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Silvana M. Demarchi, R. Martín Torrez Irigoyen, Sergio A. Giner

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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  
 5 Silvana M. Demarchi<sup>a,b</sup>, R. Martín Torrez Irigoyen<sup>a,b</sup> and Sergio A. Giner<sup>a,c,d\*</sup>

6  
 7 <sup>a</sup> *Centro de Investigación y Desarrollo en Criotecnología de Alimentos (CIDCA),*  
 8 *CONICET-CIC, Universidad Nacional de La Plata, 47 y 116 La Plata (B1900 AJJ),*  
 9 *Argentina.*

10 <sup>b</sup> *Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 1 y 47 La Plata,*  
 11 *Argentina.*

12 <sup>c</sup> *Facultad de Ingeniería, Universidad Nacional de La Plata, 1 y 47 La Plata,*  
 13 *Argentina.*

14 <sup>d</sup> *Comisión de Investigaciones Científicas (CIC), Provincia de Buenos Aires, 526 e/ 10 y*  
 15 *11, La Plata, Argentina.*

16  
 17 \*Corresponding author. Address: 47 y 116, (1900) La Plata, Argentina.

18 Tel: +54-221-4249287. E-mail address: [saginer@ing.unlp.edu.ar](mailto:saginer@ing.unlp.edu.ar)

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 <sup>2</sup> /s)
$D_0$	pre-exponential factor in Eq. (4) (m <sup>2</sup> /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 <sup>2</sup> °C)
$k$	kinetic constant for quality loss (s <sup>-1</sup> )
$k_0$	pre-exponential factor in Eq. (6.1) (s <sup>-1</sup> )
$k_1, k_2$	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)
$\rho_{d0}$	dry mass of product referred to the initial volume (kg/m <sup>3</sup> )
$\rho_F$	density of fresh formulation (kg/m <sup>3</sup> )

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  $\mu$ 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  $D$  (m<sup>2</sup>/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  $D_0$  (m<sup>2</sup>/s) is the pre-exponential factor,  $E_a$  (J/mol) is the drying activation energy,  
200  $R=8.314$  J K<sup>-1</sup> mol<sup>-1</sup> 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/ m<sup>2</sup> °C) represents an effective heat transfer coefficient,  $\rho_{d0}$  (kg/m<sup>3</sup>) 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  $\rho_F$  (kg/m<sup>3</sup>) 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<sup>-1</sup> mol<sup>-1</sup> is  
 244 the ideal gas constant and  $k_0$  (s<sup>-1</sup>) 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  $3.1 \times 10^{-10}$  and  $1.8 \times 10^{-9}$   
341  $\text{m}^2/\text{s}$  for SAF and between  $4.2 \times 10^{-10}$  and  $2.0 \times 10^{-9}$   $\text{m}^2/\text{s}$  for PAF were found. Other  
342 authors working with vacuum dried fruit pulps have informed similar results: between  
343  $7.0 \times 10^{-10}$  and  $3.3 \times 10^{-9}$   $\text{m}^2/\text{s}$  for coconut presscake, at 8.3 kPa and temperatures from  
344 65 to 75 °C (Jena & Das, 2007); between  $1.6 \times 10^{-9}$  and  $9.2 \times 10^{-9}$   $\text{m}^2/\text{s}$  for mango pulp,  
345 at the same conditions (Jaya & Das, 2003); and between  $2.3 \times 10^{-9}$  and  $4.0 \times 10^{-9}$   $\text{m}^2/\text{s}$   
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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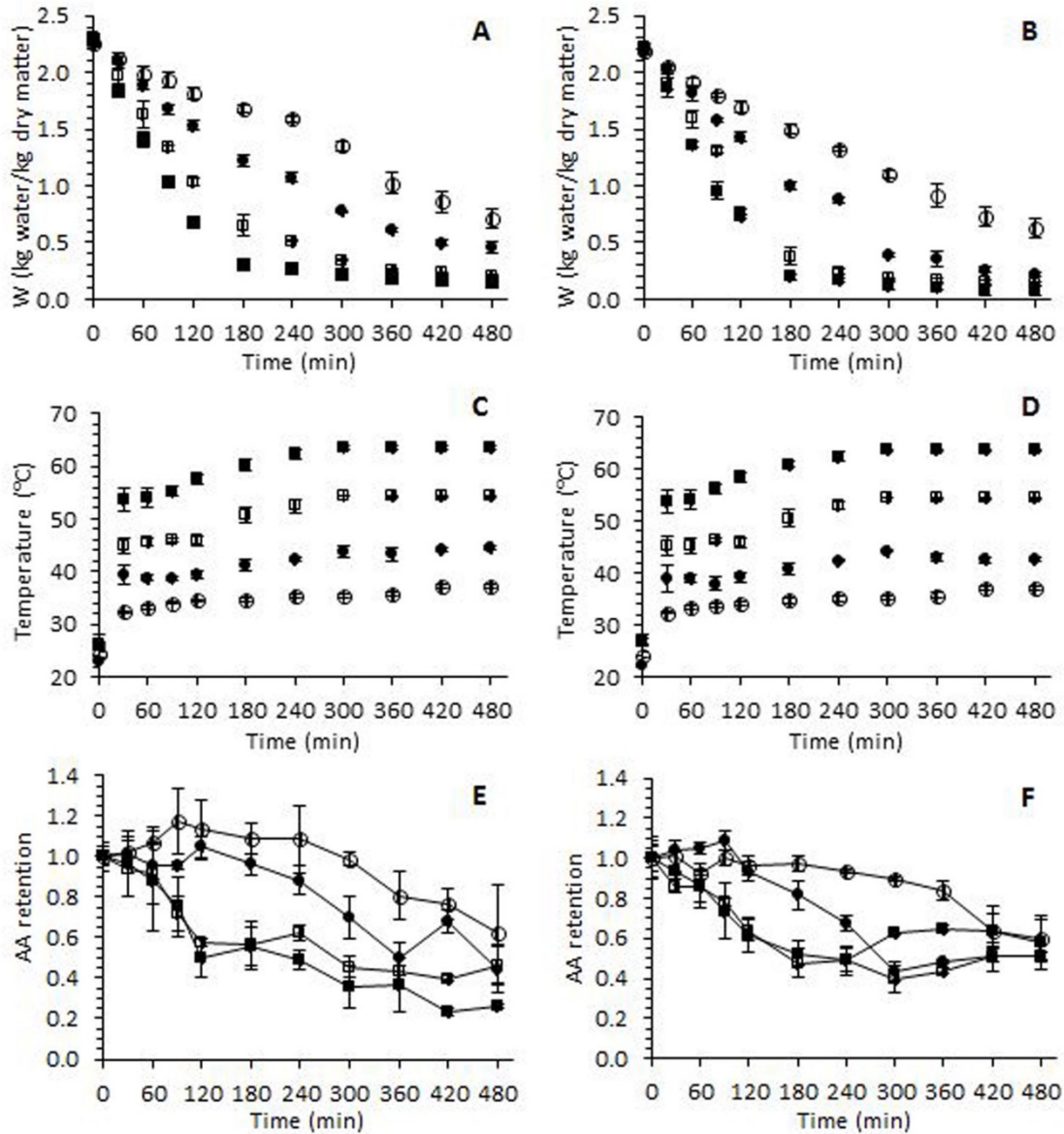
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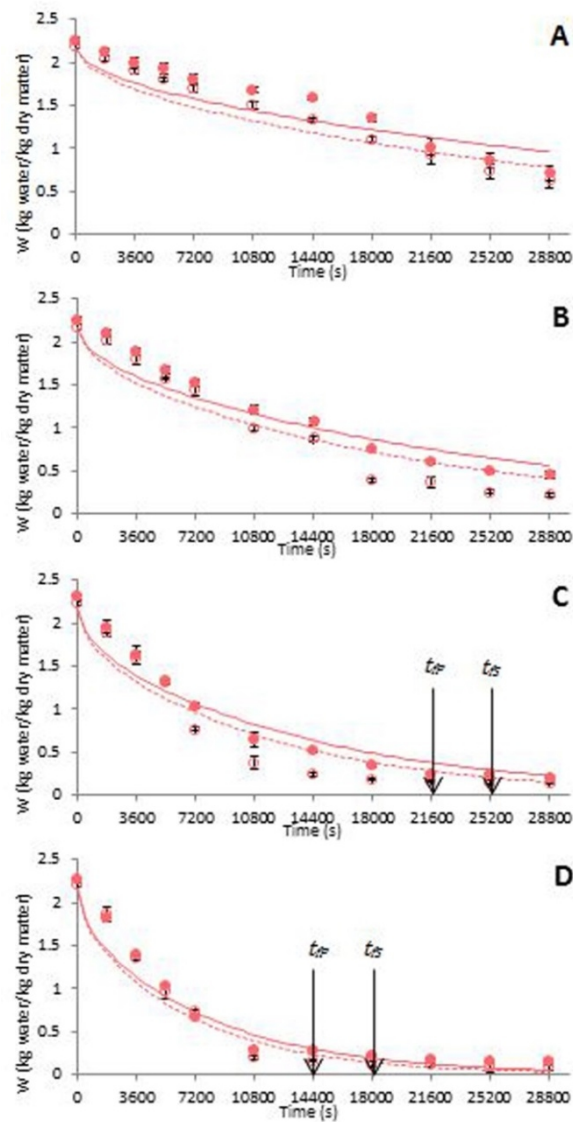
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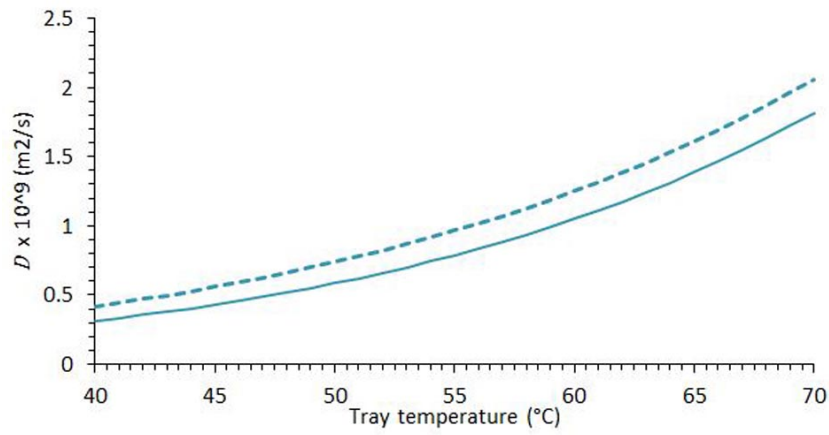


**Figure 1.** Variation of moisture content (A, B), product temperature (C, D) and ascorbic acid retention (E, F) during vacuum drying of sucrose-added (left) and polydextrose-added (right) formulations. Mean values  $\pm$  standard deviation are plotted for tray temperatures of 40°C (○), 50°C (●), 60°C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

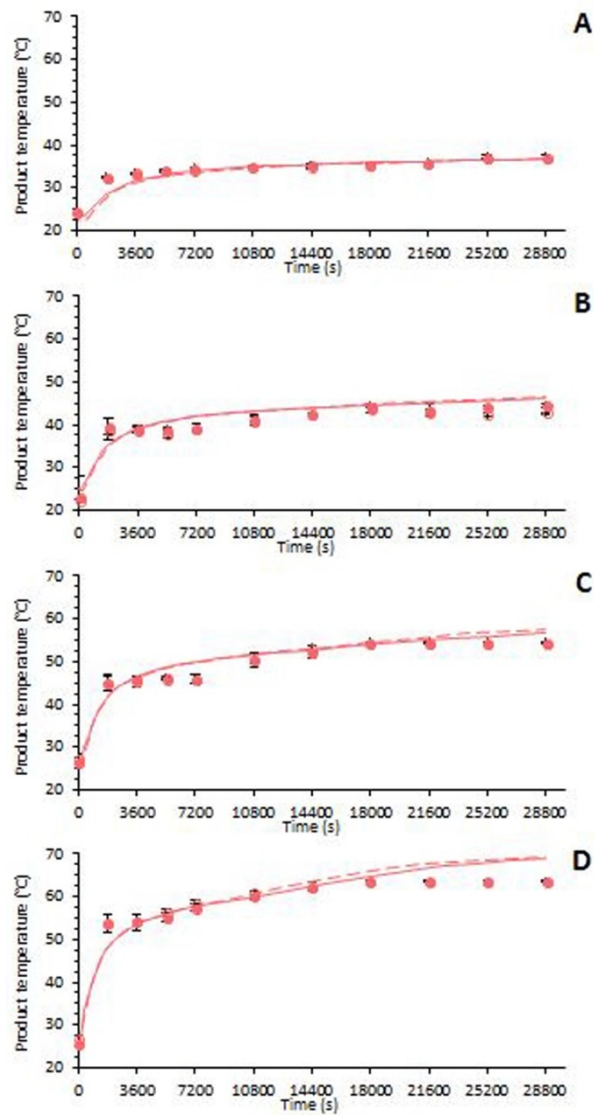




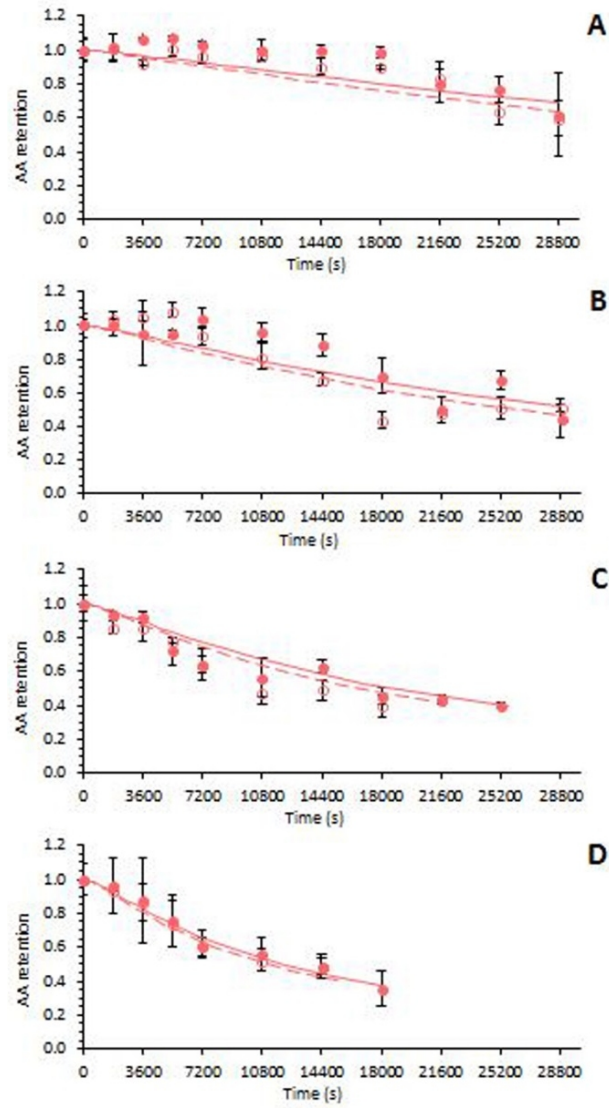
**Figure 2.** Experimental (symbols) and predicted (lines) vacuum drying kinetics for sucrose-added (●—) and polydextrose-added (○-- --) formulations at 40°C (A), 50°C (B), 60°C (C) and 70°C (D).  $t_{js}$  and  $t_{jp}$  are the times required to reach the intended  $W$  for the corresponding leathers.



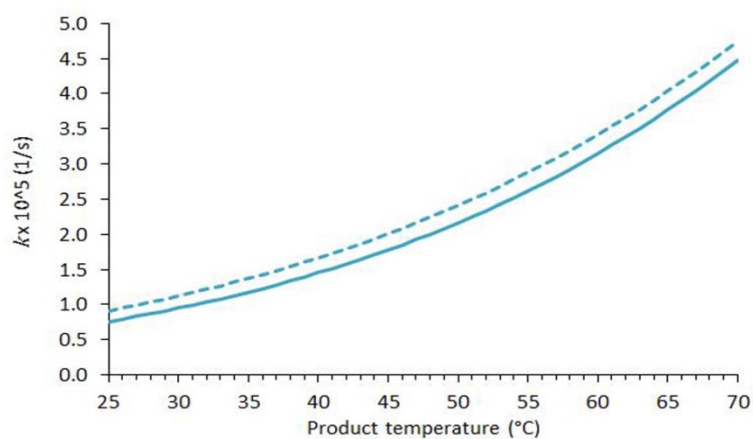
**Figure 3.** Water diffusion coefficient ( $D$ ) for sucrose-added (—) and polydextrose-added (---) formulations, predicted by Eq. (4) as a function of tray temperature.



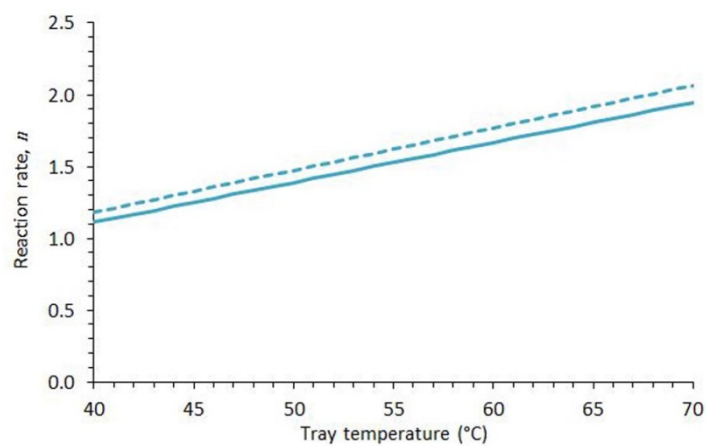
**Figure 4.** Experimental (symbols) and predicted (lines) thermal histories for sucrose-added (●—) and polydextrose-added (○-- ) formulations at 40°C (A), 50°C (B), 60°C (C) and 70°C (D).



**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 <sup>2</sup> /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 <sup>2</sup> °C)	30.183	33.212
	$r^2$	0.9620	0.9476
Eq. (6.1)	$k_0$ (s <sup>-1</sup> )	5.6772	2.6189
	$E_{aq}$ (J/mol)	33506	31137
	$n_1$	6.07x10 <sup>-5</sup>	8.99x10 <sup>-5</sup>
	$n_2$	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 raw 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 <sup>a</sup>	300 <sup>b</sup>	360 <sup>c</sup>	240 <sup>d</sup>
Experimental AA retention	0,3962 <sup>a</sup>	0,3542 <sup>a</sup>	0,4388 <sup>a</sup>	0,4876 <sup>a</sup>
Predicted AA retention	0,3952 <sup>a</sup>	0,3759 <sup>a</sup>	0,4272 <sup>a</sup>	0,4238 <sup>a</sup>