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 attempted to fit the experimental data of drying curves, but the normalized Newton model was the one presenting the best results. Samples blanched in hot water or in the 0.1% edible oil emulsion had faster drying rates than untreated samples. When compared to blanching, and on the contrary to what was expected, pre-treating with the 0.1% edible oil emulsion did not increase the drying rate in a higher extent. Pre-treatments did not imply a noteworthy difference in total drying time. However, they had an important role accelerating initial drying rates, thus preventing moulds and bacterial growth and consequently increasing farmers' income.

Keywords: pre-treatments; solar drying; kinetics; modeling; raisins

Short title: Effect of pre-treatments on kinetics of solar dried grapes

Nomenclature

a, b parameters of equations 2 and 5

a_w water activity

C	Guggenheim constant
Co, Ko	pre-exponential factor of equations 8 and 9, respectively
H_1	heat of condensation of pure water vapour (J mol^{-1})
H_m	heat of sorption of the monolayer of water (J mol^{-1})
H_q	heat of sorption of the multilayers (J mol^{-1})
k_1, k_2	parameters of the two-term model (equation 5)
k	drying rate of equations 1, 2 and 3
K	factor that corrects properties of the multilayer molecules with respect to the bulk liquid
N	parameter of equations 3 and 4
Rg	universal gas constant
s	standard deviation of the experimental error
t	time (min)
T	absolute temperature (K)
X	water content on dry basis (kg_{water} $kg_{dry\ matter}^{-1}$)
Xe	average equilibrium water content on dry basis (kg_{water} $kg_{dry\ matter}^{-1}$)
Xm	monolayer water content on dry basis (kg_{water} $kg_{dry\ matter}^{-1}$)
X_0	initial average water content on dry basis (kg_{water} $kg_{dry\ matter}^{-1}$)

1. Introduction

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

Through the years, several empirical treatments were applied on grape berries prior to drying, such as oil-surfactant emulsions, caustic treatments, sulphuring or olive oil. Pre-treatments usually have a dual effect, accelerating the drying rate, and most of the time also improving 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 in a 'hot' or 'cold' technique, being the 'cold' dipping done with immersions at ambient temperature. 'Hot' dipping increases the drying rate to a faster extent than 'cold' dipping, but originates cracks in the waxy cuticle which diminish the quality of produced raisins. 'Cold' dipping improves their quality originating an attractive colour make-up, without any damage on the berries. 'Cold dip' used alkaline oil emulsions with olive oil and wood ashes in ancient times, but nowadays is 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 are vegetable oil based, 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 and changes the waxy layer structure of grape skin, expediting the drying process and reducing browning. Ethyl oleate effect on air-drying kinetics of raisins has been pointed out by several authors as accelerating drying rates (Mahmutõglu, Emír, & Saygi, 1996; Pangavhane, Sawhne, & Sarsavadia, 1999; Peri & Riva, 1984; Pointing & McBean, 1970; Saravacos & Marousis, 1988).

Blanching (or dipping in plain hot water) increases drying rate, by removing or breaking the cuticular wax and inducing cracks on the grape skin (Striegler, Berg, & Morris, 1996). It has the advantage of not adding chemicals to grapes, originating 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 on 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 on the most widely used models for sun / solar drying of fruits, vegetables and cereals on thin-layer is presented on

Table 1, including type of equipment and dried products. The models include: an equation analogous to the Newton's law of cooling and first applied to drying by Lewis, also known as the Exponential model (equation 1); the Henderson and Pabis model (equation 2), similar to the first term of Fick's series solution; the Page (equation 3) and modified Page (equation 4) models; the two-term model (equation 5) and the Fick's simplified series solution.

Some of these models were tested to achieve the main objective of this work, which was to quickly assess kinetics and total drying time of field solar drying of grapes submitted to different pre-treatments.

2. Materials and Methods

2.1. Description of the solar dryer

This study was carried out in a solar drier at Mirandela, North of Portugal (Direcção Regional de Agricultura de Trás-os-Montes) (Fig. 1). According to the classification of Fuller (1993), this is a mixed mode or hybrid cabinet dryer. The solar dryer consisted of a collector for pre-heating the air, a drying chamber and a solar chimney. It is made of wood with a transparent plastic film (polyethylene) cover (Araújo et al., 1994), and is 8.10 m long, 7.50 m wide and 2 to 2.6 m high. The dryer collector is facing south for maximising solar radiation, and forms an angle of 38 degrees, which is similar to local latitude. It has a 30 cm opening through all its length, for air entrance. In this area, the air is pre-dried before moving to the dehydration chamber. The drying chamber comprises 18 (6x3) sets of 5 trays each (90 trays total). Two exhaust air fans are placed on the back wall.

2.2 Description of grape samples

Red seedless grapes from the *Monukka* cultivar were purchased from a local farmer in the region (Trás-os-Montes, Portugal). Grape clusters were cut into smaller pieces and the bigger peduncles removed. Some of the grapes were blanched in hot water or in a 0.1% water emulsion of sunflower oil (3às Sovena) at 99^{o}C, for approximately 15 seconds. These preparative techniques may be observed in Fig. 2. The proportion of grapes to solution was approximately 2 kg/l and bath temperature was monitored. The remaining grapes were simply washed in cold water (untreated samples). These pre-treatments were chosen aiming at obtaining a 'more natural' product and also due to their easier application in the available facilities close to the solar dryer.

Determination of the grapes' initial water content (berries with small peduncles) was performed according to the AOAC – 984.25 method (AOAC, 2010), and water content during drying was mathematically calculated. The grapes' initial dimensions were measured using a sliding vernier calliper (Measy 2000 Typ 5921, Swiss), and the Brix Degree (g sucrose/g solution) of fresh grapes was determined in triplicate with a hand refractometer (Atago, Tokyo, Japan).

2.3 The drying experiments

The pre-treated material was weighed and divided between the wood trays (approximately 5 kg per tray). Initial load was approximately 250 kg of grapes. The mass of samples was daily determined using a farmer weighing device with $\pm$ 100g accuracy, until reaching a constant value. Four replicates were performed in the solar dryer for each pre-treatment.

Six K thermocouples and two air humidity probes were placed in different positions of the solar drier. Temperature and air humidity were acquired on-line by a squirrel datalogger (Grant Instruments 1023, Cambridge, England) every 15 minutes. Air velocity was determined with a vane anemometer with $\pm$ 0.01 m/s accuracy (Airflow LCA 6000, Buckinghamshire, England), twice a day.

2.4 Modelling considerations

Several models were attempted to fit drying data, including the two-term model, the Newton model, and two simplified forms of the series solution of Fick's diffusion equation, with one term and two terms.

The Newton model was normalised in order to the initial water content, to allow a clearer comparison between pre-treatments (equation 6):

$$\frac{X}{X_0} = \frac{Xe}{X_0} + \left(1 - \frac{Xe}{X_0}\right) \exp(-k\,t) \qquad (6)$$

where X is the average water content on dry basis ($kg_{water}\ kg_{dry\ matter}^{-1}$), X_0 the average initial water content and Xe the average equilibrium water content and t the time (min).

The average equilibrium water content value for grapes drying, to include in the normalised Newton model, was determined by the GAB equation (7), with data of grape sorption isotherms presented by Vázquez, Chenlo, Moreira, & Carballo (1999).

$$\frac{Xe}{Xm} = \frac{C\,K\,a_w}{(1 - K\,a_w)\,(1 - K\,a_w + C\,K\,a_w)} \qquad (7)$$

Xm is the water content on dry basis corresponding to the monolayer value, C the Guggenheim constant, a_w the water activity and K a factor correcting properties of the multilayer molecules with respect to the bulk liquid (Bizot, 1983). C and K reflect the temperature effect:

$$C = Co\,\exp\left(\frac{H_1 - H_m}{Rg\,T}\right) \quad (8)$$

$$K = Ko\,\exp\left(\frac{H_1 - H_q}{Rg\,T}\right) \quad (9)$$

where *Co* and *Ko* are constants, H_1 the heat of condensation of pure water vapour (J mol^{-1}), H_m the heat of sorption of the monolayer of water, H_q the heat of sorption of the multilayers, and *Rg* the universal gas constant.

2.5 Statistical Analysis

The drying rate (*k* – in equation 6) was estimated by non-linear regression analysis using the package Solver of MICROSOFT Excel 2002 (Microsoft® corporation, Redmond, WA, USA). The 95% standard error of the parameter (SE) and statistical indicators of the quality of the regression [coefficient of determination (R^2) and standard deviation of the experimental error (s)] were also calculated (Box, Hunter, & Hunter, 1978). The evaluation criterion for selecting the best model was the standard deviation of the experimental error (s).

3. Results and Discussion

The grapes initial average diameter was 1.50 ± 0.14 cm, and the initial water content ranged from 81.0 % ± 1.3 (wet basis), 83.0 % ± 1.6 and 83.0 % ± 2.0, respectively for untreated grapes, grapes blanched in hot water and grapes blanched in the edible oil solution. Brix Degree ranged between 19.0 % ± 0.9 for the fully ripened grapes and 13.0 % ± 1.2 for unripe grapes. Air velocity in the solar dryer ranged between 9 and 34 cm/s (respectively measured in the front and back of the solar dryer). For an average air temperature of 25.38°C and average air relative humidity of 44.21%, observed during the field experiments, the value of 0.0677 was calculated for the equilibrium water content, using the GAB equation (equation 7).

From all the tested models, the normalized Newton model (equation 6) was the one that better fitted experimental drying curves data, with the lowest standard deviation of the experimental error (s). Table 2 presents the estimated values of drying rates (k) of the Newton model, the corresponding 95% standard error of the parameter (SE), the coefficient of determination (R^2) and the standard deviation of the experimental error (s) for each grapes pre-treatment.

Observing Table 2 and Fig. 3 one concludes that blanching samples in hot water enhanced the drying rate, in comparison with untreated samples. This is in accordance to what was referred in the literature (Striegler, Berg, & Morris, 1996; Aguilera, Oppermann, & Sanchez, 1987). Drying rates of samples blanched in the 0.1% sunflower oil emulsion, are faster than the ones for untreated samples and very similar to water blanched samples. It was expected that immersing grapes in the sunflower oil emulsion would expedite drying in a larger extent than simple water blanching. Sunflower oil consists of oleic acid and, as referred before, this oil-surfactant changes the waxy layer structure of grape skin and is one of the main constituents of commercial drying oils. However, commercial drying oils are usually used in 'cold' dipping. The results indicate that if a 'hot' dipping is planned, the addition of sunflower oil to the water is not worth the cost and water blanching is sufficient.

Differences in the drying rate of untreated samples did not imply a noteworthy difference in total drying time. Water content of untreated grapes is similar to the water content of blanched ones, in the last drying phases. However, although pre-treatments do not significantly decrease total drying time, they have an important role for preventing moulds and bacterial grow by accelerating initial drying phases.

Regarding data available in the literature, particularly for grapes, the obtained drying rate values (Newton model) are very similar to the ones presented by Togrul and Pehlivan (2004) and in the same order of magnitude of the ones presented by El-Sebaii, Aboul-Enein, Ramadan, & El-Gohari (2002). These were the only values found for grapes drying rates, using the Newton model.

Drying rate values presented in this work, are almost one order of magnitude lower than the ones estimated in previous experiments (Ramos et al., 2010). Lower drying rates may be attributable to decreasing blanching time from 30 to 15 s. *Dominga* grapes used in the previous experiments were subjected to a 30 s water blanching, and experiments performed at 30 and 40^{o}C where chosen for comparison. In the present study, average product temperature during drying was around 34^{o}C. However, the two studies are difficult to compare because different grape cultivars and different air conditions drying patterns were used.

4. Conclusions

It was found that the normalized Newton model presented the best fit to experimental data of grapes solar drying. Comparing estimated drying rates of the normalised Newton model, one concluded that samples blanched in hot water or in the 0.1% edible oil water emulsion had faster drying rates than untreated samples. On the contrary to what was expected, it was not observed that pre-treating grapes with the 0.1% edible oil emulsion increased the drying rate in a higher extent than blanching.

Pre-treatments enhanced the drying rates, but differences in total drying time were not significant. Although pre-treatments did not significantly decrease total drying time, they play an important role in preventing moulds and bacterial grow in initial drying phases and consequently increasing farmers income.

Drying rate values are very similar to those reported for grapes in the literature (obtained with the Newton model).

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Figures captions

Fig. 1. Solar dryer located at the North of Portugal - Mirandela.

Fig. 2. Preparative techniques for solar drying.

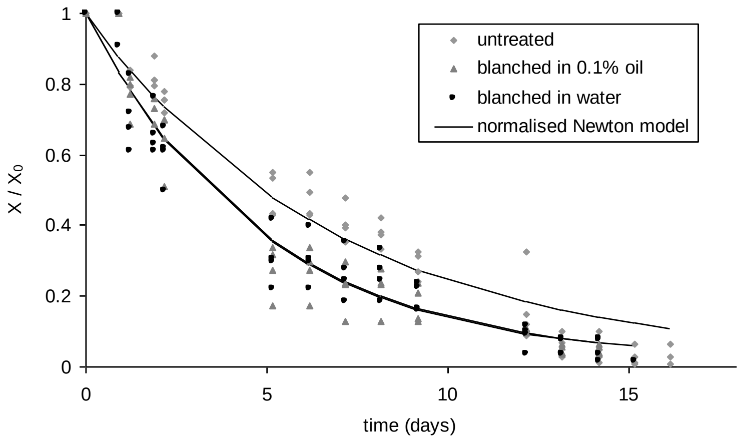

Fig. 3. Effect of different pre-treatments on grape drying kinetics.

Tables captions

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

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

Table 2. Grapes drying rates and statistical indicators of the normalised Newton model.

sample	*k x 10^4 (min^{-1})*	*R^2*	*s*
untreated	1.011± 0.075	0.9390	0.0769
blanched in hot water	1.415 ± 0.115	0.9472	0.0747
blanched in 0.1% oil	1.433 ± 0.113	0.9506	0.0721