 *2.1. Fruit processing*

83

84 Ripe whole rosehip fruits (*Rosa rubiginosa* L., syn. *Rosa eglanteria* L.) harvested in El
85 Bolsón, Province of Río Negro, Argentina, were boiled for 30 min in an industrial
86 cooker, adding 0.2 kg of drinking water per kg of fresh fruit. The softened fruits were
87 processed with a pulping machine and passed through a 0.5 mm sieve to remove seeds
88 and non-edible matter. A homogeneous pulp was obtained which was concentrated by
89 evaporation to 14 °Brix. Then the pulp (average moisture content 85.4% or 5.85 kg
90 water/kg dry matter) was cooled, frozen and stored at -20 °C until using.

91

92 *2.2. Rosehip leather formulations*

93

94 The two formulations analysed here derive from those studied in a previous work
95 (Demarchi et al., 2014), which were enhanced by an increase in fruit solids content and
96 in sweetness, based on sensory tests (not published data).

97 In order to prepare a sucrose-added formulation (SAF) and a polydextrose-added
98 formulation (PAF), the mass of rosehip pulp required for all the drying experiments was
99 thawed at 4 °C, homogenized and divided in two portions, each of them combined with
100 the solid ingredients, as shown in Table 1. Commercial sucrose (Chango Premium
101 refined white sugar, Tabacal Agroindustria, Argentina) was purchased on a local
102 market. Polydextrose (Winway I Polydextrose powder) and sucralose (Splenda
103 Micronized Sucralose) were provided by Tate & Lyle (UK). Citric acid from Cicarelli
104 (Argentina) was used. Ingredients were homogenized with an electric blender (Braun
105 Multiquick Advantage, MR4050, 400 W, Spain). Then, formulations were kept in
106 sealed jars at 4 °C for 24 h, until dried.

107

108 *2.3. Drying conditions*

109

110 A vacuum oven (Arcano, China) connected to a diaphragm vacuum pump (Vacuubrand
111 PC 500 Series - CVC 3000, Germany) were used. Pressure and temperature during
112 drying were automatically controlled by a digital system. Sucrose- and polydextrose-
113 added formulations were dehydrated at an absolute pressure of 5 kPa and tray
114 temperatures of 40, 50, 60 and 70 °C, [conditions usually applied in the food industry to
115 assure the boiling of water \(Greensmith, 1998\)](#). For a convenient sampling, formulations
116 were distributed in plastic Petri dishes (0.048 m internal diameter). Initial mass (0.012
117 kg exactly weighed per Petri dish) was determined in order to achieve an initial
118 thickness of 0.006 m, required to obtain 0.002 m thickness finished leathers, according
119 to previously published data (Leiva Díaz et al., 2009).

120

121 *2.4. Experimental design*

122

123 Three dependent variables, i.e. moisture content (W), temperature (T) and ascorbic acid
124 content (Q) of the product, were recorded along vacuum drying, in order to model and
125 compare their variation in time (t) for the different formulations and drying
126 temperatures. Aiming to assure a randomized design with representative data, both
127 formulations were processed at the same time in each drying run, conducting duplicated
128 runs for every tray temperature, so eight drying experiments were performed.
129 Dependent variables were measured at fixed times during 8 h drying runs: every 30
130 minutes during the first two hours, and then every 60 minutes. Four replicates of W vs t ,
131 T vs t and Q vs t were determined for each formulation and tray temperature.

132

133 *2.5. Determination of moisture content and product temperature vs time*

134

135 During the drying runs, samples of SAF and PAF were taken from the oven at the fixed
136 sampling times, braking the vacuum for a few seconds, in order to determine their
137 moisture content by weighing, assuming constant dry matter. After weighing, the
138 samples were covered, sealed with Parafilm® paper and stored at -80 °C for subsequent
139 ascorbic acid (AA) content determination. In two aleatory chosen samples of each
140 formulation, which were not removed from the oven, thermocouples were fixed to
141 follow the product thermal history. Moisture content data obtained by weight
142 differences was verified by AOAC method 984.25 (AOAC, 1998) in the stored samples,
143 at the moment of taking aliquots for AA quantification.

144 Initial moisture content (W_0) and initial temperature (T_0) were measured in both
145 formulations immediately before the start of every drying run, while aliquots of the
146 fresh material were sealed and stored at -80 °C for determination of initial AA content
147 (Q_0).

148

149 *2.6. Determination of ascorbic acid content vs time*

150

151 Samples stored at -80 °C were removed from the freezer and kept sealed until reaching
152 room temperature. Then, they were opened, homogenized (those that were not gelled)
153 and aliquots were taken for moisture content verification and for HPLC quantification
154 of ascorbic acid (AA). A methodology adapted from Kafkas et al. (2006) and Nojavan
155 et al. (2008) was applied. The analyte was extracted dispersing 0.5 g of sample in 2.5 ml
156 of 5% (w/v) metaphosphoric acid (HPO_3) solution. The dispersion was centrifuged at 4
157 °C and 15000 rpm for 15 minutes to recover the supernatant. An RP C18 column (250 x
158 4.6 mm) coupled with an RP C18 pre-column (20 x 4.6mm), both from Spherical,
159 Optimals ODS-H, Capital HPLC (UK) were used, along with an UV-Visible detector
160 (wavelength of detection: 245nm). The mobile phase consisted of a mixture of 0.5%
161 (w/v) metaphosphoric acid and acetonitrile, in a 93:7 ratio. Isocratic elution was
162 conducted at 25 °C using a flow rate of 1 ml/min, with an injection volume of 20 μ l. For
163 the calibration curve, [HPLC grade L-ascorbic acid \(\$C_6H_8O_6\$ \) dissolved in the mobile
164 phase at various concentrations was employed](#), obtaining a linear correlation between
165 the peak area and the analyte concentration in a range from 5 to 200 mg/l. Results were
166 expressed as mg AA/g dry matter.

167

168 *2.7. Mathematical modelling*

169

170 To simultaneously model the variations of moisture content, temperature and AA
171 content during drying, a system of coupled differential equations [had to be](#) solved. In
172 the first place, migration of water by diffusion in a plane sheet was considered to
173 describe the drying kinetics. As the external resistance to the mass transfer is negligible
174 under vacuum conditions, Eq. (1) was used, which is the analytical solution of the
175 unsteady state diffusion equation of water in a solid (Crank, 1975) integrated over the
176 leather thickness:

177

$$178 \quad W_d = \frac{W - W_e}{W_0 - W_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{4 e_0^2}\right) \quad (1)$$

179

180 This expression predicts the variation of the mean moisture content W (kg water/kg dry
181 matter) as a function of time t (s) under conditions of strict internal control to the mass
182 transfer, being W_d the dimensionless moisture content, W_0 and W_e , the initial and
183 equilibrium moisture contents respectively, while D (m²/s) is the Fickian effective
184 diffusion coefficient and e_0 (m), the initial leather thickness. Experimental data was
185 modelled considering 10 terms of Eq. (1) and $W_e = 0$, so the following expression was
186 used:

187

$$188 \quad W = W_0 \frac{8}{\pi^2} \sum_{n=0}^9 \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{4 e_0^2}\right) \quad (2)$$

189

190 Then, an expression for drying rate was derived from Eq. (2) as follows:

191

$$192 \quad \frac{dW}{dt} = W_0 \frac{8}{\pi^2} \sum_{n=0}^9 \left(-\frac{(2n+1)^2 \pi^2 D}{4 e_0^2}\right) \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D t}{4 e_0^2}\right) \quad (3)$$

193

194 In turn, the diffusion coefficient D was related to temperature by an Arrhenius type
195 function (Eq. (4)):

196

$$197 \quad D = D_0 \exp\left(-\frac{E_a}{R(T_b + 273,15)}\right) \quad (4)$$

198

199 where D_0 (m²/s) is the pre-exponential factor, E_a (J/mol) is the drying activation energy,
200 $R=8.314$ J K⁻¹ mol⁻¹ is the ideal gas constant and T_b (°C) is the tray temperature.
201 Equations (2) and (3) are functionally adequate because the possible decrease of D
202 during drying (which is not considered here) is compensated by the volumetric
203 shrinkage (not considered in the model either), so that the ratio D/e_0^2 remains
204 approximately constant (Torrez Irigoyen & Giner, 2014).

205 Regarding product thermal histories, the heating rate was modelled applying an energy
206 balance (Eq. (5)) taking the sheet as the control volume, to describe the variation of the
207 average product temperature T (°C) during drying, over a tray set at a temperature T_b
208 (°C):

209

$$210 \quad \frac{dT}{dt} = \frac{h_{eff}}{\rho_{d0} C_p e_0} (T_b - T) - \frac{L_w}{C_p} \left(-\frac{dW}{dt}\right) \quad (5)$$

211

212 Here, h_{eff} (W/ m² °C) represents an effective heat transfer coefficient, ρ_{d0} (kg/m³) is the
 213 dry mass of the product referred to the initial volume, while C_p (J/kg dry matter °C)
 214 stands for the product specific heat and L_w (J/kg), for the heat of desorption of water.
 215 The following considerations were made:

216

$$217 \quad \rho_{d0} = \rho_F / (1 + W_0) \quad (5.1)$$

218

219 where ρ_F (kg/m³) is the density of the fresh formulation, corresponding to a moisture
 220 content W_0

221

$$222 \quad C_p = 837.4 + 4187 W \quad \text{for } W > 0.7 \quad (5.2)$$

223

$$224 \quad C_p = 1637 + 3567 W \quad \text{for } W \leq 0.7 \quad (5.3)$$

225

$$226 \quad L_w = 2.49 \times 10^6 - 1953 T \quad (5.4)$$

227

228 C_p correlations were taken from Mohsenin (1980), while coefficients in Eq. (5.4) were
 229 based on Kiefer's correlation of liquid-vapor saturation pressure for pure water (Giner,
 230 2001).

231 Finally, a kinetic model of variable order (Eq. (6)) was applied to predict the AA
 232 content as a function of time during drying:

233

$$234 \quad -\frac{dQ}{dt} = kQ^n \quad (6)$$

235

236 where $-dQ/dt$ represents the rate of AA degradation, being Q its concentration at time t
 237 expressed as mg AA/g dry matter. A kinetic constant k affected by moisture content (W)
 238 and product temperature (T) was considered, with a reaction order n depending on the
 239 tray temperature (T_b), so that:

240

$$241 \quad -\frac{dQ}{dt} = k_0 \exp\left(-\frac{E_{aq}}{R(T + 273.15)}\right) Q^{(n_1 + n_2 T_b)} \quad (6.1)$$

242

243 The symbol E_{aq} (J/mol) is the activation energy for quality loss, $R=8.314$ J K⁻¹ mol⁻¹ is
 244 the ideal gas constant and k_0 (s⁻¹) stands for the pre-exponential factor, which represents
 245 the molecular collision frequency and is here related with moisture content by Eq. (6.2):

246

$$247 \quad k_0 = k_1 + k_2 W \quad (6.2)$$

248

249 *2.8. Fitting method*

250

251 The fitting of differential equation parameters implies an inverse problem that cannot be
252 solved by the usual methods employed for integral equations. In this work, both the
253 integration of the differential equations with time and the parameter optimization were
254 performed using the *OptiPa* software (Hertog et al., 2007). The aim was to fit
255 parameters D_0 , E_a , h_{eff} , k_1 , k_2 , E_{aq} , n_1 and n_2 , to minimize the sum of squared residuals
256 (SSR) between numerically integrated values (Eq. (3) to (6.2)) and the experimental
257 data set for each formulation (W , T and Q as a function of t at different tray
258 temperatures). As the models were simultaneously solved, the fitting criterion was to
259 minimize a combined SSR, i.e., the sum of SSR for moisture content, temperature and
260 AA content, each of them weighted by the inverse of the variance of the corresponding
261 experimental data (Torrez Irigoyen & Giner, 2017). The calculation procedure was as
262 follows: given the initial values ($t = t_0$, $W = W_0$, $T = T_0$, $Q = Q_0$), and initial values for
263 the eight parameters to be adjusted, calculations started at $t = t_0$. The drying rate ($-$
264 dW/dt) estimated by Eq. (3) was used in the macroscopic energy balance (Eq. (5)) to
265 determine dT/dt . The values of W , T and Q were used to calculate dQ/dt by Eq. (6). The
266 differential equation system was numerically solved by the function *ode 23s*, obtaining
267 W , T and Q corresponding to the next time value. This sequence was repeated for
268 increasing times until reaching the final time ($t_f = 28800$ s). Then, with predicted and
269 experimental curves of W vs t , T vs t and Q vs t , the software calculated the combined
270 SSR. Based on this value, an optimization program *lsqnonlin* estimated new parameter
271 values from the previous ones and the combined SSR by solving a nonlinear equation
272 system. With the new values, another integration process was initiated followed by
273 optimization, and the combined algorithm was repeated until the combined SSR
274 between experimental and calculated values reached a minimum.

275

276 2.9. Statistical analysis

277

278 Data was analyzed using the *Origin* software (Origin, 2009). To assess the effect of
279 formulations and tray temperatures on drying kinetics, thermal histories and quality
280 kinetics, the F -test for datasets comparison (function *fitcmpdata*) was applied, allowing
281 the comparison of entire curves between drying runs, and also two-way ANOVAs were
282 performed for data at specific drying times. For mean value's comparison, Tuckey test
283 was used.

284

285 3. Results and Discussion

286

287 3.1. Experimental data

288

289 Fig. 1 shows the evolution of moisture content, product temperature and AA retention
290 during vacuum drying of both formulations at different tray temperatures. As it can be
291 seen from Figures 1.A and 1.B, the drying rate increased with the tray temperature (T_b)
292 and was always higher for PAF. The samples' moisture content after 8 h drying runs

293 were significantly affected by T_b and formulation (two-way ANOVA, $\alpha=0.05$). The
294 moisture content intended for rosehip leathers (0.23 kg water/kg dry matter for SAF and
295 0.17 kg water/kg dry matter for PAF, corresponding both to $a_w = 0.6$) was only reached
296 during experiments conducted at 60 and 70 °C. Nevertheless, data obtained at tray
297 temperatures of 40 and 50 °C is relevant for kinetic modelling purpose, providing a
298 wide temperature range for relevant parameters fitting, as activation energies for drying
299 and for quality loss.

300 Thermal histories (Figures 1.C and 1.D) had a characteristic shape, with a rapid increase
301 in the first 60 minutes, reaching a maximum constant value at the end. Such maximum
302 values were considerably lower than the corresponding T_b and that difference increased
303 with T_b . Thermal histories were not affected by composition (F -test for datasets
304 comparison, $\alpha=0.05$). So, the fact that PAF dehydrated faster than SAF in spite of
305 reaching the same temperatures in the same times, revealed differences in the sorption
306 behaviour of the formulations, due to the type of saccharide present in the matrix and its
307 degree of interaction with the water.

308 With respect to nutritional retention (expressed in relation to the initial value of AA
309 concentration on dry basis), it decreased faster for higher T_b (Figures 1.E and 1.F). The
310 apparent rising of AA retention for sucrose formulation dried at 50°C from 360 to 420
311 min (Figure 1.E) and for polydextrose formulation dried at 70 °C from 240 to 300 min
312 (Figure 1.F) were not significant (Tukey test, $\alpha=0.05$). After 8 hours process, the
313 average AA retention was the same (0.53) for any T_b and formulation, being lower
314 (0.27) only for SAF at 70 °C (Tukey test, $\alpha=0.05$). Other authors, who have investigated
315 AA degradation in rosehip, have found that long thermal treatments (between 8 and 24
316 h) in the temperature range of 50 to 90 °C result in similar retention values, around 50%
317 (Erenturk et al., 2005; Pirone et al., 2007).

318

319 3.2. Mathematical modelling results

320

321 A set of fitted parameters was obtained for each formulation, providing acceptable
322 predictions of its moisture content, temperature and AA content during vacuum drying
323 at tray temperatures between 40 and 70 °C. Complete experimental data of Q vs t was
324 modelled for tray temperatures of 40 and 50 °C whereas, for practical reasons, data of Q
325 vs t obtained at 60 and 70 °C was only modelled from $t = 0$ to the time corresponding to
326 the leathers intended W . Fitted values are shown in Table 2, along with the
327 corresponding coefficients of determination (r^2). As the value of k_2 obtained for both
328 formulations was not relevant in Eq. (6.2), a pre-exponential factor k_0 not depending on
329 W was finally fitted.

330

331 3.2.1. Drying kinetics

332

333 Experimental and predicted values of W vs t are shown in Fig. 2 for every formulation
334 and tray temperature (T_b). In general, calculated values were lower during the first 2 or

335 3 hours of drying, whereas the opposite occurred towards the end of the process. The
336 goodness of fit was acceptable, being higher for $T_b = 70^\circ\text{C}$.

337 Fig. 3 shows the diffusion coefficient (D) predicted for both formulations as a function
338 of tray temperature. For every T_b in the studied range, D values for PAF were found to
339 be higher than the corresponding for SAF, according to the higher drying rate
340 experimentally observed for PAF ($\alpha=0.05$). D values between 3.1×10^{-10} and 1.8×10^{-9}
341 m^2/s for SAF and between 4.2×10^{-10} and 2.0×10^{-9} m^2/s for PAF were found. Other
342 authors working with vacuum dried fruit pulps have informed similar results: between
343 7.0×10^{-10} and 3.3×10^{-9} m^2/s for coconut presscake, at 8.3 kPa and temperatures from
344 65 to 75 °C (Jena & Das, 2007); between 1.6×10^{-9} and 9.2×10^{-9} m^2/s for mango pulp,
345 at the same conditions (Jaya & Das, 2003); and between 2.3×10^{-9} and 4.0×10^{-9} m^2/s
346 for pumpkin slices, at 5 kPa and temperatures from 50 to 70 °C (Arévalo-Pinedo &
347 Murr, 2006). Regarding activation energy for drying, the fitted values were in
348 agreement with those reported by Ashraf et al. (2012), who found values from 34 to 55
349 kJ/mol for the drying of date paste of various thicknesses, at 20 kPa between 60 and
350 80°C.

351

352 3.2.2. Thermal histories

353

354 In Fig. 4, experimental and predicted data of the product temperature as a function of
355 time is shown for every formulation and tray temperature. As for the heat transfer
356 coefficients, fitted values were lower than those reported for hot air dried foods (Ratti &
357 Crapiste, 1995), which is expected because the heat transfer is limited under vacuum
358 conditions. It can be seen from experimental data in Fig. 4, that thermal histories for
359 both formulations are the same ($\alpha=0.05$). However, fitting of Eq. (5) led to a higher h_{eff}
360 for PAF (see Table 2). This compensated for its higher drying rate (dW/dt), and then, the
361 same heating rate (dT/dt) was predicted for both formulations.

362

363 3.2.3. Quality kinetics

364

365 Experimental data of AA retention as a function of time is shown in Fig. 5, along with
366 the values predicted by Eq. (6.1) expressed in terms of retention (Q/Q_0). For tray
367 temperatures of 60 and 70 °C (Figures 5.C and 5.D), data and models were plotted only
368 until the time corresponding to the leather's intended W .

369 Concerning the quality loss model, a kinetic constant k depending only on product
370 temperature was found, as shown in Fig. 6, according to the values of k_0 and E_{aq} fitted
371 for each formulation. Several authors have modelled the dependence of k on both
372 moisture content and product temperature during different drying processes: Erenturk et
373 al. (2005) in rose hip; Villota & Karel (1980) in a model system with
374 carboxymethylcellulose; Khraisheh et al. (2004) in starch-rich foods. In this work, no
375 significant, explicit effect of moisture content on quality loss was found. This does not
376 mean, however, that degradation kinetics of AA is not affected by moisture content. In

377 fact it is and is proven by numerous scientific works for isothermal conditions: Lee &
378 Labuza (1975) in a cellulose model system with different water activities; Goula &
379 Adamopoulos (2006) in tomato pulp; Uddin et al. (2001) in kiwi. What actually happens
380 is that the effect of W is not perceived when fitting the parameters of Eq. (6.1) for each
381 rosehip formulation, because different values of T_b are covered. That is, if the quality
382 variation (dQ/dt) is analysed for a given formulation, comparing samples with the same
383 temperature but different W (necessarily for different T_b), the effect of W on dQ/dt is
384 compensated by the differences in thermal histories, so that the sample with higher W
385 requires less time to reach the same temperature. Thus, the kinetic constant k appears to
386 depend mainly on the product temperature. However, the effect of W on quality loss
387 became evident when comparing samples with the same thermal history but different W ,
388 i.e., when contrasting both formulations at the same T_b . In this case, a higher kinetic
389 constant was fitted for PAF over the whole product temperature range (Fig (6)). Note
390 that the higher drying rate exhibited by PAF generated samples with the same thermal
391 history but lower W than those of SAF at the same times.

392 Finally, according to the values of n_1 and n_2 fitted for each formulation, a reaction order
393 varying between 1.11 and 2.06 was obtained, as shown in Fig. 7. This is in agreement
394 with numerous works, mentioned in a review by Santos & Silva (2008), where first and
395 second order kinetics are applied to model the degradation of AA in processed fruits and
396 vegetables, depending on the O_2 partial pressure.

397

398 3.3. Further discussion

399

400 In agreement with the lower kinetic constant obtained for SAF (see Fig. 6), a slightly
401 lower AA degradation rate was predicted for this formulation, although, after 8 hours
402 drying, the retention **tended** to a mean value of 0.53 for both formulations a $T_b = 40$ and
403 $50\text{ }^\circ\text{C}$ (see Figures 5.A and 5.B). However, the data of interest for practical purposes
404 **was** the AA retention in the finished products, for $T_b = 60$ and $70\text{ }^\circ\text{C}$. Table 3 shows
405 these values, together with the corresponding drying times. It can be seen that, for both
406 tray temperatures, SAF required 60 minutes more than PAF to achieve the intended W ,
407 even when it **was** higher for SAF (0.23 kg water/kg dry matter) than for PAF (0.17 kg
408 water/kg dry matter). Thus, although AA **degraded** faster in PAF, the same nutritional
409 retention was observed for both formulations (two-way ANOVA, $\alpha = 0.05$). Besides,
410 the drying rate also compensated for the effect of tray temperature. In this case, an
411 increase of $10\text{ }^\circ\text{C}$ in T_b (from 60 to $70\text{ }^\circ\text{C}$) implied a reduction of 120 minutes in the
412 drying time of each formulation (see Table 3), resulting in products with the same AA
413 retention. Kurozawa et al. (2014) also observed that nutritional retention in fruits was
414 related to the total processing time. Erenturk et al. (2005) confirmed that low
415 temperatures (between 40 and $50\text{ }^\circ\text{C}$) were not favourable for rose hip drying while, at
416 $70\text{ }^\circ\text{C}$, products with high vitamin C retention were obtained, due to the shorter drying
417 time required.

418

419 4. Conclusions

420

421 The simultaneous modelling of the variations of moisture content, product temperature
422 and ascorbic acid content during the vacuum drying of rosehip leathers lead to
423 satisfactory predictions of drying kinetics, thermal histories and quality loss kinetics at
424 different tray temperatures.

425 A set of model parameters was fitted for each formulation, representing well the
426 different behaviour of sucrose and polydextrose systems. The latter shown a higher
427 drying rate and higher quality degradation rate, with identical thermal histories. The
428 reaction order for ascorbic acid degradation varied approximately from first to second
429 order, as a function of the tray temperature during vacuum drying.

430 For tray temperatures of 40 and 50 °C, the final moisture content intended for rosehip
431 leathers was not reached in the time covered by the experiments (8 hours). Drying at
432 temperatures below 50 °C is therefore not recommended because the process is longer
433 and the ascorbic acid retention is the same or even lower than those observed at higher
434 temperatures.

435 When drying both formulations at 60 and 70 °C, the differences in drying rate were
436 sufficient to compensate for both the saccharide effect (quality degrades faster in
437 polydextrose-added formulation) and the tray temperature effect (quality degrades faster
438 at 70 °C), so that the same nutritional retention was obtained in all cases. Then, drying
439 at 70 °C is recommended in order to minimize processing times.

440 The mathematical model solved here is novel and improves existing practice, since
441 parameters are directly fitted from the differential equation system, without the need of
442 considering drying as an isothermal process.

443 The solution of the complex inverse problem described in this work provides now a tool
444 that can be combined with equipment simulation models to allow a more complete
445 design of food processing including quality losses. This would contribute to better
446 decision making when operating dryers for the production of nutritive, fruit-based,
447 snack foods.

448

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450

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454

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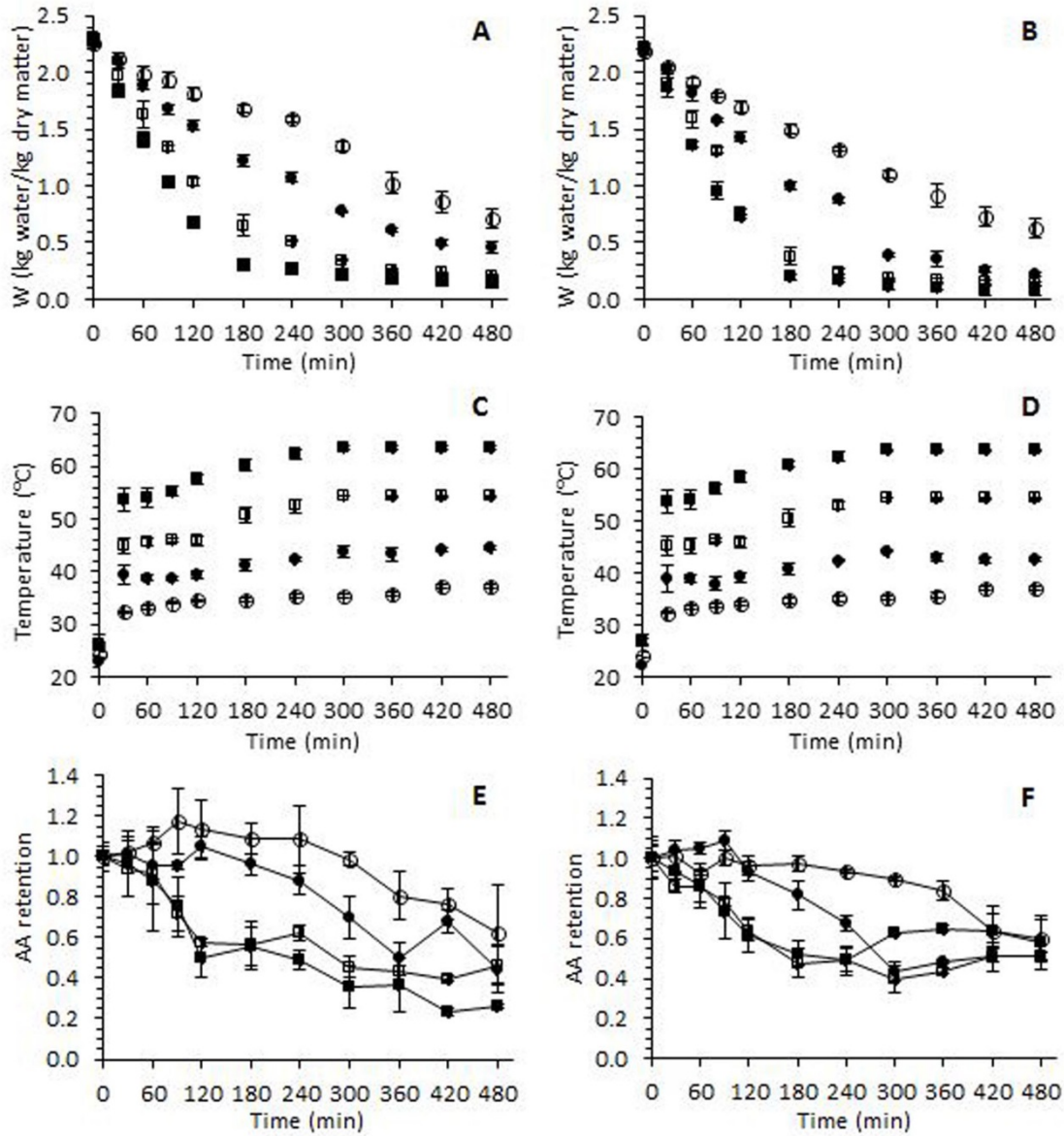


Figure 1. Variation of moisture content (A, B), product temperature (C, D) and ascorbic acid retention (E, F) during vacuum drying of sucrose-added (left) and polydextrose-added (right) formulations. Mean values \pm standard deviation are plotted for tray temperatures of 40°C (○), 50°C (●), 60°C (□) and 70°C (■).

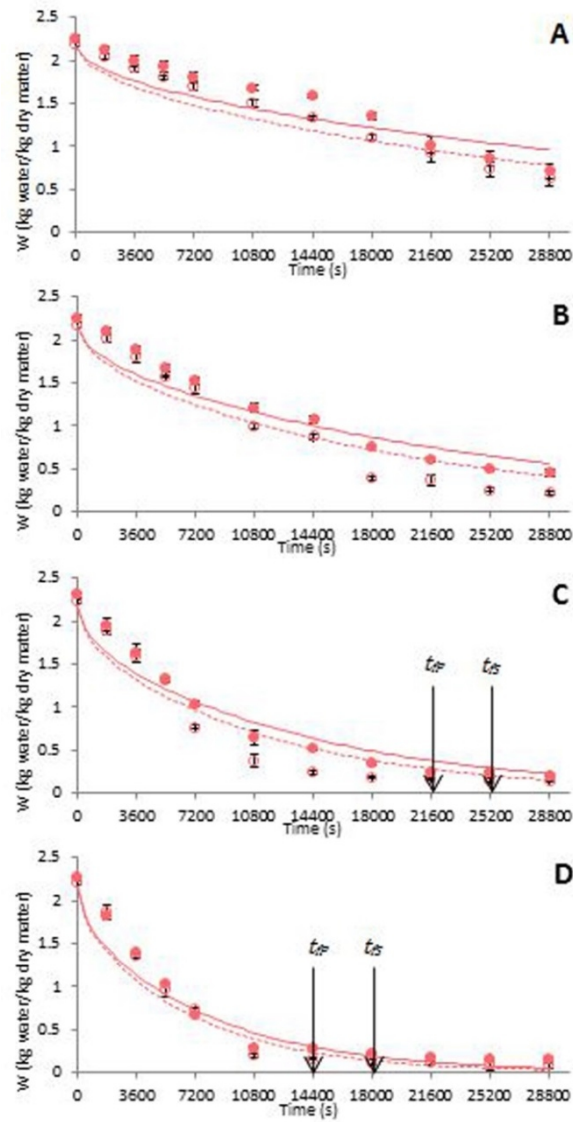


Figure 2. Experimental (symbols) and predicted (lines) vacuum drying kinetics for sucrose-added (●—) and polydextrose-added (○-- --) formulations at 40°C (A), 50°C (B), 60°C (C) and 70°C (D). t_{js} and t_{jp} are the times required to reach the intended W for the corresponding leathers.

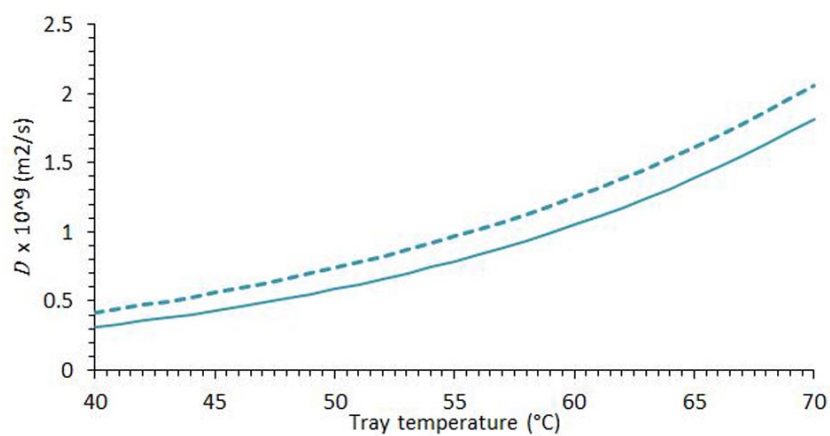


Figure 3. Water diffusion coefficient (D) for sucrose-added (—) and polydextrose-added (---) formulations, predicted by Eq. (4) as a function of tray temperature.

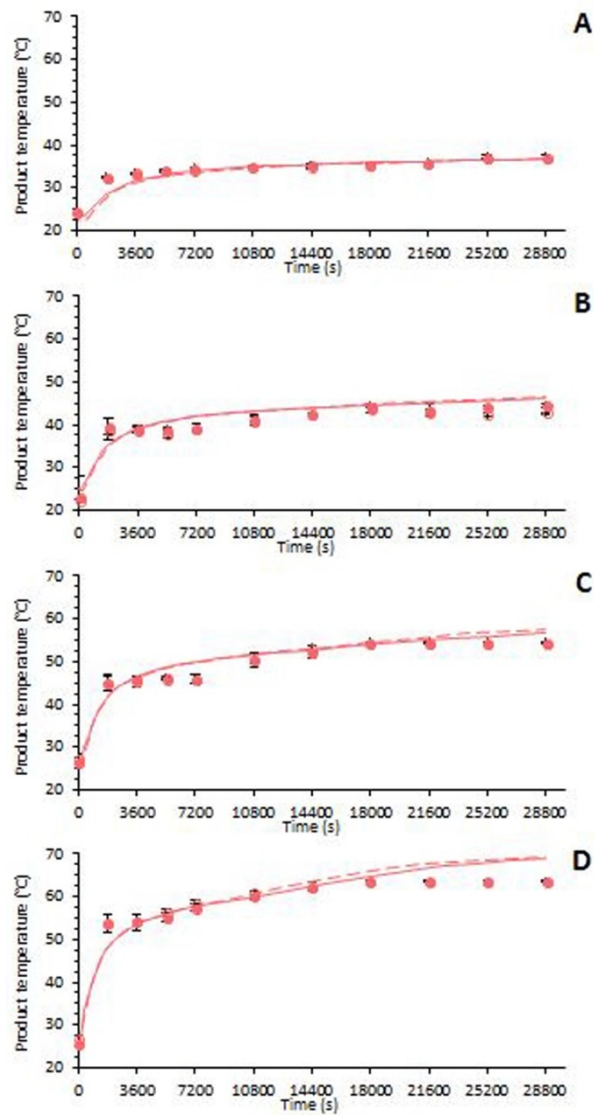


Figure 4. Experimental (symbols) and predicted (lines) thermal histories for sucrose-added (●—) and polydextrose-added (○- -) formulations at 40°C (A), 50°C (B), 60°C (C) and 70°C (D).

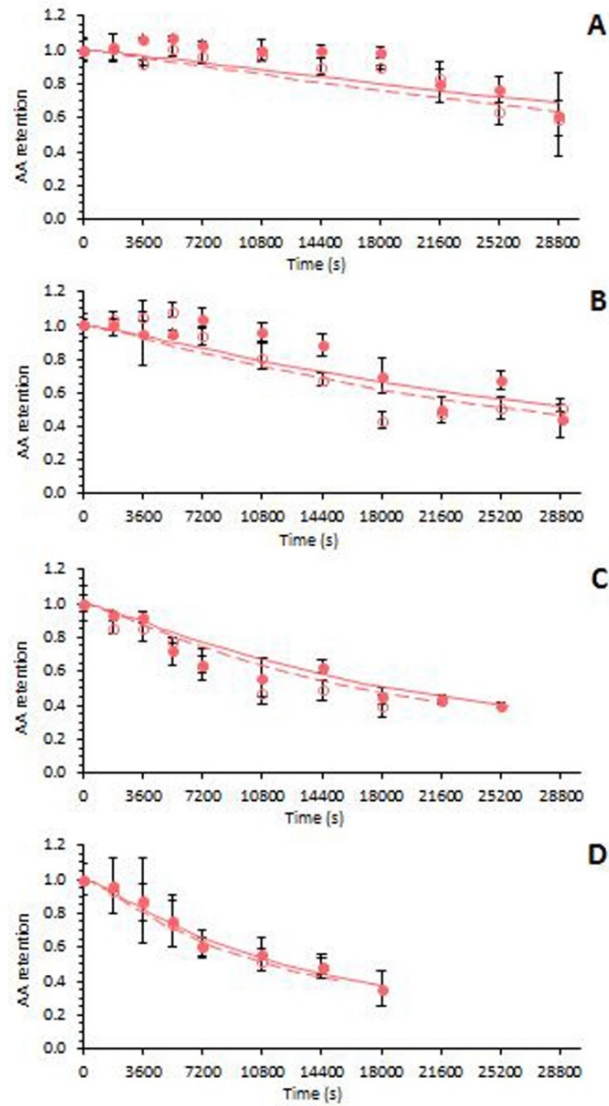


Figure 5. Experimental (symbols) and predicted (lines) ascorbic acid retention as a function of time, for sucrose-added (●—) and polydextrose-added (○- -) formulations at 40°C (A), 50°C (B), 60°C (C) and 70°C (D).

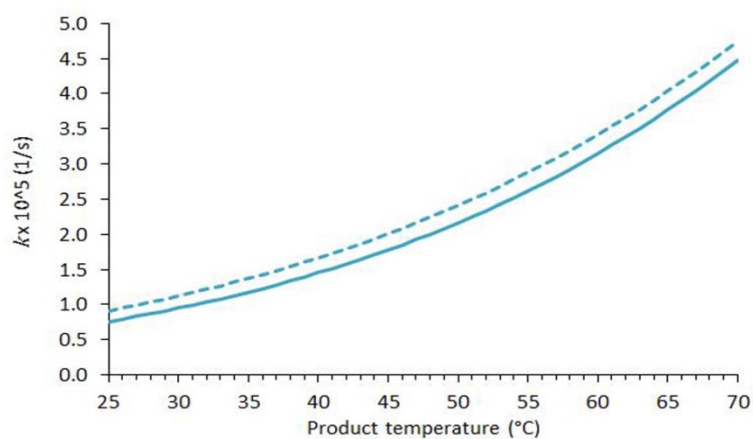


Figure 6. Kinetic constant k for ascorbic acid degradation during vacuum drying of sucrose-added (—) and polydextrose-added (- - -) formulations, as a function of product temperature.

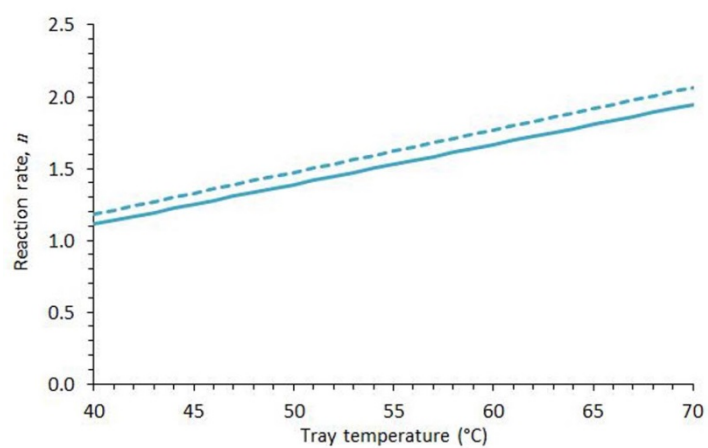


Figure 7. Reaction order n for ascorbic acid degradation, predicted by Eq. (6.1) as a function of tray temperature, during vacuum drying of sucrose-added (—) and polydextrose-added (---) formulations.

Highlights

Rosehip leather formulations added with sucrose or polydextrose were vacuum dried.

Tray temperatures between 40 and 70°C were applied.

Thermal histories, drying and quality kinetics were simultaneously modelled.

Quality degrades faster in polydextrose-added formulation dried at 70 °C.

However, due to the higher drying rate, quality is the same as for lower temperature.

Table 1. Composition of the rosehip leather formulations.

Formulation	Ingredients (% w/w)				
	Fruit pulp	Sucrose	Polydextrose	Citric acid	Sucralose
SAF	77.95	21.00	---	1.00	0.05
PAF	77.92	---	21.00	1.00	0.08

Table 2. Fitting parameters determined for equations that predict moisture content, temperature and quality of rosehip leather formulations as a function of time during vacuum drying.

Model	Parameter	Fitted value	
		SAF	PAF
Eq. (3) and (4)	D_0 (m ² /s)	0.1644	0.0334
	E_a (J/mol)	52243.8	47341.3
	r^2	0.9630	0.9520
Eq. (5)	h_{eff} (W/m ² °C)	30.183	33.212
	r^2	0.9620	0.9476
Eq. (6.1)	k_0 (s ⁻¹)	5.6772	2.6189
	E_{aq} (J/mol)	33506	31137
	n_1	6.07x10 ⁻⁵	8.99x10 ⁻⁵
	n_2	0.0278	0.0295
	r^2	0.8790	0.8520

Table 3. Drying times and nutritional retention of SAF and PAF leathers, vacuum dried at 60 and 70°C. Different letters in the same row indicate significantly different values ($\alpha=0.05$).

	SAF		PAF	
	$T_b = 60\text{ }^\circ\text{C}$	$T_b = 70\text{ }^\circ\text{C}$	$T_b = 60\text{ }^\circ\text{C}$	$T_b = 70\text{ }^\circ\text{C}$
Drying time (min)	420 ^a	300 ^b	360 ^c	240 ^d
Experimental AA retention	0,3962 ^a	0,3542 ^a	0,4388 ^a	0,4876 ^a
Predicted AA retention	0,3952 ^a	0,3759 ^a	0,4272 ^a	0,4238 ^a