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Abstract

Two different pre-treatments were applied to grapes prior to drying in a mixed mode solar dryer. Grapes were blanched in water and in a 0.1% sunflower oil water emulsion, both at 99°C and for approximately 15 seconds. Several models were tested to fit the experimental data of drying curves but the normalized Newton model gave the best fit results. Samples blanched in hot water or in the 0.1% edible oil emulsion had faster drying rates than untreated samples. Contrary to what was expected, pre-treating with the 0.1% edible oil emulsion did not increase the drying rate to a higher extent than blanching. Pre-treatments did not give a noteworthy difference in the total drying time. However, they had an important role in accelerating initial drying rates, thus preventing moulds and bacterial growth and consequently increasing farmers' income.

Keywords: Pre-treatments; Solar drying; Kinetics; Modeling; Raisins

Nomenclature

a, b	parameters of equations 2 and 5
a_w	water activity
C	Guggenheim constant
k_1, k_2	parameters of the two-term model (equation 5)
k	drying rate of equations 1, 2, 3, 4 and 6 (day^{-1})
K	factor that corrects properties of the multilayer molecules with respect to the bulk liquid
N	parameter of equations 3 and 4
s	standard deviation of the experimental error
t	time (min)
T	absolute temperature (K)
X	water content on dry basis ($\text{kg}_{\text{water}} \text{kg}_{\text{dry matter}}^{-1}$)
X_e	average equilibrium water content on dry basis ($\text{kg}_{\text{water}} \text{kg}_{\text{dry matter}}^{-1}$)
X_m	monolayer water content on dry basis ($\text{kg}_{\text{water}} \text{kg}_{\text{dry matter}}^{-1}$)
X_0	initial average water content on dry basis ($\text{kg}_{\text{water}} \text{kg}_{\text{dry matter}}^{-1}$)

1 Introduction

Fruits are an essential part of a healthy human diet but mostly forgotten by a fast-living society. This gap may be bridged to a large extent by consuming dried fruits which are convenient. Dried grapes have functional properties due to their high concentrations of polyphenols, antioxidants, flavonoids and minerals (Williamson & Carughi, 2010).

Over the years, several empirical treatments were applied to grape berries prior to drying, such as oil-surfactant emulsions, caustic treatments, sulphuring or olive oil. Pre-treatments usually have a dual effect to accelerate the drying rate and, most of the time, improve quality (Grncarevic & Radler, 1971). Acceleration of the drying rate reduces total drying time and consequently increases production. On the other hand, quality improvement is mainly achieved by generating light-coloured raisins with better sanitation (Pangavhane, Sawhney, & Sarsavadia, 1999).

Pre-treatments may be applied using a ‘hot’ or ‘cold’ technique, where ‘cold’ dipping is carried out with immersions at ambient temperature. ‘Hot’ dipping increases the drying rate to a faster extent than ‘cold’ dipping, however, cracks in the waxy cuticle originate which diminish the quality of produced raisins. ‘Cold’ dipping improves their quality by giving rise to an attractive colour make-up, without damaging the berries. ‘Cold dip’ treatments used alkaline oil emulsions, with olive oil and wood ashes, in ancient times

but nowadays they are prepared with specially formulated drying oils (‘dipping oils’) and food grade potassium carbonate (K_2CO_3) (Whiting, 1992). The drying oils are derived from animal tallow or vegetable oil, and mainly consist of ethyl oleate and oleic acid. Ethyl oleate is widely used in ‘cold’ dipping, due probably to its inoffensive nature when compared with other food additives such as sodium hydroxide (NaOH) or sulphur. This product is an oil-surfactant which changes the waxy layer structure of grape skin thus expediting the drying process and reducing browning. The ethyl oleate effect on air-drying kinetics of raisins has been pointed out by several authors to accelerate drying rates (Mahmutoglu, Emir, & Saygi, 1996; Pangavhane et al., 1999; Ponting & Mcbean, 1970; Saravacos, Marousis, & Raouzeos, 1988; Peri & Riva, 1984).

Blanching (or dipping in plain hot water) increases drying rate, by removing or breaking the cuticular wax and inducing cracks in the grape skin (Striegler, Berg, & Morris, 1996). It has the advantage of not adding chemicals to grapes, thus giving a more ‘natural’ product.

Most grapes are usually dried using solar energy. There are several different solar dryers, including direct, indirect and mixed modes (Fuller, 1993; Bala & Woods, 1994). An extensive review of solar dryers, applied to food drying at small scale, was compiled by Murthy (2009). Modelling is essential to design solar dryers, and to predict and simulate drying processes. An overview of

Table 1: Most common thin-layer models for sun / solar drying of fruits, vegetables and cereals

<i>Model</i>	<i>Equipment</i>	<i>Product</i>	<i>Reference</i>
Newton	indirect solar dryer	grains	Bala and Woods (1994)
	solar dryer	banana	Phoungchandang and Woods (2000)
$\frac{X - X_e}{X_0 - X_e} = \exp(-k t)$ (1)	indirect natural-convection solar dryer	grape, fig, green peas, tomato and onion	El-Sebaii, Aboul-Enein, Ramadan, and El-Gohary (2002)
	mixed-mode forced-convection solar dryer with electrical heater	onion	Bennamoun and Belhamri (2003)
	sun-drying	apricot, grape, fig, peach and plum	Togrul and Pehlivan (2004)
	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
Henderson & Pabis	sun-drying	fig	Doymaz (2005)
	indirect forced-convection solar dryer	grape	Yaldiz, Ertekin, and Uzun (2001)
$\frac{X - X_e}{X_0 - X_e} = a \exp(-k t)$ (2)	sun-drying	apricot, grape, fig, peach and plum	Togrul and Pehlivan (2004)
	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
Page	sun-drying	fig	Doymaz (2005)
	direct solar dryer / sun-drying	grape	Mahmutoglu, Emir, and Saygi (1996)
$\frac{X - X_e}{X_0 - X_e} = \exp(-k t^N)$ (3)	indirect forced-convection solar dryer	grape	Yaldiz, Ertekin, and Uzun (2001)
	sun-drying	apricot, grape, fig, peach and plum	Togrul and Pehlivan (2004)
Modified Page	indirect forced-convection solar dryer	grape	Yaldiz, Ertekin, and Uzun (2001)
	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
$\frac{X - X_e}{X_0 - X_e} = \exp(-(k_1 t)^N)$ (4)	sun-drying	apricot, grape, fig, peach and plum	Togrul and Pehlivan (2004)
	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
Two-term	sun-drying	apricot, grape, fig, peach and plum	Togrul and Pehlivan (2004)
	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
$\frac{X - X_e}{X_0 - X_e} = a \exp(-k_1 t) + \dots + b \exp(-k_2 t)$ (5)	sun-drying	fig	Doymaz (2005)
	sun-drying	grape	Riva and Peri (1986)
Fick's simplified series Solution	sun-drying	grape	Riva and Peri (1986)
	direct solar dryer / sun-drying	grape	Mahmutoglu, Emir, and Saygi (1996)

66 the most widely used models for sun / solar dry-
 67 ing of fruits, vegetables and cereals in thin-layer
 68 is presented in Table 1, including type of equip-
 69 ment and dried products. The models include:
 70 an equation analogous to the Newton's law of
 71 cooling and first applied to drying by Lewis, also
 72 known as the Exponential model (equation 1);
 73 the Henderson and Pabis model (equation 2),
 74 similar to the first term of the Fick's series so-
 75 lution; the Page (equation 3) and modified Page
 76 (equation 4) models; the two-term model (equa-
 77 tion 5) and the Fick's simplified series solution.
 78 Some of these models were tested to achieve the
 79 main objective of this work, which was to quickly
 80 assess kinetics and total drying time for the field
 81 solar drying of grapes submitted to different pre-
 82 treatments.

83 2 Materials and Methods

84 2.1 Description of the solar dryer

85 This study was carried out in a solar drier at Mi-
 86 randela in Northern Portugal (Direcção Regional
 87 de Agricultura de Trás-os-Montes) (Fig. 1). Ac-
 88 cording to the classification of Fuller (1993), this
 89 is a mixed mode or hybrid cabinet dryer. The so-
 90 lar dryer consisted of a collector for pre-heating
 91 the air, a drying chamber and a solar chimney. It
 92 is made of wood, with a transparent plastic film
 93 (polyethylene) cover (Araújo et al., 1994), and is
 94 8.10 m long, 7.50 m wide and 2 to 2.6 m high.
 95 The dryer's collector faced south to maximise so-
 96 lar radiation, and formed an angle of 38 degrees,
 97 which is similar to local latitude. It had a 30 cm
 98 opening over all its length, for air entrance. In
 99 this area, the air is pre-dried before moving to
 100 the dehydration chamber. The drying chamber
 101 comprises 18 (6x3) sets of 5 trays each (90 trays
 102 total). Two exhaust air fans are placed on the
 103 back wall.

104 2.2 Description of grape samples

105 Red seedless grapes from the *Monukka* cultivar
 106 were purchased from a local farmer in the region
 107 (Trás-os-Montes, Portugal). Grape clusters were
 108 cut into smaller pieces and the bigger peduncles
 109 removed. Some of the grapes were blanched in

110 hot water or in a 0.1% water emulsion of sun-
 111 flower oil, (3às Sovena) both at 99°C and for
 112 approximately 15 seconds. These preparative
 113 techniques are shown in Fig. 2. The propor-
 114 tion of grapes to solution was approximately 2
 115 kg l⁻¹ and the bath temperature was monitored.
 116 The remaining grapes were washed in cold water
 117 (untreated samples). These pre-treatments were
 118 chosen with the aims to obtain a 'more natural'
 119 product and easier application in the available
 120 facilities close to the solar dryer.

121 Determination of the grapes' initial water con-
 122 tent (berries with small peduncles) was per-
 123 formed according to the AOAC – 984.25 method
 124 (AOAC, 2000), and water content during dry-
 125 ing was mathematically calculated. The grapes'
 126 initial dimensions were measured using a sliding
 127 vernier calliper (Measy 2000 Typ 5921, Swiss),
 128 and the Brix Degree (g sucrose/g solution) of
 129 fresh grapes was determined in triplicate with a
 130 hand refractometer (Atago, Tokyo, Japan).

131 2.3 The drying experiments

132 The pre-treated material was weighed and di-
 133 vided between the wood trays (approximately
 134 5 kg per tray). The initial load was approxi-
 135 mately 250 kg of grapes. The mass of samples
 136 was daily determined using a farmer's weighing
 137 device, with ± 100g accuracy, until reaching a
 138 constant value. Four replicates were performed
 139 in the solar dryer for each pre-treatment.

140 Six K thermocouples and two air humidity
 141 probes were placed in different positions of the
 142 solar drier. Temperature and air humidity were
 143 acquired on-line by a squirrel datalogger (Grant
 144 Instruments 1023, Cambridge, England) every
 145 15 minutes. Air velocity was determined with
 146 a vane anemometer, with ± 0.01 m s⁻¹ accuracy
 147 (Airflow LCA 6000, Buckinghamshire, England),
 148 twice a day.

149 2.4 Modelling considerations

150 Several models were tested to fit drying data, in-
 151 cluding the two-term model, the Newton model,
 152 and two simplified forms of the series solution
 153 of Fick's diffusion equation, with one term and
 154 two terms. The Newton model was normalised



Figure 1: Solar dryer located in Northern Portugal - Mirandela



Figure 2: Preparative techniques for solar drying

155 to the initial water content, in order to al-
156 low a clearer comparison between pre-treatments
157 (equation 6):

$$\frac{X}{X_0} = \frac{X_e}{X_0} + \left(1 - \frac{X_e}{X_0}\right) \exp(-k t) \quad (6)$$

158 where X is the average water content on dry basis
159 ($\text{kg}_{\text{water}} \text{kg}_{\text{dry matter}}^{-1}$), X_0 the average initial
160 water content, X_e the average equilibrium water
161 content, k the drying rate (day^{-1}) and t the time
162 (min).

163 The average equilibrium water content value for
164 grapes' drying, to include in the normalised New-
165 ton model, was determined by the GAB equation
166 (7), using data from grape sorption isotherms
167 presented by Vázquez, Chenlo, Moreira, and
168 Carballo (1999).

$$\frac{X_e}{X_m} = \frac{C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \quad (7)$$

169 X_m is the water content on a dry basis corre-
170 sponding to the monolayer value, C the Guggen-
171 heim constant, a_w the water activity and K
172 a factor correcting properties of the multilayer
173 molecules with respect to the bulk liquid (Bizot,
174 1983). C and K reflect the temperature effect.

175 2.5 Statistical Analysis

176 The drying rate (k - in equation 6) was es-
177 timated by non-linear regression analysis using
178 the package Solver of MICROSOFT Excel 2002
179 (Microsoft® Corporation, Redmond, WA, USA).
180 The 95% standard error of the parameter (SE)
181 and statistical indicators of the quality of the
182 regression [coefficient of determination (R^2) and
183 standard deviation of the experimental error (s)]
184 were also calculated (Box, Hunter, & Hunter,
185 1978). The evaluation criterion for selecting the
186 best model was the standard deviation of the ex-
187 perimental error (s).

188 3 Results and Discussion

189 The grapes' initial average diameter was 1.50 ±
190 0.14 cm, and the initial water content ranged
191 from 81.0 % ± 1.3 (wet basis), 83.0 % ± 1.6
192 and 83.0 % ± 2.0, respectively for untreated

193 grapes, grapes blanched in hot water and grapes
194 blanched in the edible oil solution. Brix Degree
195 ranged between 19.0 % ± 0.9 for the fully ripened
196 grapes and 13.0 % ± 1.2 for unripe grapes. Air
197 velocity in the solar dryer ranged between 9 and
198 34 cm s^{-1} (respectively measured in the front
199 and back of the solar dryer). For an average air
200 temperature of 25.38°C and average air relative
201 humidity of 44.21%, observed during the field
202 experiments, the value of 0.0677 $\text{kg}_{\text{water}} \text{kg}_{\text{dry}}$
203 matter^{-1} was calculated for the equilibrium wa-
204 ter content, using the GAB equation (equation
205 7).

206 Of all the tested models, the normalized Newton
207 model (equation 6) was the one that best fitted
208 the data for experimental drying curves, with the
209 lowest standard deviation of the experimental er-
210 ror (s). Table 2 presents the estimated values for
211 drying rate (k) of the Newton model, the corre-
212 sponding 95% standard error of the parameter
213 (SE), the coefficient of determination (R^2) and
214 the standard deviation of the experimental error
215 (s) for each grapes' pre-treatment.

216 The plots of the fits of the normalized Newton
217 model to the three series of data (untreated and
218 two pre-treatments) are shown in Fig. 3. The
219 two lower curves corresponding to blanched sam-
220 ples in hot water and edible oil solution are over-
221 laid, due to very similar drying rates (Table 2).
222 One concludes that blanching samples in hot wa-
223 ter enhanced the drying rate, in comparison with
224 untreated samples. This is in accordance to what
225 was reported in the literature (Aguilera, Opper-
226 mann, & Sanchez, 1987; Striegler et al., 1996).
227 Drying rates of samples blanched in the 0.1%
228 sunflower oil emulsion are also faster than the
229 ones for untreated samples. It was expected that
230 immersing grapes in the sunflower oil emulsion
231 would expedite drying to a larger extent than
232 simple water blanching. Sunflower oil consists
233 of oleic acid and, as mentioned before, this oil-
234 surfactant changes the waxy layer structure of
235 grape skin and is one of the main constituents
236 of commercial drying oils. However, commercial
237 drying oils are usually used in 'cold' dipping. The
238 results indicate that if a 'hot' dipping is planned,
239 the addition of sunflower oil to the water is not
240 worth the cost and water blanching is sufficient.
241 Differences in the drying rate of untreated sam-
242 ples did not imply a noteworthy difference in

Table 2: Drying rates and statistical indicators of the normalised Newton model for grapes

<i>sample</i>	<i>k</i> (<i>day</i> ⁻¹)	<i>R</i> ²	<i>s</i>
untreated	0.1456 ± 0.01078	0.9390	0.0769
blanched in hot water	0.2038 ± 0.01652	0.9472	0.0747
blanched in 0.1% oil	0.2064 ± 0.01626	0.9506	0.0721

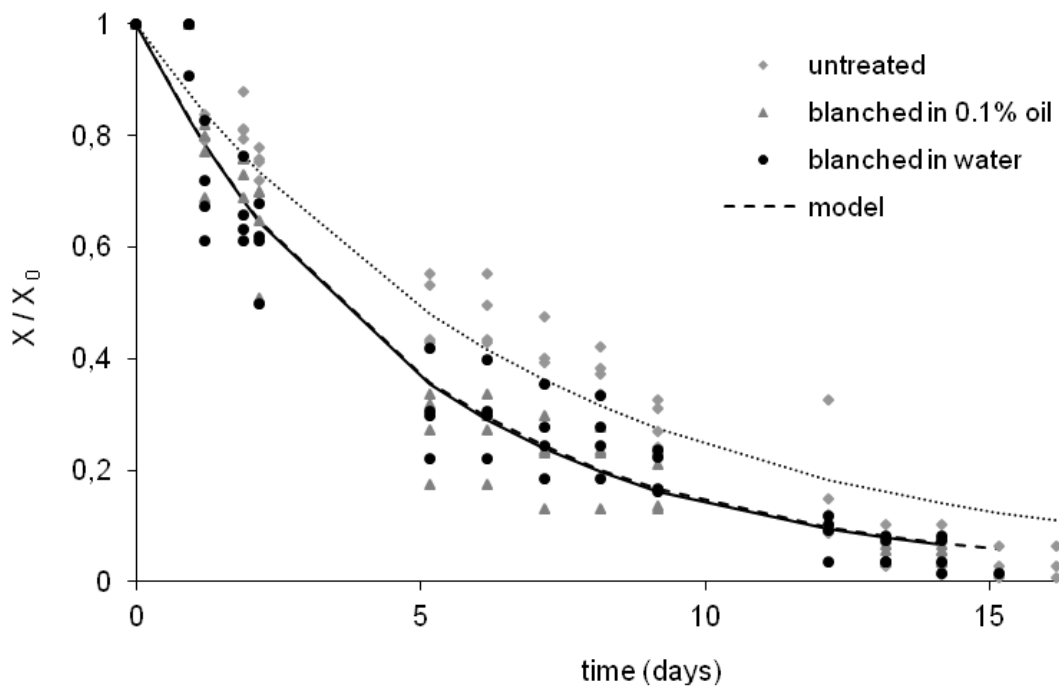


Figure 3: Effect of different pre-treatments on grape drying kinetics

243 total drying time. Water content of untreated
 244 grapes is similar to the water content of blanched
 245 ones, in the last drying phase. However, although
 246 pre-treatments do not significantly decrease total
 247 drying time, they have an important role to
 248 prevent the growth of moulds and bacteria, by
 249 accelerating the initial drying phase.
 250 Regarding data available in the literature, particu-
 251 larly for grapes, the obtained drying rate values
 252 (Newton model) are very similar to the ones pre-
 253 sented by Togrul and Pehlivan (2004) and have
 254 the same order of magnitude as the ones pre-
 255 sented by El-Sebaii, Aboul-Enein, Ramadan, and

256 El-Gohary (2002). These were the only values
 257 found for grapes' drying rates, using the Newton
 258 model.
 259 Drying rate values presented in this work, are
 260 almost one order of magnitude lower than the
 261 ones estimated in previous experiments (Ramos,
 262 Miranda, Brandão, & Silva, 2010). Lower drying
 263 rates may be attributable to a decrease in blanch-
 264 ing time from 30 to 15 s. Dominga grapes used
 265 in the previous experiments were subjected to a
 266 30 s water blanching, and experiments performed
 267 at 30 and 40°C were chosen for comparison. In
 268 the present study, the average product temper-

269 ature during drying was around 34°C. However,
 270 the two studies are difficult to compare because
 271 different grape cultivars and different air condi-
 272 tions drying patterns were used.

273 4 Conclusions

274 It was found that the normalized Newton model
 275 presented the best fit to experimental data for
 276 grapes' solar drying. Comparing estimated dry-
 277 ing rates of the normalised Newton model, one
 278 concluded that samples blanched in hot water or
 279 in the 0.1% edible oil water emulsion had faster
 280 drying rates than untreated samples. Contrary
 281 to what was expected, it was not observed that
 282 pre-treating grapes with the 0.1% edible oil emul-
 283 sion increased the drying rate to a higher extent
 284 than blanching in hot water.

285 Pre-treatments enhanced the drying rates, but
 286 differences in total drying time were not sig-
 287 nificant. Although pre-treatments did not sig-
 288 nificantly decrease total drying time, they play
 289 an important role in preventing the growth of
 290 moulds and bacteria in the initial drying phase
 291 and consequently increasing farmers' income.

292 Drying rate values are very similar to those re-
 293 ported for grapes in the literature (obtained with
 294 the Newton model).

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