

## Effect of pre-treatments on solar drying kinetics of red seedless grapes (cv. *Monukka*)

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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 ( $\text{day}^{-1}$ )
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 ( $\text{K}_2\text{CO}_3$ ) (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>
<b>Newton</b>	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)
<b>Henderson &amp; Pabis</b>	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)
<b>Page</b>	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)
<b>Modified Page</b>	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
	sun-drying	apricot, grape, fig, peach and plum	Togrul and Pehlivan (2004)
$\frac{X - X_e}{X_0 - X_e} = \exp(-(k_1 t) + \dots)$ (4)	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
	sun-drying	apricot, grape, fig, peach and plum	Togrul and Pehlivan (2004)
<b>Two-term</b>	indirect forced-convection solar dryer with heating system	prickly pear	Lahsasni, Kouthila, Mahrouz, and Jaouhari (2004)
	sun-drying	fig	Doymaz (2005)
<b>Fick's simplified series Solution</b>	sun-drying	grape	Riva and Peri (1986)
	direct solar dryer / sun-drying	grape	Mahmutoglu, Emir, and Saygi (1996)

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

## 82 2 Materials and Methods

### 83 2.1 Description of the solar dryer

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

### 103 2.2 Description of grape samples

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

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

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

### 130 2.3 The drying experiments

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

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

### 148 2.4 Modelling considerations

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



Figure 1: Solar dryer located in Northern Portugal - Mirandela



Figure 2: Preparative techniques for solar drying



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

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

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

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

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

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

## 174 2.5 Statistical Analysis

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

## 187 3 Results and Discussion

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

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

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

215 The plots of the fits of the normalized Newton  
 216 model to the three series of data (untreated and  
 217 two pre-treatments) are shown in Fig. 3. The  
 218 two lower curves corresponding to blanched sam-  
 219 ples in hot water and edible oil solution are over-  
 220 laid, due to very similar drying rates (Table 2).  
 221 One concludes that blanching samples in hot wa-  
 222 ter enhanced the drying rate, in comparison with  
 223 untreated samples. This is in accordance to what  
 224 was reported in the literature (Aguilera, Opper-  
 225 mann, & Sanchez, 1987; Striegler et al., 1996).  
 226 Drying rates of samples blanched in the 0.1%  
 227 sunflower oil emulsion are also faster than the  
 228 ones for untreated samples. It was expected that  
 229 immersing grapes in the sunflower oil emulsion  
 230 would expedite drying to a larger extent than  
 231 simple water blanching. Sunflower oil consists  
 232 of oleic acid and, as mentioned before, this oil-  
 233 surfactant changes the waxy layer structure of  
 234 grape skin and is one of the main constituents  
 235 of commercial drying oils. However, commercial  
 236 drying oils are usually used in 'cold' dipping. The  
 237 results indicate that if a 'hot' dipping is planned,  
 238 the addition of sunflower oil to the water is not  
 239 worth the cost and water blanching is sufficient.  
 240 Differences in the drying rate of untreated sam-  
 241 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> <sup>-1</sup> )	<i>R</i> <sup>2</sup>	<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

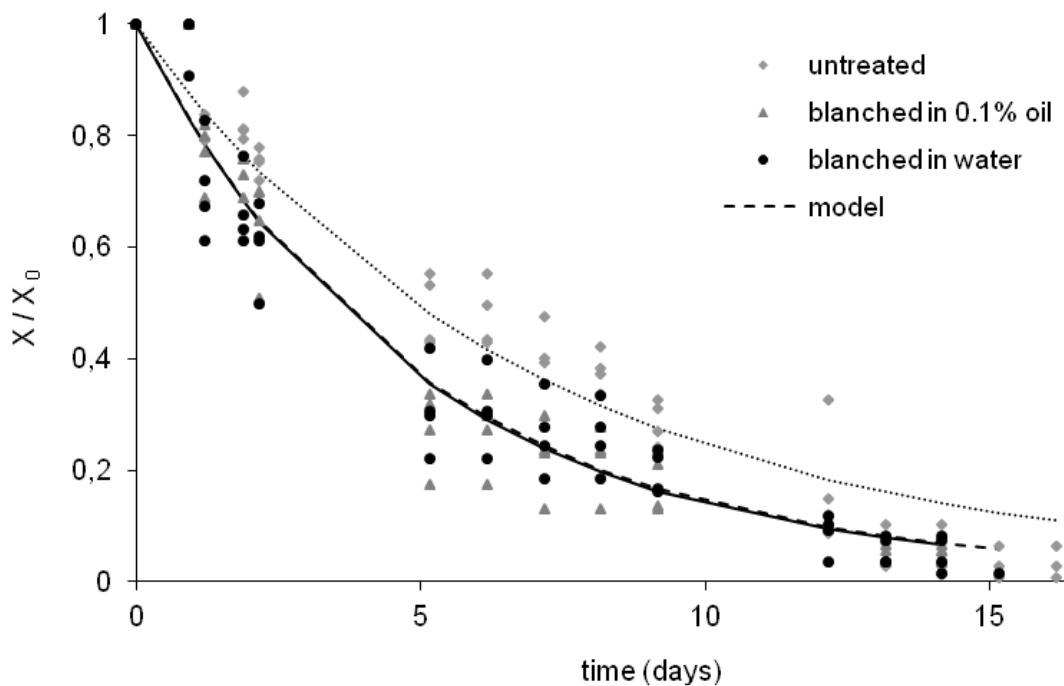


Figure 3: Effect of different pre-treatments on grape drying kinetics

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

255 El-Gohary (2002). These were the only values  
 256 found for grapes' drying rates, using the Newton  
 257 model.

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

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

## 272 4 Conclusions

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

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

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

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