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Araştırma / Research

CONVECTIVE DRYING OF CORNELIAN CHERRY FRUITS (*Cornus mas.*L): DRYING KINETICS AND DEGRADATION OF VITAMIN C

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ABSTRACT

The influence of drying air temperature and velocity on the drying kinetics and vitamin C degradation of cornelian cherry fruit (*Cornus mas.*L) was investigated using a hot-air convective dryer. Experiments were carried out at 50, 60, 70ºC air temperature and 0.4, 0.7 and 1,0 m/s air velocity. Shorter drying times were achieved with increasing air temperature and velocity. Twelve thin-layer drying models were used to determine the thin layer drying kinetics of cornelian cherry. The best appropriate model was found as the modified Henderson and Pabis model. The vitamin C degradation of cornelian cherry fruit was determined in the range of 42-54%.

Keywords: Cornelian cherry, drying kinetics, modeling, vitamin C

KIZILCIK MEYVESİNİN (*Cornus mas.* L) KONVEKTİF KURUTULMASI: KURUMA KİNETİĞİ VE C VİTAMİNİ BOZULMASI

ÖZ

Kızılcık meyvesinin (*Cornus mas* L.) kuruma kinetiği ve C vitamin bozulması üzerine hava sıcaklığı ve hava hızının etkileri bir sıcak hava-konvektif kurutucu kullanılarak incelendi. Deneyler 50, 60, 70ºC hava sıcaklığı ve 0,4, 0,7 ve 1,0 m/s hava hızlarında gerçekleştirildi. Artan hava sıcaklığı ve hava hızında daha kısa kuruma süreleri elde edildi. Kızılcığın kuruma kinetiğini belirlemek için on iki ince tabaka kuruma modeli kullanıldı. Modifiye Henderson ve Pabis modeli en uygun model olarak bulundu. Kızılcığın C vitamin bozulması %42-54 aralığında belirlendi.

Anahtar Kelimeler: Kızılcık, kurutma kinetiği, modelleme, vitamin C

1. INTRODUCTION

Cornus mas L. commonly known as cornelian cherry belongs to *Cornaceae* family and it naturally grows in Southern Europe, Armenia, Azerbaijan, Iran, and Turkey. Cornelian cherry fruit contains antioxidant, flavonoid, melatonin and vitamin C [1]. Cornelian cherry fruits have been used for cosmetic purposes and herbal medicine in Europe and China, respectively [2]. In Turkey, cornelian cherry fruits are consumed fresh or as tarhana (a traditional cereal food), marmalade, jam, soup and compote, cornelian cherry's fruits and leaves are used also against diabetes and diarrhea in Turkish folk medicine [3].

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Drying, in general terms, is a unit operation that water is removed from the material by giving heat energy to the wet material. During the drying process, simultaneous mass and heat transfers take place in unsteady state. Vegetables and fruits are seasonal products and it is difficult to preserve them fresh for a long time due to high water content that causes microbial spoilage. Dried materials, however, have the longer storage periods, therefore, consumer and process industries can provide them all year around. Drying method and conditions affect drying kinetics and quality characteristics of the dried products. Although different and new drying methods such as vacuum, microwave, infrared, freeze drying and combined techniques have become popular in recent years, hot air drying is the most favorite method for industrial usage. [4]. Thin- layer models are widely used to describe drying characteristics of the dried material to control the process and to determine the optimum process conditions for the equipment design [5]. There have been many studies about drying behavior of fruits and vegetables in convective drying in literature. Some of these studies are hawthorn [5], fig [6], peach slices [7], sweet cherry [8], potato slices [9], kale [10], berberis fruit [11], passion fruit [12] and garlic [13]. Although there have been studies on drying of cornelian cherry in literature [2, 14], no data on drying kinetics and modeling of cornelian cherry fruit have been reported yet.

The main objectives of this research were to investigate convective drying behavior of cornelian cherry, to predict the best mathematical model for drying curves, and to investigate the effect of drying air conditions on the degradation of vitamin C in cornelian cherry.

2. MATERIAL AND METHODS

2.1. Equipment

The convective drying experiments of cornelian cherry fruits were carried out in a laboratory drier. The dimensions of the rectangular tunnel were 0.30x0.28x2.50 m and it included an electrical heater controlling the temperature of drying air and an adjustable centrifugal fan. A photograph of the experimental setup is shown in Figure 1.

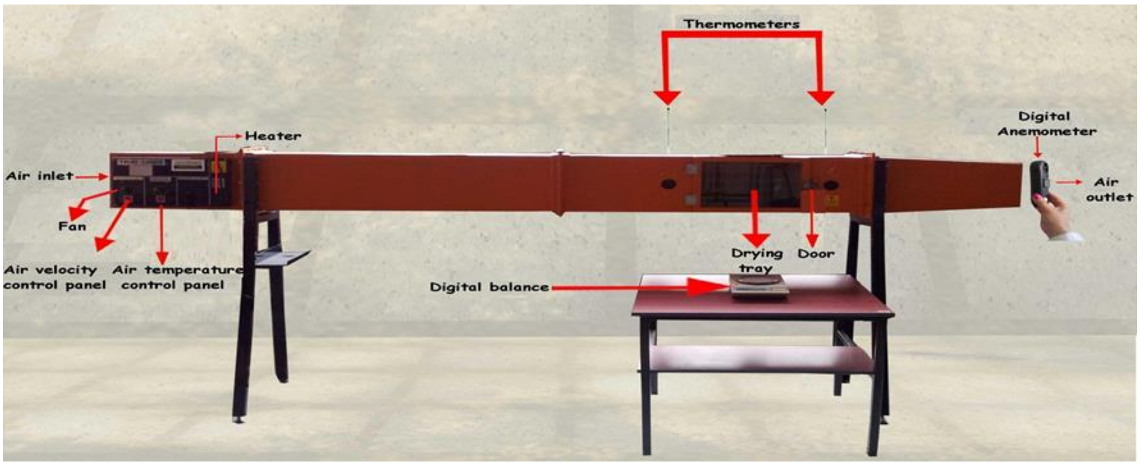

Figure 1. The convective drying system

Convective drying experiments were performed at 50, 60 and 70ºC air temperature and 0.4, 0.7 and 1,0 m/s air velocity that these values were in the range commonly used for fruit and vegetable drying [15]. The ambient air was used as drying air whose temperature and relative humidity were about 21±2ºC and 0.005± 0.001 (g H_2O/ g dry air), respectively. The air velocity was measured using an anemometer (HALT- 08) with a precision of ±0.05 m/s. The dryer was adjusted to the selected air temperature and velocity and run without loaded to achieve a steady state condition for one hour.

2.2. Raw Material

Fresh cornelian cherry fruits were obtained from the Coruh Valley, Erzurum, Turkey, in September, 2011. The oven method was used to determine initial moisture content of fresh cornelian cherry [16]. About 50 g of fresh cornelian cherry with five replicates were dried in an oven at 105ºC for 24 hours and the value of initial moisture was determined as about 75.4% (w.b.). Diameter of cornelian cherry was evaluated with a digital caliper (Powerfix) and its average value was found as 11.94±0.3 mm. Cornelian cherry fruits (about 100 g) were packed in plastics bag and stored in a refrigerator at 4ºC until used.

2.3. Drying experiments

For each experiment, about 100 g of fruits was spread as a thin layer on the stainless steel mesh tray (15x24 cm) and the tray was placed in the dryer. During the drying processes, amount of water removed was periodically recorded at an hour using a digital balance (AND Electronic Balance FX 3000, Japan) accuracy of ±0.01. Experiments were completed when fruits reached constant weight. Three replications of each experiment were performed and mean values were used.

2.4. Mathematical Modelling of Drying Curves

The dimensionless moisture ratio (MR) is calculated using following equation for drying samples at any time:

$$MR = \frac{M_t - M_e}{M_o - M_e} \qquad (1)$$

where M_o, M_e and M_t reflect initial moisture content (g H_2O·g dry solids^{-1}), equilibrium moisture content (g H_2O·g dry solids^{-1}) and moisture content at any time (g H_2O·g dry solids^{-1}) respectively. As shown in Table 1, the experimental data obtained were applied to twelve thin-layer drying models which were widely used for food and biological materials. The correlation coefficient (R^2), the reduced chi-square (X^2) and the root mean square error (*RMSE*) were used to determine the ability of each model to the experimental data. The highest value of R^2 and the lowest values of X^2 and *RMSE* indicate the most appropriate of fit. Statistica 7.0 was used for regression analysis.

$$\chi^2 = \frac{\sum_{i=1}^{N}\left(MR_{\exp,i} - MR_{\text{pre},i}\right)^2}{N - z} \qquad (2)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}\left(MR_{\exp,i} - MR_{\text{pre},i}\right)^2}{N}} \qquad (3)$$

where $MR_{exp,i}$ is the *i*th experimentally observed moisture ratio,, $MR_{pre,,i}$ is the *i*th predicted moisture ratio, the *z* is number of constants in the model and *N* is the number of data values. The drying rate (*R*) represents the variation of moisture ratio (*MR*) by time and Eq. (4) can be used to calculate drying rate.

$$R = \frac{dM_t}{dt} = \frac{M_{t+\Delta t} - M_t}{\Delta t} \qquad (4)$$

where $M_{t+\Delta t}$ is the moisture content at $t+\Delta t$ (g H_2O. g dry solids^{-1}), M_t is the moisture content at t (g H_2O. g dry solids^{-1}) and t is the drying time (min).

2.5. Determination of Vitamin C

The vitamin C content was determined by the methods described by Jagato and Danie [17] with some modification. Five grams of fresh and dried cornelian cherry samples blended were extracted with 100 mL of distilled water and then filtered and centrifuged at 3000 rpm. 2 mL of supernatant was diluted with distilled water to 5 mL and then was transferred into a polypropylene centrifuge tube. 2 mL of 10% trichloroacetic acid was added in this solution and tube was placed for 5 minutes in an ice bath and then 2 mL of Folin-Ciocalteu reagent was added onto the mixture. The mixture was homogenized and kept at dark for 10 min. The absorbance of the resulting solution was assayed at 750 nm by using a UV spectrophotometer (Shimadzu, UV-160A). Results were expressed as milligrams of vitamin C per 100 g dry matter (mg vitamin C/100 g d.m.).

3. RESULTS AND DISCUSSION

3.1. Drying Curves of Cornelian Cherry

Figure 2 shows the variation of moisture ratio with drying time of cornelian cherry fruit during the convective drying. Drying time varied between 18 and 71 hours depending on the drying conditions in the range of studies. The times required to reach the equilibrium moisture content were determined to be 4260, 3600, 3180 min at air velocities of 0.4, 0.7 and 1,0 m/s, respectively, for air temperature of 50ºC; 2760, 2400, 2040 min at air velocities of 0.4, 0.7 and 1,0 m/s, respectively, for air temperature of 60ºC; and 1500, 1260, 1080 min at air velocities of 0.4, 0.7 and 1,0 m/s, respectively, for air temperature of 70ºC.

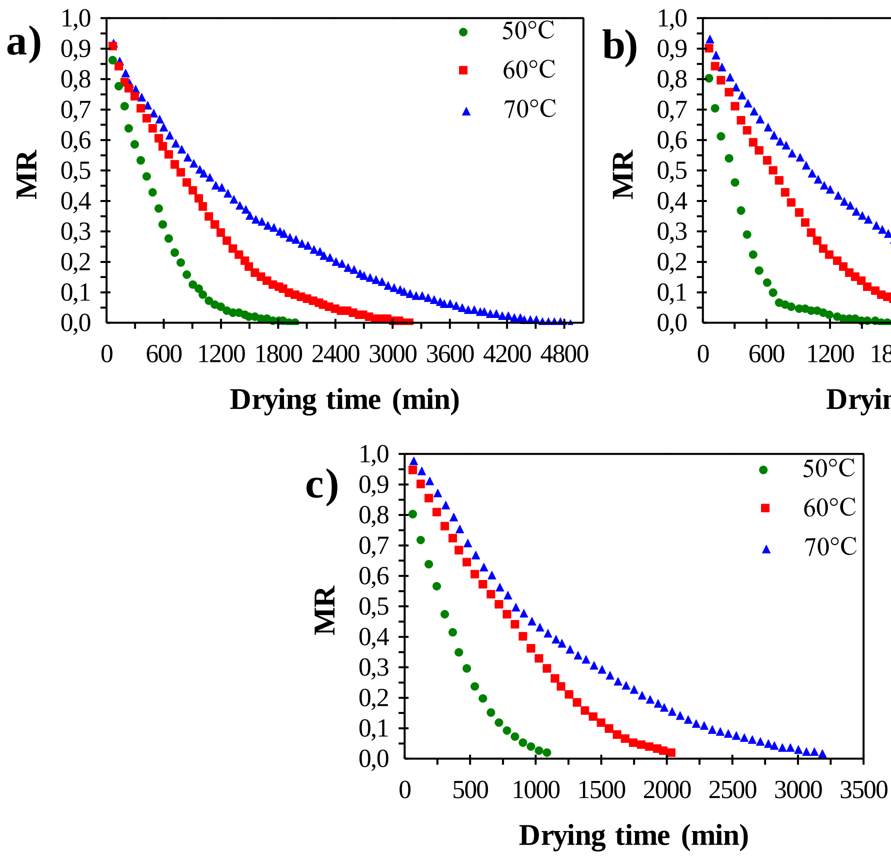

Figure 2. Drying curves of cornelian cherry (a. 0.4 m/s, b. 0.7 m/s, c. 1,0 m/s)

As shown from these results, increasing drying air temperature decreased drying time. This decrease in drying time with increased drying air temperature can be explained that higher temperature causes faster moisture evaporation which increases vapor pressure in the fruit and increased vapor pressure leads to quick migration of moisture from fruit. Similar observations were obtained for hawthorn, peach slices and sweet cherry [5, 7, 8].

Figure 3 shows the variation of moisture ratio with drying time for different air velocities at 50, 60 and 70ºC air temperature, respectively. While the longest drying times were obtained at 0.4 m/s air velocity, the shortest drying times were observed at 1.0 m/s air velocity for all temperatures. When air velocity increased from 0.4 to 1.0 m/s, the time decreased about 1070, 720 and 420 min for 50, 60 and 70ºC air temperature, respectively. The moisture evaporating from fruit creates a boundary layer containing saturated vapor around the fruit which is an external resistance for heat and mass transfer. The boundary layer around the fruit becomes thinner due to the increasing air velocity, therefore, the quality of the heat energy transferred to the fruit from the air increases and drying time reduces. These results are consistent with the observation of hawthorn [5], fig [6] and carrot pomace [18].

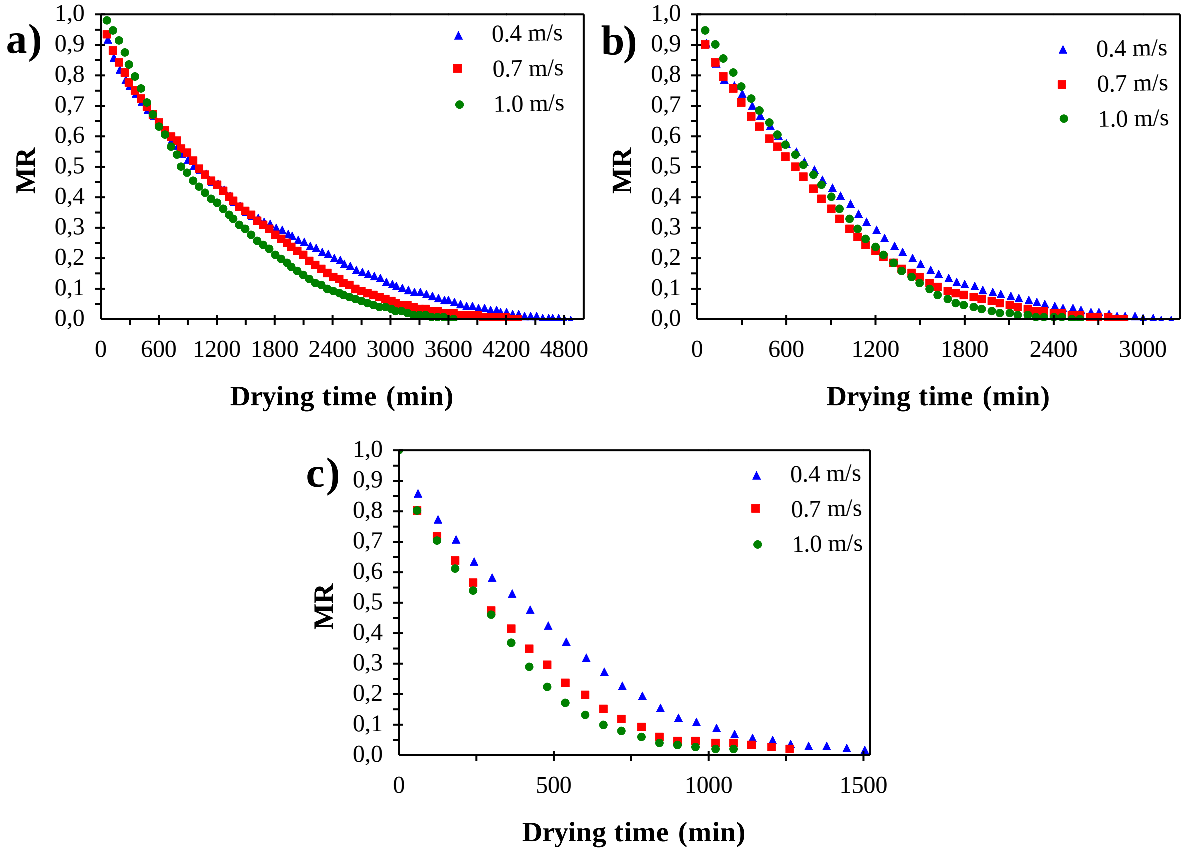

Figure 3. Drying curves of cornelian cherry at different air velocity (a. 50ºC, b. 60ºC, c. 70ºC)

The change of drying rate as a function of drying time is shown in Figure. 4. Drying rate curve is used to describe the dominant mechanism of a product during the drying. Drying mechanisms for fruits and vegetables can be by the surface diffusion, liquid/vapor diffusion and capillary action within the porous region of foods. Moisture movement in the dried material can be controlled by internal or external resistances. Vegetables and fruits have high moisture content and there is an overall constant rate period at the initial stages of drying. As it has been widely reported dominant mechanism of moisture removal from the foodstuff is diffusion, generally constant rate period is ignored in during the drying processes [19].

As shown in Figure 4, drying rate decreased continuously with drying time. This behavior shows that constant rate period was not present and drying process occurs in falling rate period for all the drying conditions. The falling rate period represents that the mass transfer mechanism in the material is controlled by molecular diffusion. It has been reported that the drying behavior of fruit and vegetables generally occurs in the falling rate period [4-12].

3.2. Mathematical Modelling of Drying Curves

The thin layer modeling approach is an essential tool in estimating the drying kinetics from the experimental data for equipment design, optimization and product quality improvements. The selection of the most suitable thin-layer drying model is also a very important in describing the drying behavior of fruits and vegetables. So to analyze the drying behavior of fruit and vegetables it is important to study the kinetics of model of each particular product [15].

The data obtained from the experiments were applied to twelve thin-layer models in Table 1. The statistical results of models calculated using non-linear regression analysis are shown in Table 2.

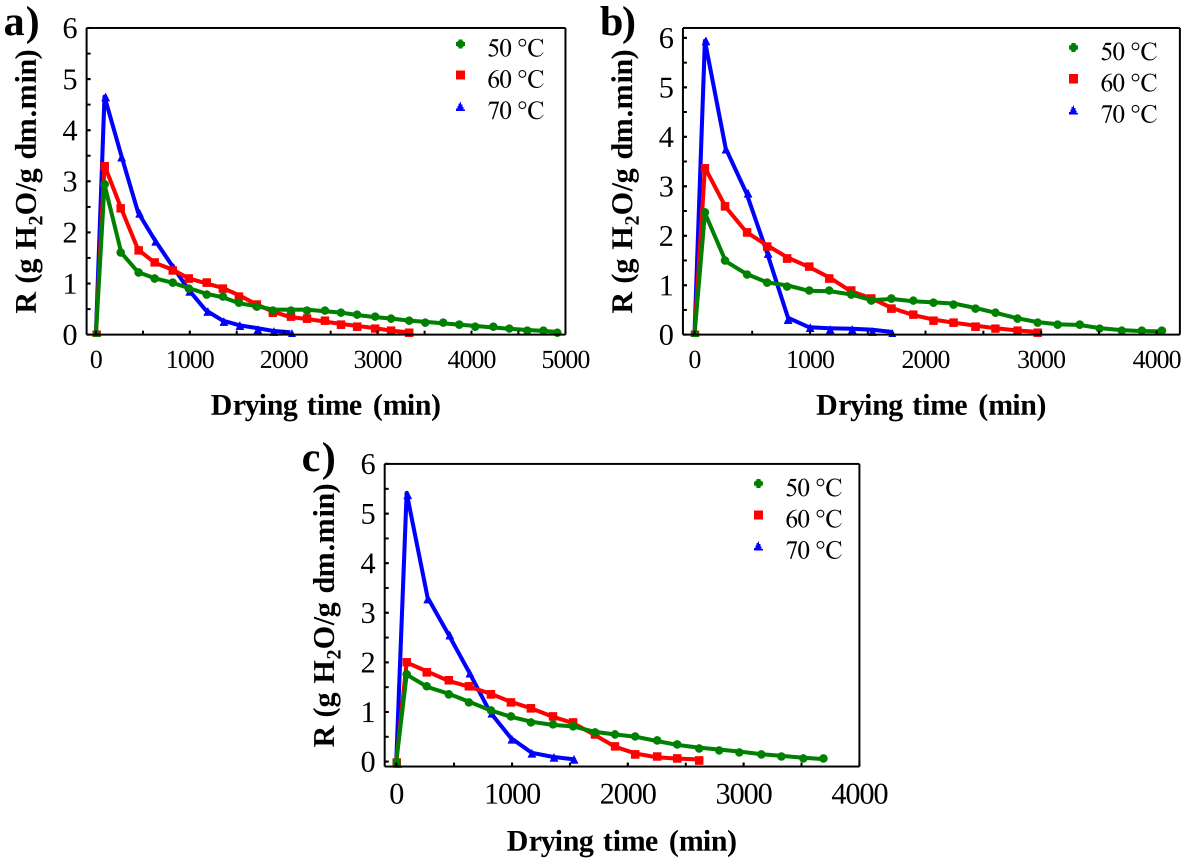

Figure 4. Drying rates of cornelian cherry (a. 0.4 m/s, b. 0.7 m/s, c. 1.0 m/s)

Table 1. Thin-layer models applied to drying curves of cornelian cherry [5]

Name of Model	Model Equation
Henderson & Pabis	MR= a exp(-kt)
Newton	MR= exp(-kt)
Page	MR= exp(-kt^n)
Wang & Singh	MR= 1+at+bt^2
Logarithmic	MR= a exp(-kt)+c
Midilli *et al.*	MR= a exp(-kt^n)+bt
Logistic	MR= b/(1+a exp(kt))
Two-term	MR= a exp(-k$_0$t)+b exp(-k$_1$t)
Verma *et al.*	MR= a exp(-kt)+(1-a)exp(-gt)
Diffusion Approach	MR= a exp(-kt)+(1-a)exp(-kbt)
Two-term Exponential	MR= a exp(-kt)+(1-a)exp(-kat)
Modified Henderson & Pabis	MR= a exp(-kt)+b exp(-gt)+c exp(-ht)

As shown in Table 2, with the highest values of R^2 and the lowest values of χ^2 and RMSE, the modified Henderson and Pabis model was found to be the most appropriate models for explaining the thin layer drying characteristic of cornelian cherry. The modified Henderson and Pabis model is a semitheoretical and complex thin layer model which it is derived from the solution of Fick's second law. This model has got three terms and six model constants. The model's first term explains the last part of the drying process of food stuff, which occurs largely in the falling rate periods, second term describes the midway part, and the third term explains the initial moisture loss of the drying process. This model has been found to successfully describe the drying kinetics of olive leave, apple slices and pumpkin [20-22].

Table 2. Statistical results of applied mathematical models

Models	Drying air velocity (m/s)	Drying air temperature								
		50°C			60°C			70°C		
		R^2	χ^2	RMSE	R^2	χ^2	RMSE	R^2	χ^2	RMSE
Henderson & Pabis	0.4	0.996	0.0000	0.0052	0.993	0.0010	0.0326	0.995	0.0008	0.0284
	0.7	0.993	0.0011	0.0333	0.994	0.0008	0.0292	0.996	0.0005	0.0239
	1.0	0.995	0.0007	0.0271	0.986	0.0026	0.0512	0.995	0.0007	0.0277
Newton	0.4	0.996	0.0000	0.00331	0.993	0.0011	0.0332	0.994	0.0008	0.0289
	0.7	0.992	0.0011	0.03336	0.994	0.0009	0.0299	0.996	0.0005	0.0238
	1.0	0.992	0.0012	0.03594	0.982	0.0034	0.0584	0.995	0.0007	0.0272
Page	0.4	0.996	0.0000	0.00346	0.996	0.0005	0.0243	0.997	0.0004	0.0202
	0.7	0.995	0.0007	0.02754	0.997	0.0004	0.0202	0.997	0.0003	0.0198
	1.0	0.998	0.0002	0.01451	0.997	0.0005	0.0238	0.996	0.0005	0.0230
Wang & Singh	0.4	0.981	0.0000	0.0081	0.994	0.0008	0.0299	0.988	0.0019	0.0443
	0.7	0.994	0.0008	0.0297	0.993	0.0010	0.0316	0.949	0.0075	0.0867
	1.0	0.997	0.0004	0.0217	0.994	0.0009	0.0305	0.987	0.0022	0.0472
Logarithmic	0.4	0.999	0.0000	0.0072	0.997	0.0003	0.0193	0.978	0.0037	0.0609
	0.7	0.993	0.0011	0.0343	0.998	0.0002	0.0170	0.996	0.0005	0.0233
	1.0	0.999	0.0001	0.0107	0.995	0.0008	0.0290	0.998	0.0003	0.0188
Midilli *et.al.*	0.4	0.942	0.0014	0.0380	0.997	0.0004	0.0202	0.890	0.0185	0.1363
	0.7	0.944	0.0087	0.0937	0.998	0.0001	0.0135	0.997	0.0003	0.0191
	1.0	0.938	0.0110	0.1052	0.997	0.0004	0.0222	0.998	0.0003	0.0185
Logistic	0.4	0.997	0.0000	0.00853	0.936	0.0102	0.1011	0.995	0.0007	0.0276
	0.7	0.997	0.0003	0.01918	0.938	0.0101	0.1005	0.996	0.0006	0.0257
	1.0	0.942	0.0102	0.10123	0.986	0.0028	0.0537	0.995	0.0009	0.0302
Two-term	0.4	0.996	0.0000	0.00527	0.994	0.0008	0.0293	0.998	0.0002	0.0171
	0.7	0.993	0.0011	0.03379	0.998	0.0002	0.0151	0.996	0.0006	0.0247
	1.0	0.995	0.0007	0.02758	0.986	0.0027	0.0524	0.995	0.0008	0.0287
Verma *et al.*	0.4	0.997	0.0000	0.0015	0.997	0.0003	0.0184	0.997	0.0003	0.0187
	0.7	0.998	0.0002	0.0168	0.998	0.0002	0.0151	0.997	0.0004	0.0215
	1.0	0.998	0.0002	0.0143	0.995	0.0008	0.0289	0.998	0.0003	0.0174
Diffusion Approach	0.4	0.996	0.0000	0.0009	0.997	0.0004	0.0222	0.995	0.0007	0.0276
	0.7	0.993	0.0011	0.0335	0.997	0.0003	0.0191	0.996	0.0004	0.0220
	1.0	0.998	0.0002	0.0153	0.996	0.0007	0.0273	0.998	0.0003	0.0180
Two-term Exponential	0.4	0.996	0.0000	0.0033	0.993	0.0011	0.0333	0.997	0.0003	0.0194
	0.7	0.992	0.0011	0.0336	0.997	0.0003	0.0193	0.997	0.0003	0.0188
	1.0	0.992	0.0013	0.0364	0.995	0.0008	0.0299	0.995	0.0007	0.0278
Modified Henderson & Pabis	**0.4**	**0.999**	**0.0000**	**0.0064**	**0.998**	**0.0003**	**0.0164**	**0.998**	**0.0002**	**0.0142**
	0.7	**0.998**	**0.0002**	**0.0151**	**0.999**	**0.0001**	**0.0119**	**0.998**	**0.0002**	**0.0169**
	1.0	**0.999**	**0.0000**	**0.0081**	**0.998**	**0.0002**	**0.0164**	**0.998**	**0.0003**	**0.0173**

3.6. Values of Vitamin C of Cornelian Cherry

Since the vitamin C is sensitive to light, heat, oxygen and pH, the processing and storage conditions significant affect degradation of vitamin C. Ascorbic acid is often used as an indicator compound of nutrient quality as it is more unstable than other nutrients in fruit and vegetable [23]. Figure 5 shows the vitamin C content of fresh and dried cornelian cherry in different drying conditions. Degradation of vitamin C varied between 42% and 54% depending on the drying conditions in the range of studies for the convective drying. As shown in Figure 4, increasing air temperature caused higher degradation of vitamin C in cornelian cherry. While the values of vitamin C retention varied from 54.3% to 57.8% at 50ºC air temperature, these values varied from 45.2% to 50.9% at 70ºC.

Similar results were reported for tomatoes [24], kiwifruit [25] and mango [26]. The vitamin C degradation decreased with increasing air velocity (Figure 5). This behavior can be explained with the drying curves in Figure 3. As shown in Figure 3, the increasing air velocity reduced drying time and the shorter exposed time for fruit with hot air caused the lower degradation of vitamin C. The same behavior was observed for drying of papaya [27].

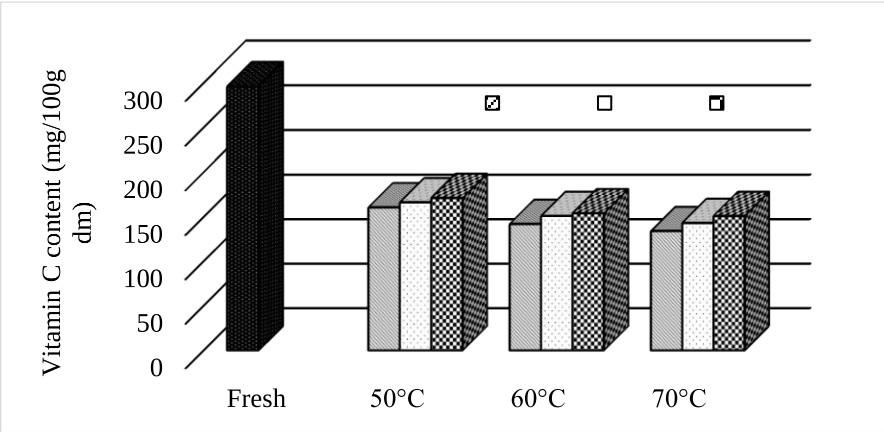

Figure 5. Vitamin C content of fresh and dried cornelian cherry at different drying conditions

4. CONCLUSIONS

Drying behavior of cornelian cherry fruit was investigated using a hot-air convective drier between drying air temperatures of 50 and 70°C and velocities of 0.4 and 1.0 m/s.

- The higher air temperature and velocity occurred the lower drying time.
- The drying process took place in a falling rate periods.
- Modified Henderson and Pabis model was found to be the best model for describing the thin layer drying characteristic of cornelian cherry among applied twelve models.
- The least degradation of vitamin C occurred at 50°C of air temperature and 1.0 m/s air velocity. Increased temperature and decreased air velocity increased degradation of vitamin C in cornelian cherry.

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