PAPER

THE EFFECT OF BLANCHING PRE-TREATMENT ON THE DRYING KINETICS, THERMAL DEGRADATION OF PHENOLIC COMPOUNDS AND HYDROXYMETHYL FURFURAL FORMATION IN POMEGRANATE ARILS

H. VARDİN[1] and F.M. YILMAZ*[2]

[1]Harran University, Engineering Faculty, Food Engineering Dept., 63040, Şanlıurfa, Turkey

[2]Adnan Menderes University, Engineering Faculty, Food Engineering Dept., 09010, Aydın, Turkey

*Corresponding author. Tel.: +90 2562137503; Fax +90 2562136686

E-mail address: fatih.yilmaz@adu.edu.tr

ABSTRACT

This study examined the effect of blanching pre-treatment on the drying kinetics, thermal degradation of phytonutrients and hydroxymethylfurfural (HMF) formation in pomegranate arils. Pre-treated and untreated arils were dried in a cabinet dryer operated at temperatures of 55, 65 and 75°C. The efficiency of the drying process was assessed according to the effective moisture diffusivity and activation energy values. Effective moisture diffusivities ranged from 0.59×10^{-9} to 5.62×10^{-9} $m^2 s^{-1}$ and activation energies for drying were 31.82 and 76.11 kJ/mol for pre-treated and untreated arils, respectively. Six thin-layer drying models were tested, and Page and Modified Page models were found to be the most suitable. The final quality of pomegranate arils was evaluated according to their total phenolic and total anthocyanin contents, their antioxidant capacities and the rate of HMF formation. The blanching pre-treatment prior to drying produced higher retention of antioxidant compounds with less HMF content and superior sensory properties. Sensory analysis results revealed that pre-treated arils were preferred to untreated arils.

Keywords: pomegranate, drying kinetics, antioxidants, HMF, thermal degradation, blanching

1. INTRODUCTION

The pomegranate is a native plant to an area covered by Persia, Anatolia, Mesopotamia and India, and has been cultivated in the USA and Mediterranean countries (MENA *et al.,* 2013). Significant attention has been given to pomegranate fruits in recent years because of the desirable aroma, flavor and characteristic bright red color (SHAHBAZ *et al.,* 2014). Pomegranate fruits are used for the manufacture of various food products and fruit juice concentrates. Fresh pomegranates are harvested during late September, October and November. Even though there is significant demand for fresh pomegranates during the whole year, geographical and seasonal restrictions limit the fresh pomegranate supply to the market. Therefore, many food preservation techniques have been investigated to extend the shelf life of the pomegranate fruits such as canning, freezing, modified-atmosphere packaging and controlled storage of the products in addition to drying (VIUDA-MARTOS *et al.,* 2012). Traditionally dried pomegranate arils are called 'Anardana', which is widely consumed in Southern Asia and Persia. Anardana is an alternative pomegranate product enabling people to serve dried arils the whole year round. Anardana production keeps increasing together with increasing acres of pomegranate plantations in other parts of the world. Drying is one of the oldest food preservation methods that have been used from ancient times up to the modern day. The drying process extends the shelf life of the products by lowering water activity, and therefore inhibiting microbial and biochemical decay of the food (KAMİLOGLU *et al.,* 2014). However, the drying process may negatively affect food quality parameters such as the nutritional quality, the bioactive compound content, the color, and the texture (FAZAELİ *et al.,* 2013). Therefore, it is necessary to investigate the optimum drying conditions for the production of high quality, desirable and shelf life –extended foods [AKDAŞ and BAŞLAR, 2015; STURM *et al.,* 2012). Pre-treatment applications, and different drying methods and conditions, are currently being investigated for the production of high quality products (CHAETHONG and PONGSAWATMANİT, 2015; ADEDEJİ *et al.,* 2008]. The balance between low cost, fast production techniques and high quality of the final product should be established to ensure consumer acceptability. The consumer acceptability and the market value of the products are influenced by both qualitative and quantitative factors. In general, consumers tend to prefer foods at a reasonable price with a high functional compound content and improved color characteristics. Especially in recent years, together with the improvements in welfare and education, most people from all over the world have become more and more demanding with regard to functional foods (SIRO *et al.,* 2008). The major functional compounds in fruit and vegetable products are vitamins, pigments, flavonoids and phenolic acids (ZULUETA *et al.,* 2007). Phenolic compounds have been shown to be associated with inhibiting cardiovascular diseases, tumor formation and cancer development (ACOSTA-ESTRADA *et al.,* 2014; BONDIA-PONS *et al.,* 2009). However, food-processing steps can also exert negative effects on vulnerable food compounds such as vitamins, pigments and phenolic acids (CHONG *et al.,* 2009; MOUSA *et al.,* 2002). Even though most of the drying process is completed in cabinet-type dryers in the food industry, there are few studies in published literature evaluating the bioactive-compound degradation kinetics and the formation of harmful compounds. Thus information on the final quality parameters is essential for enabling better process control and the manufacture of dried goods with a higher antioxidant capacity. The objective of this study is to evaluate the drying kinetics of pomegranate arils and determine the proper drying conditions to produce dried arils with higher nutritional value. Blanched and unblanched pomegranate arils were dried using cabinet dryers at different temperatures.

The association between the thermal-processing steps and the phytonutrient content of pomegranates were determined at different temperatures. The heat and mass transfer characteristics of the dried foods determine their drying mechanisms. Hence, mathematical methods are useful in predicting the drying behavior of food commodities. This study also looked at mathematical models to determine which model best described the kinetics of the drying process in the context of degradation of phenolics and anthocyanins, as well as the formation of HMF during the process.

2. MATERIALS AND METHODS

2.1. Materials

Fresh pomegranates (*Punica granatum* L., cv. *Hicaz*) were purchased from a wholesale market hall in Şanlıurfa, Turkey, and immediately transported to the laboratory. Fruits were kept at 4°C before commencement of the tests. Folin-Ciocalteu, gallic acid and DPPH (1,1-diphenyl-2-picrylhydrazyl) were obtained from the Merck Co. (Darmstadt, Germany), and 5-(hydroxymethyl)furfural (HMF) and acetone from the Sigma Chemical Co. (St. Louis, Mo, USA). All other chemicals used were of analytical grade.

2.2. Preparation of pomegranate arils

The pomegranates were peeled manually, and the arils were separated from the fruits. The arils were separated into two groups. Half of the group was pre-treated by dipping into water with 0.1% citric acid at 80 ± 2°C for 2 minutes and afterwards immediately transferred to the cabinet dryer (i.e. pre-treated). The ratio of blanching water and pomegranate arils was 20 mL/g. After blanching, the arils were drained using soft filter papers. The other half of the arils was dried directly without any pre-treatment.

2.3. Drying procedure

The pre-treated and untreated arils were immediately transferred for cabinet drying. Cabinet drying was carried out in the dryer (Kendro Laboratory Products, Germany) at three different temperatures (55, 65 and 75°C) at an air velocity of 1.2 m/s. During drying, moisture loss was recorded and almost 10 g of samples were removed from the dryer at thirty-minute intervals. The samples were stored at −20°C until the extraction procedure.

2.4. Mathematical modeling

Page, Modified Page, Henderson and Pabis, Wang and Singh, Two Term and Logarithmic models (Table 1) were used for modeling the drying kinetics of the pomegranate arils. In these models, the moisture ratio (*MR*) was simplified to Equation 1, below, instead of $(M-M_e)/(M_0-M_e)$, as the value of M_e is relatively small compared to M or M_0.

$$MR = M/M_0 \quad (1)$$

where M is the moisture content at time t, M_0 is the initial moisture content and M_e is the equilibrium moisture content. Goodness of fits were determined according to the evaluation of R^2 and root mean square error (RMSE). Higher values of R^2 and smaller RMSE values (Equation 2) indicated a better fit of the experimental data to the model. The

correlation coefficient (R^2) and root mean square error (RMSE) were taken into consideration to select the best model.

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}(MR_{exp.i} - MR_{pre.i})^2\right]^{1/2} \quad (2)$$

Table 1. Models used for determining thin-layer drying curves.

Model	Equation	Reference
Page	$MR = \exp(-kt^n)$	(PAGE, 1949)
Modified Page	$MR = \exp[-(kt)^n]$	(OVERHULTS *et al.*, 1973)
Henderson and Pabis	$MR = a\exp(-kt)$	(HENDERSON and PABIS, 1961)
Wang and Singh	$MR = 1+at+bt^{28}$	(WANG and SINGH, 1978)
Two Term	$MR = a\exp(k_0t)+ b\exp(k_1t)$	(HENDERSON, 1974)
Logarithmic	$MR = a\exp(-kt) + c$	(YAGCİOGLU *et al.*, 1999)

2.5. Computation of effective moisture diffusivity and activation energy

Fick's second law was adapted to spherical shapes for unstable diffusion conditions as follows (CRANK, 1975):

$$MR = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp(-n^2\pi^2\frac{D_{eff}t}{r^2}) \quad (3)$$

For extended drying periods (Equation 4) can be further simplified as follows (DOYMAZ, 2012):

$$ln(MR) = ln(\frac{6}{\pi^2}) - (\frac{\pi^2 D_{eff}t}{r^2}) \quad (4)$$

Plotting ln(MR) versus time enables calculation of the effective moisture diffusivity and a straight line can be obtained with a slope of (K) as expressed in (Equation 5) below:

$$K = \frac{\pi^2 D_{eff}}{r^2} \quad (5)$$

The activation energy for diffusion was determined from the slope of the Arrhenius-type equation (Equation 6):

$$D_{eff} = D_0 exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

2.6. Modeling the degradation of total phenolic and total anthocyanin contents

Thermal degradation of most bioactive compounds follows first order kinetics (Equation 7):

$$C_t = C_0\, x\, exp\,(\pm k_0\, x\, t) \quad (7)$$

Where C_t and C_0 are the total phenolic (TP) and total anthocyanin (TA) contents after heating time t and t=0 minutes, respectively, and k is the kinetic constant. The natural logarithms of the ratios of C_t and C_0 against time were plotted, and by using the slope of this graph, half-life ($t_{1/2}$) was deduced according to Equation 8:

$$t_{1/2} = \frac{ln2}{k} \quad (8)$$

2.7. Extraction of bioactive compounds

The arils were firstly homogenised with 80% acetone (0.01% HCl) using a pestle and mortar. Extraction was carried out in a shaking incubator (Labline, USA) operated at 50°C and 180 rpm for 60 minutes. Then, the slurry was centrifuged at 6000 rpm for 8 minutes (Hitachi CT6E, Taiwan), and the supernatant was collected in falcon tubes and stored at −40°C until analysis.

2.8. Determination of total phenolic (TP) content

The TP contents of the samples were determined by the Folin-Ciocalteu method (SINGLETON and ROSSI, 1965) using the gallic acid standard curve. The absorbance of each sample was read at 750 nm in a spectrophotometer (Libra, Biochrom, UK) against the blank, and the results were expressed as mg of gallic acid equivalent per kilogram of pomegranate aril (mg GAE kg^{-1}).

2.9. Determination of total anthocyanin (TA) content

The TA contents of the samples were determined using a pH-differential method (GIUSTI and WROLSTAD, 2001) by a UV-vis spectrophotometer (Biochrom Libra, UK). The pomegranate extracts were mixed with pH 1.0 (0.025 M potassium chloride) and pH 4.5 (0.4 M sodium acetate) buffers, and the absorbance values were recorded at 520 and 700 nm. The results were expressed as mg of cyanidin 3-glucoside per kilogram dry weight of the pomegranate aril.

2.10. Determination of antioxidant capacity

The antioxidant capacity of the samples was estimated by DPPH (1,1-diphenyl-2-picrylhydrazyl) assay as described by KARAASLAN *et al.*, 2004a. An 0.1 mL amount of various concentrations of the extracts diluted in ethanol was added to 2.9 mL of 0.1 mM of the DPPH solution. The decrease in absorbance at 517 nm was measured after 30 minutes of incubation at room temperature. The inhibition concentration (EC_{50}) – the amount of sample concentration (g/mL db) necessary to decrease the initial DPPH concentration by 50% – was calculated after plotting the percentage inhibition versus the extract concentration curve.

2.11. Determination of hydroxymethylfurfural (HMF)

The HMF contents of the arils were determined using a spectrophotometric method (ACAR *et al.*, 1999). Briefly, 5 g of dried sample was crushed and diluted with distilled water up to 50 mL. Then, 5 mL of this solution was mixed with p-toluidine solution (10 g/100 mL) and 1 mL of barbituric acid solution was added to the mixture after 2 minutes.

The absorbance of the mixture was noted on the spectrophotometer at 55 nm and calculations were done using the HMF standard calibration curve.

2.12. Sensory analysis

Dried samples (pre-treated and untreated at three different temperatures for a total of 6 samples) were randomly coded and served to panelists. Samples were analyzed organoleptically by 20 trained panelists in terms of color, shape, texture, flavor-aroma and overall acceptability. Evaluation was scored on a ten-point scale (0–4, very bad – bad; 5–9, acceptable – excellent), according to GOULD (1977).

2.13. Statistical analyses

Experimental data were subjected to analysis of variance (ANOVA) using SPSS version 15.0 software (SPSS Inc., Chicago, IL, USA) and *P* values less than 0.05 were taken into consideration. The Duncan test was used as a post hoc test after applying the homogeneity test. The parameters of kinetic models were determined by using Sigma Plot software (Sigma Plot 10.0 Windows version, SPSS Inc.). All the experiments were repeated three times.

3. RESULTS AND DISCUSSIONS

3.1. Drying kinetics and modelling

The initial moisture content of the fresh and pre-treated pomegranate arils were 79.82 ± 0.44% and 80.13 ± 0.67% (w.b.), respectively. The samples were dried until they had 16% (w.b.) moisture content by considering sensory properties and current literature data. A graphical representation of MR values versus time belonging to pre-treated samples is shown in Fig. 1.

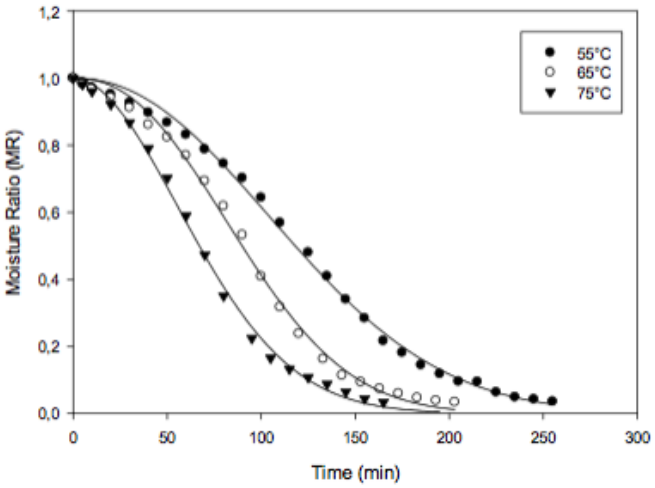

Figure 1. Drying curve of pre-treated pomegranate arils (plotted by the page model) in cabinet dryer.
(*MR* Moisture Ratio: The ratio of dry basis moisture content at any time to initial dry basis moisture content).

As expected, the drying temperature had a significant effect on the drying kinetics of the samples. The time required to dry pre-treated pomegranate arils in a cabinet dryer were 168, 204 and 237 minutes at 75, 65 and 55 °C, respectively, while for untreated samples the values were 244, 448 and 945 minutes at the same temperatures. It is clear that pre-treatment application had a significant effect on the drying time of the arils. In a pomegranate drying study using an air circulating oven (v = 1.3 m/s), drying times were reported to be 330, 520 and 1020 minutes at 55, 65 and 75°C, respectively (BAŞLAR *et al*., 2014). Six thin layer drying models were evaluated by fitting the experimental data and considering the highest R^2 and lowest RMSE values. The results showed that Page and Modified Page models were the most relevant models in all drying conditions. Model constants with statistical evaluations are demonstrated in Table 2. Mathematical models used in drying applications are useful for designing new or improved existing drying systems. Such models are directly related to the temperature and velocity of the drying medium inside the mechanical dryer as well as the energy cost (BABALIS and BELESSIOTIS, 2004).

3.2. Effective moisture diffusivity and activation energy of the drying process

Knowing the effective moisture diffusivity is necessary for designing and modeling mass transfer processes (SHARMA and PRASAD, 2004). The *Deff* values of the pre-treated samples in the cabinet dryer ranged from 2.87×10^{-9} to 5.62×10^{-9} m^2/s and the untreated samples from 0.59×10^{-9} to 2.92×10^{-9} m^2/s (Table 3). Higher *Deff* values were observed in pre-treated samples that are associated with faster removal of moisture and thus the faster drying of samples. Similar effective moisture diffusivity results were demonstrated by studies investigating pomegranate aril drying (DOYMAZ, 2012; BAŞLAR *et al*., 2014; KARAASLAN *et al*., 2014b; MINAEI *et al*., 2011;HII *et al*., 2009). The *ln(Deff)* value was plotted against the reciprocal of absolute temperature to determine the activation energy and Equation (6) was used to determine the activation energy. The activation energy may be defined as the energy barrier that must be overcome in order to activate moisture diffusion. Therefore, determination and comparison of the *Ea* values are important in drying applications (KARAASLAN *et al*., 2014b). The activation energy was 31.82 kJ/mol for the pre-treated arils and 76.11 kJ/mol for untreated arils. Pre-treatment of the samples brought about a significant decrease in the activation energies of the samples. BAŞLAR *et al*.,(2014) reported the *Ea* value as 44.798 kJ/mol for cabinet drying of pomegranate arils. In a pomegranate aril drying study, pre-treated (dipping in alkali emulsion of ethyl oleate) samples had lower activation energy than the control group (DOYMAZ, 2012).

3.3. The changes in total phenolic compounds and anthocyanin content

Anthocyanins are responsible for giving the characteristics red color to pomegranate arils, and the arils are rich in anthocyanins and other colorless phenolic compounds. Numerous studies have showed the health benefits of phenolics present in pomegranate arils (KARAASLAN *et al*., 2014a). However, the stabilities of these compounds can easily be affected by temperature increases and the presence of oxygen (VERBEYST *et al*., 2010). Therefore, the determination of such substances is important for process optimization. The anthocyanin content of the samples declined from 824.65 ± 87.27 (mg kg^{-1}, d.b.) to 813.83 ± 79.91 (mg kg^{-1}, d.b.), and total phenolic compounds declined from 7433.04 ± 685.51 (mg kg^{-1}, d.b.) to 6863.86 ± 630.27 (mg kg^{-1}, d.b.) as pre-treatment was applied.

Table 2. Statistical data of the six thin-layer mathematical models applied to the drying data.

Condition	T (°C)	Model	R^2	RMSE	k	n	a	b	k_0	k_1	c
UNTREATED	55	**1**	**0.9914**	0.0203	3.1471	1.9017					
		2	**0.9914**	0.0203	0.0010	1.8922					
		3	0.9124	0.0637	0.0014		1.0919				
		4	0.9897	0.0458			0.0004	5.3849			
		5	0.9114	0.0651			0.5394	0.5448	0.0009	0.0009	
		6	0.9108	0.0039	0.0029		6.2423				-5.348
	65	**1**	**0.9955**	0.0309	4.6778	2.076					
		2	**0.9955**	0.0310	0.0080	2.076					
		3	0.9068	0.0779	0.0074		1.1079				
		4	0.9845	0.0614			0.0027	1.8017			
		5	0.9073	0.0774			0.5481	0.5561	0.0078	0.0078	
		6	0.8345	0.0547	0.0058		4.2418				-4.154
	75	**1**	**0.9873**	0.0323	8.8847	1.8517					
		2	**0.9873**	0.0323	0.0058	1.8488					
		3	0.9271	0.0738	0.5724		1.1417				
		4	0.9577	0.0617			0.0029	2.1854			
		5	0.9303	0.0716			0.5673	0.5673	0.0060	0.0060	
		6	0.9668	0.0515	0.0073		5.2346				-4.132
PRE-TREATED	55	**1**	**0.9964**	0.0183	6.0977	1.9132					
		2	**0.9962**	0.1830	0.0063	1.9132					
		3	0.9249	0.0770	0.0061		1.1105				
		4	0.9840	0.0369			0.0023	0.5421			
		5	0.9248	0.0762			0.5537	0.5487	0.0061	0.0061	
		6	0.8978	0.0184	0.6913		1.2710				-2.026
	65	**1**	**0.9960**	0.0187	4.6787	2.0874					
		2	**0.9960**	0.0188	0.0081	2.0874					
		3	0.9528	0.0854	0.0799		1.1104				
		4	0.9852	0.0451			0.0034	1.8446			
		5	0.9061	0.0839			0.5572	0.5572	0.0071	0.0071	
		6	0.8632	0.1239			3.0045				-0.353
	75	**1**	**0.9816**	0.0425	0.0014	1.4628					
		2	**0.9816**	0.0425	1.4631	1.4628					
		3	0.9611	0.0849	0.0110		1.0921				
		4	0.9633	0.0624			0.0082	1.4365			
		5	0.9616	0.0850			0.5473	0.5473	0.0103	0.0103	
		6	0.9684	0.0058	0.0068		1.3641				-0.285

As demonstrated in Table 4, more anthocyanin and phenolic contents were preserved in the samples dried at 55°C compared to other samples, while the increase in temperature caused more phenolic and anthocyanin degradation. The TA concentration of the pre-treated samples decreased to 19% in a cabinet dryer at 75°C, to 25% at 65°C, and to 29% at 55°C. The TA in untreated samples in a cabinet dryer declined to 13%, 19% and 22% under the same temperature regimes. A decrease of TP content of the arils was also observed.
The TP content of the pre-treated samples in the cabinet dryer dropped to 36% in the cabinet dryer at 75°C, to 41% at 65°C and to 54% at 55°C. The TP content of the untreated

samples in the cabinet dryer declined to 22%, 28%, and 33% under the same conditions at 75, 65, 55°C, respectively (Table 4). It is clear that both TP and TA are preserved better in pre-treated samples. BAŞLAR *et al*. (2014) reported increasing TP retention with increasing temperature. The TP retentions of pomegranate arils in their study were 78.61, 81.82 and 84.11% for 55, 65 and 75°C, respectively. BCHIR *et al*. (2012) reported that the phenolic content of the arils decreased to 40% (w.b.), and the anthocyanin content decreased to 25% (w.b.) for cabinet drying of pomegranates, which are much lower than our results.

Table 3. Effective Moisture Diffusivities and Activation Energies of Drying.

Experimental Samples	Temp (°C)	D_{eff} (m^2/s)	*Ea* (kJ/mol)	R^2
Untreated Cabinet	55	0.59×10^{-9}	76.11	0.9708
	65	1.71×10^{-9}		
	75	2.92×10^{-9}		
Pre-treated Cabinet	55	2.87×10^{-9}	31.82	0.9844
	65	3.77×10^{-9}		
	75	5.62×10^{-9}		

Table 4. Effect of Drying Temperatures and Pre-treatment Application on Half-Life ($t_{1/2}$), Drying Time and Total Phenolic (TP) – Total Anthocyanin (TA) Contents of Pomegranate Arils Dried in a Cabinet Dryer.

Pre-treated					Untreated				
Temperature (°C)	$t_{1/2}$ (min)	R^2	Drying Time (min)	C_t/C_0 at drying time	Temperature (°C)	$t_{1/2}$ (min)	R^2	Drying Time (min)	C_t/C_0 at drying time
Kinetic Results of TP degradation									
55	211	0.982	237	0.54	55	629	0.958	945	0.33
65	173	0.964	204	0.41	65	190	0.984	448	0.28
75	140	0.938	168	0.36	75	147	0.965	244	0.22
Kinetic results of TA degradation									
55	124	0.974	237	0.29	55	793	0.988	945	0.22
65	75	0.988	204	0.25	65	154	0.970	448	0.19
75	53	0.990	168	0.19	75	83	0.975	244	0.13

3.4. Thermal degradation kinetics of total phenolic compounds and anthocyanins

The time-dependent TP and TA degradation data were used to develop an Arrhenius model to predict the bioactive compounds' degradation during the drying. Table 5 shows that the model adequately fits the degradation kinetics ($0.9131 < R2 < 0.9754$). A higher *Ea* value implies the increasing temperature dependence of TP–TA degradation. Table 5 shows the *Ea*, half-life ($t_{1/2}$) and final TP–TA contents at the drying point. TA degradation was less sensitive to heat treatment under both these conditions compared to TP degradation. In addition, pre-treated samples have a higher degradation rate compared to untreated samples. However, the final TP and TA contents were higher in pre-treated samples despite the higher degradation rate they experienced (Table 4). The final concentrations of TP and TA in untreated samples were lower than pre-treated samples, even if *Ea* values were lower. So, it is important to evaluate drying kinetics and phytonutrient degradation kinetics in combination. Also, the necessity to control the time

to terminate the drying at a desired point is crucial. BAŞLAR *et al*. (2014) reported higher retention of TP and TA with increasing temperature, while on the other hand they demonstrated higher degradation rates of TP and TA at higher temperatures. They also concluded that the combination of time and temperature in the drying process is important.

Table 5. Activation Energy (E.) Values Obtained from Arrhenius Model for Total Phenolic (TP) and Total Anthocyanin (TA) Degradation.

Condition	Arrhenius model E_a (kJ mol^{-1})	R^2
TP degradation kinetic		
Pre-treated	32.53	0.9428
Untreated	72.65	0.9641
TA degradation kinetic		
Pre-treated	41.60	0.9131
Untreated	102.27	0.9754

3.5. Antioxidant capacities of dried pomegranate arils

The antioxidant capacities of the final products were significantly affected by pre-treatment application. Pre-treated arils had a higher antioxidant capacity than untreated arils (Fig. 2). The resulting higher antioxidant capacity of the pre-treated arils is linked to the shorter drying operation, which may protect the bioactive compounds. The temperature also had a significant effect on the antioxidant capacities of dried arils (Fig. 2).

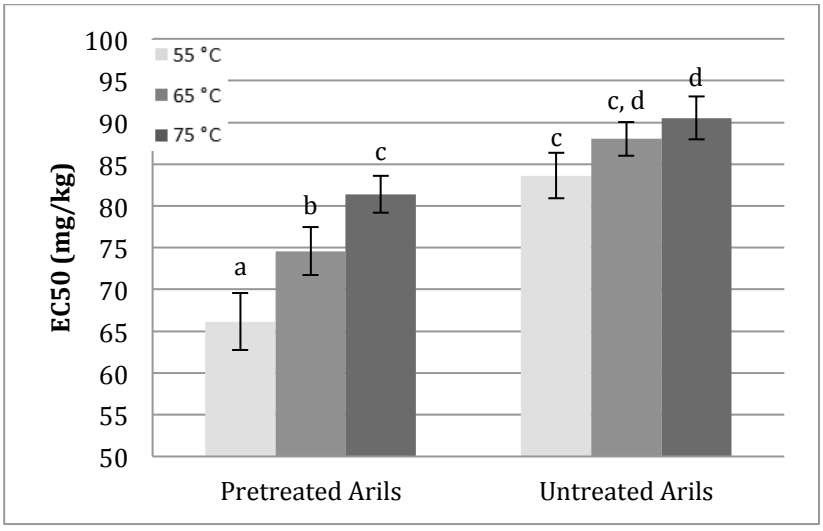

Figure 2. Antioxidant capacities of dried pomegranate arils depending on the drying conditions.

The highest antioxidant capacity value belonged to the pre-treated arils dried at 55°C. The antioxidant capacities were decreased as temperature increases, and this may result from degradation of heat sensitive bioactive compounds. The correlation between the antioxidant capacity and antioxidant compounds of the dried pomegranates were evaluated individually. The correlations among the data were determined using Pearson's correlation coefficient. The correlations between the TPC and antioxidant capacity (r = - 0.833) and TA and antioxidant capacity (r = - 0.774) were found to be statistically significant ($P < 0.01$).

3.6. Formation of HMF (hydroxymethylfurfural)

Several factors, such as dry matter content (or ˚Bx), aw, processing or storage temperature may affect the HMF formation in the dried fruits and concentrated juices (LAVELLI and VANTAGGI, 2009). The content of HMF in the dried pomegranate arils is depicted in Fig. 3. A higher HMF content was found in untreated samples in this study.. In addition, increasing temperature led to higher HMF content in the final product. HMF contents of the dried samples were between 5.22 and 16.34 mg/kg. The lowest HMF content was found in pre-treated samples dried at 55°C. The harsh effect of temperature increase on the HMF content of dried samples has been illustrated in other studies (ZANONİ *et al.*, 1999; PEKKE *et al.*, 2013; WOJDYŁO *et al.*, 2014).

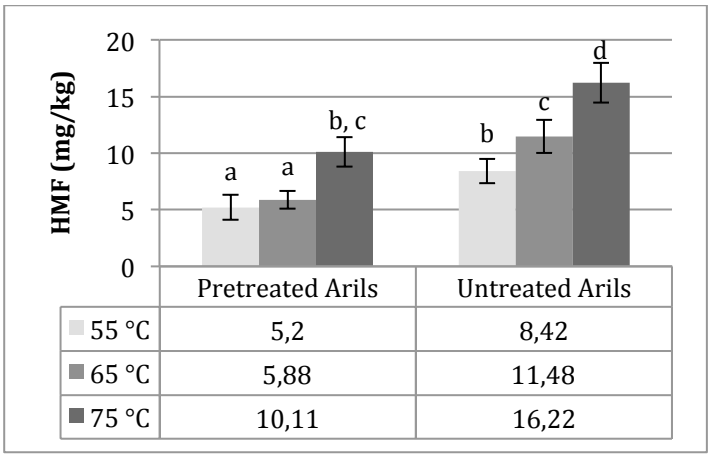

Figure 3. The effect of pre-treatment conditions and temperature on HMF formation.

3.7. Sensory analysis

The untreated and pre-treated samples had statistically significant differences in color, shape, texture and overall acceptability, while there were no statistically significant differences in flavor and aroma ($P < 0.05$). The pre-treated samples were more *acceptable–excellent* to the panelists across all sensory properties. Apart from color, the temperature had no statistically significant effect on the sensory properties of the dried samples. The average score for the overall acceptability of pre-treated samples was 8.76, and 5.34 for untreated samples.

4. CONCLUSIONS

The use of controlled drying conditions and pre-treatment applications may assist the production of better quality dried arils. Drying rates were considerably higher for pre-treated arils under all drying conditions. The drying process was completed in a shorter time for pre-treated samples, and thus, pre-treated arils had a higher phenolic and anthocyanin content in comparison to untreated samples, even if the thermal degradation rate of the bioactive compounds were higher in the pre-treated samples. Pre-treated samples had a higher antioxidant capacity and lower HMF content at all temperatures. This study is a good example that reflects the necessity of evaluating the kinetics of drying and the bioactive compounds' degradation together.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. M. Karaaslan (Harran University) for his valuable technical help and also would like to acknowledge all members of the Food Engineering Dept. (Harran University) for their helpful assistance.

NOMENCLATURE

M		Moisture content	g/g dry solid
M_0		Initial moisture content	g/g dry solid
M_e		Equilibrium moisture content	g/g dry solid
MR		Moisture ratio	dimensionless
t		Time	min
D_{eff}		Effective moisture diffusivity	m^2/s
RMSE		Root mean square error	
N		Number of observations	
n		constant, positive integer	
r		radius	m
$MR_{exp,}$	i^{th}	moisture ratio value experimentally determined	
$MR_{pre,}$	i^{th}	predicted moisture ratio value	
R		Gas constant	8.314 $J.mol^{-1}.K^{-1}$
R^2		Determination of coefficient	
E_a		Activation energy	$kJ.mol^{-1}$
C		Concentration of total phenolic compound or anthocyanin	mg/kg d.b.
C_t		Concentration of total phenolic compound or anthocyanin at time t	mg/kg d.b.
C_0		Initial concentration of total phenolic compound or anthocyanin	mg/kg d.b.
d.b.		Dry basis	
w.b.		Wet basis	
rpm		revolution per minute	

REFERENCES

Acar J., Alper N. and Evren V. 1999. Meyve ve Sebze Teknolojisi Kalite Kontrol Laboratuvar Kılavuzu, Hacettepe University Press, Ankara, p. 165.

Acosta-Estrada B.A., Gutierrez-Uribe J.A. and Serna-Saldivar S.O. 2014. Bound phenolics in foods- a review. Food Chem. 152:46.

Adedeji A.A., Gachovska T.K., Ngadi M.O. and Raghavan G.S.V. 2008.Effect of pre-treatments on drying characteristics of okra. Drying Technol. 26:1251.

Akdaş S. and Başlar M. 2015. Dehydration and degradation kinetics of bioactive compounds for mandarin slices under vacuum and oven drying conditions. J. Food. Process. Pres. 39:1098.

Babalis S.J. and Belessiotis V.G. 2004. Influence of the drying conditions on the drying constants and moisture difffusivity during the thin-layer drying of figs. J. Food. Eng. 65:449.

Başlar M., Karasu S., Kiliçli M., Us A.A. and Sagdıc O. 2014. Degradation kinetics of bioactive compounds and antioxidant activity of pomegranate arils during the drying process. Int. J. Food. Eng. 10**:**839.

Bchir B., Besbes S., Karoui R., Attia H., Paquot M. and Blecker C. 2012. Effect of air-drying conditions on physic-chemical properties of osmotically pre-treated pomegranate seeds. Food Bioprocess Tech. 5:1840.

Bondia-Pons I., Aura A.M., Vuorela S., Kolehmainen M., Mykkanen H. and Poutanen K. 2009. Rye phenolics in nutrition and health. J. Cereal Sci. 49:323.

Chaethong K.and Pongsawatmanit R. 2015. Influence of sodium metabisulfite and citric acid in soaking process after blanchıng on qualıty and storage stability of dried chili. J. Food. Process. Pres. 39:2161.

Chong C.H., Law C.L., Cloke M., Abdullah L.C. and Wan Daud W.R. 2009.Drying models and quality analysis of sun-dried Ciku. Drying Technol. 27:985.

Crank J. 1975. The Mathematics of diffusion, Oxford University Press, London, p.182.

Doymaz İ. 2012. Prediction of drying characteristics of pomegranate arils. Food Anal. Method. 5:841.

Fazaeli M., Yousefi S. and Emam-Djomeh Z. 2013. Investigation on the effects of microwave and conventional heating methods on the phytochemicals of pomegranate (*Punica granatum* L.) and black mulberry juices. Food. Res. Int. 50:568.

Giusti M. and Wrolstad R.E. 2001. Characterization and measurement of anthocyanins by UV visible spectroscopy. Wiley, New York.

Gould W.A. 1977. Food Quality Assurance, The AVI Publisher, West-port-CT, p. 93.

Henderson S.M. 1974. Progress in developing the thin layer drying equation, Trans. ASAE., 17:1167.

Henderson S.M. and Pabis S. 1961.Grain drying theory. I. Temperature effect on drying coefficient. J. Agr. Eng. Res. 6:169.

Hii C.L., Law C.L. and Cloke W. 2009. Modeling using a new thin layer drying model and product quality of cocoa. J. Food. Eng. 90:191.

Kamiloglu S., Pasli A.A., Ozcelik B. and Capanoglu E. 2014 Evaluating the in vitro bioaccessibility of phenolics and antioxidant activity during consumption of dried fruits with nuts. Food. Sci. Technol. 56:284.

Karaaslan M., Vardin H., Varlikliöz S. and Yılmaz F.M. 2014a. Antiproliferative and antioxidant activities of turkish pomegranate (*punica granatum* l.) accessions. Int. J. Food. Sci. Technol. 49:82.

Karaaslan M., Yilmaz F.M., Cesur Ö., Vardin H., Ikinci A. and Dalgiç A.C. 2014b. Drying kinetics and thermal degradation of phenolic compounds and anthocyanins in pomegranate arils dried under vacuum conditions. Int. J. Food. Sci. Technol. 49:595.

Lavelli V. And Vantaggi C. 2009. Rate of antioxidant degradation and color variations in dehydrated apples as related to water activity. J. Agric. Food Chem. 57(11):4733.

Mena P., Vegara S., Marti N., Garcia-Viguera C., Saura D. and Valero M. 2013. Changes on indigenous microbiota, colour, bioactive compounds and antioxidant activity of pasteurised pomegranate juice. Food Chem. 141:2122.

Minaei S., Motevali A., Najafi G. and Seyed S.R.M. 2011. Influence of drying methods on activation energy, effective moisture diffusion and drying rate of promegranate arils (*Punica Granatum*). Aust. J. Crop. Sci. 6:584.

Mousa N.a nd Farid M. 2002. Microwave vacuum drying of banana slices, Drying Technol., 20:55.

Overhults D.D., White G.M., Hamilton M.E. and Ross I.J. 1973. Drying soybeans with heated air. Trans. ASAE. 16:195.

Page G.E. 1949. MSc. Thesis, Factors influencing the maximum rates of air drying shelled corn in thin layers, Purdue University.

Pekke M.A., Pan Z., Atungulu G.G. and Smith G. 2013. Drying characteristics and quality of bananas under infrared radiation heating. Int. J. Agric. Biol. Eng. 6:58.

Shahbaz H.M., Ahn J.J., Akram K., Kim H.Y., Park E.J. and Kwon J.H. 2014. Chemical and sensory quality of fresh pomegranate fruits exposed to gamma radiation as quarantine treatment. Food Chem. 145:312.

Sharma G. and Prasad S. 2004. Effective moisture diffusivity of garlic cloves undergoing microwave-convective drying, J. Food. Eng., 65:609.

Singleton V.L. and Rossi J.A. 1965. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. Am. J. Enol. Vitic. 16:144.

Siro I., Kapolna E., Kapolna B. and Lugasi A. 2008. Functional food. Product development, marketing and consumer acceptance - a review. Appetite 51:456.

Sturm B., Hofacker W.C. and Hensel O. 2012. Optimizing the drying parameters for hot-air-dried apples. Drying Technol. 30**:**1570.

Wang C.Y. and Singh R.P. 1978. Use of variable equilibrium moisture content in modeling rice drying. Trans. ASAE, 78:6505.

Wojdyło A., Figiel A., Lech K., Nowicka P. and Oszmiański J. 2014. Effect of convective and vacuum-microwave drying on the bioactive compounds, color, and antioxidant capacity of sour cherries. Food Bioprocess Tech. 7:829.

Verbeyst L., Oey I., Plancken L.V., Hendrickx M. and Loey A.V. 2010. Kinetic study on the thermal and pressure degradation of anthocyanins in strawberries. Food Chem. 123:269.

Viuda-Martos M., Ruiz-Navajas Y., Martin-Sanchez A., Sanchez-Zapata E., Fernandez-Lopez J., Sendra E., Sayas-Barbera E., Navarro C.and Perez-Alvarez J.A. 2012. Chemical, physico-chemical and functional properties of pomegranate (*Punica granatum* L.) bagasses powder co-product. J. Food Eng. 110:220.

Yagcioglu A., Degirmencioglu A. and Cagatay F. 1999. Drying characteristics of laurel leaves under different drying conditions, In Proceedings of the 7th International Congress on Agricultural Mech. and Energy, Adana, Turkey, 565.

Zanoni B., Peri C., Nani R. and Lavelli V. 1999. Oxidative heat damage of tomato halves as affected by drying. Food. Res. Int. 31:395.

Zulueta A., Esteve M.J., Frasquet I. and Frigola A. 2007. Vitamin C, vitamin A, phenolic compounds and total antioxidant capacity of new fruit juice and skim milk mixture beverages marketed in Spain. Food Chem. 103:1365.

Paper Received June 24, 2017 Accepted September 27, 2017