Sun Drying of Cornelian Cherry Fruits (*Cornus mas* L.) Bilgehan POLATOĞLU¹, Ayşe Vildan BEŞE^{2*}

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ABSTRACT

In this study, the sun drying behavior of cornelian cherry fruits was investigated. The drying rate curve of cornelian cherry was shown that the drying process took place in the falling rate period. Twelve thinlayer mathematical models were used for explaining the thin layer drying kinetics of cornelian cherry. The approximation of diffusion model was found to be the most appropriate model for the process. The Fick's diffusion model was used to calculate the effective moisture diffusion coefficients (D_{eff}) of cornelian cherry. The value of D_{eff} was obtained as 1.20x10⁻¹¹ m²/s. The vitamin C degradation of dried cornelian cherry was determined as about 51.1%.

Keywords: Cornelian cherry, Drying kinetics, Modeling, Effective diffusivity, Vitamin C

Kızılcık Meyvesinin (Cornus mas L.) Güneşte Kurutulması

ÖZ

Bu çalışmada, kızılcık meyvesinin güneşte kuruma davranışı incelenmiştir. Kızılcığın kuruma hız eğrisi, kuruma işleminin azalan hız periyodunda gerçekleştiğini göstermiştir. Kızılcığın ince tabaka kuruma davranışını açıklamak için on iki ince tabaka matematik modeli kullanılmıştır. Difüzyon yaklaşım modelinin işlem için en uygun model olduğu belirlenmiştir. Kızılcığın etkin nem difüzyon katsayısını (D_{eff}) hesaplamak için Fick'in difüzyon modeli kullanılmıştır. D_{eff} 'in değeri 1.20x10⁻¹¹ m²/s olarak hesaplanmıştır. Kurutulan kızılcığın C vitamin bozulması yaklaşık % 51.1 olarak belirlenmiştir. **Anahtar kelimeler:** Kızılcık, Kuruma kinetiği, Modelleme, Etkin yayılma, C vitamini

1. Introduction

Cornus mas L. commonly known as cornelian cherry naturally grows in Southern Europe and southwest Asia. Cornelian cherry fruits have been used for food, cosmetic purposes and herbal medicine in Asia, Europe and China (Dinda et al., 2016). Cornelian cherry fruit contains antioxidant, flavonoid, melatonin and vitamin C. It has been reported that cornelian cherry juice is richer in various essential elements as Ca, Mn, Na, Zn, K and Fe than obtained juices from the plum, apple and pear (Cindrić et al., 2012).

Drying is a unit operation that the water is removed from the material by giving heat energy to the moisture material. The water inside the fruit is transferred to the surface through diffusion and is removed from the surface with evaporation. The 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. The dried materials, however, have longer storage periods, therefore consumer and process industries can provide them all year round. Sun drying is one of the oldest methods used to preserve human's food as grain, fish, fruits, vegetables etc. Despite many disadvantages such as length of drying time, weather uncertainties, insect infestation and contamination of the product with dust, sun drying is still practiced in many places throughout the world as a traditional method (Sahdev, 2014). The thin- layer models are widely used to describe drying characteristics of the dried material to control the process, to determine the optimum process conditions for the equipment design and to minimize the total energy requirements. The thin- layer models can be classified into three groups as theoretical, semitheoretical and empirical. As the theoretical models have too many assumptions which lead to significant errors, their use is limited in equipment design. The semitheoretical models, derived from Fick's second law, are easier and they have fewer assumptions, so they are widely used. Although the empirical models are similar to the semitheoretical models, they provide limited information about drying characteristic of dried material strongly depend on experimental data (Kucuk et al., 2014).

Many studies have been reported the sun drying behavior of some fruits and vegetables such as corn kernels (Sahdev and Kumar, 2013), apricot (Togrul, 2005), ciku (Chong et al., 2009), mulberry (Doymaz 2004), fig (Doymaz, 2005), seedless and seeded grapes (Doymaz, 2012), aromatic plants (Akpınar, 2006), *Gundelia tournefortii* L. (Evin 2012), green bean and okra (Doymaz, 2011), cork planks (Costa and Pereria, 2013), and some leafy vegetables (Sob kola et al., 2007). No data on sun drying of cornelian cherry fruit have been reported yet in literature.

The main objectives of this research were to investigate the sun drying behavior of cornelian cherry, to predict the best thinlayer model for drying curve, to calculate effective diffusivity coefficient and to determine amount of vitamin C in dried cornelian cherry.

2. Materials and Methods

2.1. 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 (AOAC, 1984). About 50 g of fresh cornelian cherry with five replicates were dried in an oven at 105 °C for 24 hours and the value of initial moisture was determined as about 75.4 % (w.b). The diameter of cornelian cherry was evaluated with a digital caliper (Powerfix) and its average value was found as 11.94 \pm 0.3 mm.

2.2. Drying process

The sun drying experiments were performed in September 2011 in Erzurum. Erzurum is located in the eastern region of Turkey and its geographic coordinates are 39° 53' North, 41°16' East. Fruits were distributed in a single layer on a stainless steel mesh tray (15x25 cm) and the tray was located on the open top floor of a four-floor building to benefit from the sky's direct radiation. The fruits (about 100 g) were exposed to sunlight between 8.00 a.m. and 18:00 p.m. hours. The measurements were made only during these periods. During the drying processes, the amount of water removed was periodically recorded at five hours using a digital balance (AND Electronic Balance FX 3000, Japan) accuracy of ± 0.01 . Experiments were completed when fruits reached constant weight.

3. Results and Discussion 3.1. Mathematical modelling of drying curves

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

$$MR = \frac{M_t - M_e}{M_o - M_e} \tag{1}$$

where M_o , M_e and M_t reflect initial moisture content (g H₂O/g dry matter), equilibrium moisture content (g H₂O/ g dry matter) and moisture content at any time (g H₂O/g dry matter), respectively.

As shown in Table 2, the experimental data obtained were applied to twelve thin-layer drying models which were widely used for food and biological materials. The correlation coefficient (\mathbb{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 \mathbb{R}^2 and the lowest values of X^2 and *RMSE* indicate the most appropriate of fit.

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

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

where $MR_{pre,i}$ is the *i*th predicted moisture ratio, $MR_{exp,i}$ is the *i*th experimentally observed moisture ratio, the *z* is number of constants in the model and *N* is the number of the 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.

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

where *R* is the drying rate (g H₂O/g dry matter. s), $M_{t+\Delta t}$ is the moisture content at $t+\Delta t$ (g H₂O/ g dry matter), M_t is also the moisture content at t (g H₂O/ g dry matter) and t is the drying time(min).

3.2. Determination of effective moisture diffusivity (D_{eff})

Fick's second law has been widely used to describe the transport of moisture from the material at unsteady state:

$$\frac{\partial M}{\partial t} = Deff \nabla^2 M \tag{5}$$

Eq. (6) is obtained from solution of Eq. (5) for only radial diffusion in a spherical body with the assumption of negligible external resistance and shrinkage, uniform initial moisture distribution, constant diffusivity and temperature (Crank, 1975).

$$MR = \frac{M_t - M_e}{M_o - M_e} = \frac{M_t}{M_0} = \frac{6}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \cdot \pi^2 \cdot D_{eff}}{r_0^2} t\right)$$
(6)

(7)

For long drying periods, Eq. (6) can be simplified by taking only the first term of the series then, following equation is obtained:

$$MR = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D_{eff}}{r_0^2} t\right)$$

Eq. (7) equation can be linearized as follows:

$$ln(MR) = ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 \cdot D_{eff}}{r_0^2}t\right)$$
(8)

3.3. Determination of vitamin C

The vitamin C content was determined by the methods described by Jagato and Dani (1982) with little modification. Five grams of fresh and dried cornelian cherry samples blended were extracted with 100 mL 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 in to a polypropylene centrifuge tube. 2 mL of tri-chloro acetic acid (10%) was

added in this solution and tube was placed for 5 minutes in an ice bath and then 2 mL 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 UV spectrophotometer (Shimadzu, UV-160A, Japan). Results were expressed as milligrams of vitamin C per 100 g dry matter (mg vitamin C/100 g d.m.).

Table 1 shows the variation of ambient air temperature, relative humidity and wind velocity in time for a typical drying day. During the drying process, the mean values of ambient air temperature, relative humidity and wind velocity fluctuated about \pm 2 °C, \pm 4% and \pm 0.5 m/s, respectively. This information was obtained from the Meteorology Unit in Erzurum.

Table 1. Variation of ambient air temperature, relative humidity and wind velocity during the sun drying of cornelian cheery on a typical day in September in Erzurum.

| Day times | 800 | 1000 | 1200 | 14 ⁰⁰ | 1600 | 1800 |
|-----------------------|-----|------|------|------------------|------|------|
| Temperature (°C) | 15 | 18 | 24 | 22 | 20 | 17 |
| Relative humidity (%) | 39 | 36 | 32 | 28 | 37 | 46 |
| Wind Speed (m/s) | 3 | 2 | 2 | 2 | 3 | 2 |

4.1. Drying curves of cornelian cherry

Figure 1 (a) shows the variation of moisture ratio with drying time of cornelian cherry fruit for the sun drying. The moisture ratio reduced exponentially with time. Figure 1 (b) shows the changes in drying rate as a function of drying time.



Figure 1. Drying curves of cornelian cherry (**a.** the variation of moisture ratio with drying time, **b.** the changes in drying rate as a function of drying time)

Drying rate decreased continuously with drying time. This behavior of curves shows that the drying process of cornelian cherry occurred in falling rate period and constant rate period was not present for the sun drying. The behavior represents that the mass transfer mechanism in the cornelian cherry is controlled by molecular diffusion. Similar results have been reported for as corn kernels (Sahdev and Kumar, 2013), apricot (Togrul, 2005), ciku (Chong et al., 2009), seedless and seeded grapes (Doymaz, 2012), green bean and okra (Doymaz, 2011) and hawthorn (Aral and Bese, 2016).

4.2. Evaluation of mathematical models

The experimental data were applied to twelve thin-layer models shown in Table 2.

The statistical analysis results of the models were calculated using non-linear regression analysis and they are summarized in Table 3. The approximation of diffusion model were found to be the most appropriate models for explaining the thin layer drying characteristic of cornelian cherry for the sun drying with the highest values of R^2 and the lowest values of X^2 and *RMSE*.

It is reported that the approximation of diffusion model is the best model describing the thin layer characteristics for green bean (Doymaz, 2011), tomato (Sacılık et al., 2006), and pumpkin (Yaldız and Ertekin, 2007).

4.3. Effective moisture diffusivity

The effective diffusivity was calculated using Eq. (8). *lnMR* versus time was plotted and the value of D_{eff} was determined as 1.20x10⁻¹¹ m²/s from the slope of straight line. This obtained value of D_{eff} for cornelian cherry was in general range of 10⁻¹¹-10⁻⁹ m²/s for fruits and vegetables (Aral and Beşe, 2016). A comparison of D_{eff} values of some food materials in literature, and the obtained D_{eff} value in this study is shown in Table 4.

| Model | Model Name | Model Equation |
|-------|----------------------------|--|
| No | | |
| 1 | Page | MR= exp(-kt ⁿ) |
| 2 | Newton | MR= exp(-kt) |
| 3 | Logistic | $MR = b/(1 + a \exp(kt))$ |
| 4 | Two-term | $MR = a \exp(-k_0 t) + b \exp(-k_1 t)$ |
| 5 | Logarithmic | $MR = a \exp(-kt) + c$ |
| 6 | Verma et al. | $MR = a \exp(-kt) + (1-a)\exp(-gt)$ |
| 7 | Midilli et al. | MR= a exp(-kt ⁿ)+bt |
| 8 | Wang & Singh | MR= 1+at+bt ² |
| 9 | Approximation of diffusion | $MR = a \exp(-kt) + (1-a)\exp(-kbt)$ |
| 10 | Henderson & Pabis | MR= a exp(-kt) |
| 11 | Two-term Exponential | MR= a exp(-kt)+(1-a)exp(-kat) |
| 12 | Modified Henderson & Pabis | $MR = a \exp(-kt) + b \exp(-gt) + c \exp(-ht)$ |

Table 2. Thin-layer models applied to drying curves of cornelian cherry (Kucuk et al., 2014).

Table 3. Model constants and statistical results of applied mathematical models.

| Model No | Model constants | R ² | X ² | RMSE |
|----------|---|----------------|----------------|--------|
| 1 | k=0.00036, n=1.001 | 0.996 | 0.0000 | 0.0025 |
| 2 | k=0.00027 | 0.996 | 0.0000 | 0.0025 |
| 3 | k=0.00036, a=1.636, b=2.654 | 0.997 | 0.0000 | 0.0031 |
| 4 | k_0 =0.00028, k_1 =0.100, a=1.024, b=0.00 | 0.997 | 0.0000 | 0.0054 |
| 5 | k=0.0003, a=1.017, c=0.011 | 0.997 | 0.0000 | 0.0053 |
| 6 | k=0.00, a=-1030,34, g=0.00 | 0.996 | 0.0000 | 0.0030 |
| 7 | k=188.16, a=1.00, b=0,00, n=0.00 | 0.995 | 0.0001 | 0.0106 |
| 8 | a=-0.00014, b=0.00 | 0.905 | 0.0008 | 0.0293 |
| 9 | k=0.0017, a= - 0.163, b=0.178 | 0.999 | 0.0000 | 0.0024 |
| 10 | k=0.00028, a=1.025 | 0.997 | 0.0000 | 0.0051 |
| 11 | k=6.438, a=0.0004 | 0.996 | 0.0000 | 0.0026 |
| 12 | k=0.0003, a=0.394, b=0.236, c=0.394, | 0.997 | 0.0000 | 0.0059 |
| | g=0.0003, h=0.0004 | - ' / / / | | |

| Material | D_{eff} (m ² /s) | References | |
|--------------------|-------------------------------|--------------------------|--|
| Cornelian cherry | 1.23X10 ⁻¹¹ | This study | |
| Fig | 2.47X10 ⁻¹⁰ | Doymaz (2005) | |
| Okra | 1.52X10 ⁻¹¹ | Doymaz (2011) | |
| G. tournefortii L. | 2.48x10 ⁻¹⁰ | Evin (2012) | |
| Seedless grapes | 1.02×10^{-11} | Dormon (0.010) | |
| Seeded grapes | 1.66×10 ⁻¹¹ | Doyinaz (2012) | |
| Pineapple | 6.89x10 ⁻¹⁰ | Olanipekun et al. (2015) | |

Table 4. Effective diffusivity values dried some food materials under open sun.

4.4. Vitamin C

Since the vitamin C is sensitive to light, heat, oxygen and pH, the processing and storage conditions significantly affect degradation of vitamin C. The fresh cornelian cherry had 296 ±0.12 mg/100 g dry matter value of vitamin C. After the drying processing, this value was determined as 145±0.06 mg /100 g dry matter. The degradation of vitamin C was approximately 51.1%. As the long drying period leads to more exposure to the atmospheric oxygen and the sun light of fruit, some quality aspects such as vitamin C are adversely affected (Arslan and Özcan, 2010).

4. Conclusion

Drying behavior of cornelian cherry fruit was investigated under open-sun in this study. Drying process of cornelian cherry occurred in the falling rate. The experimental data to twelve thin models layer and the approximation of diffusion model was found to be the best models for describing the thin layer drying characteristic of cornelian cherry for the sun drying. Effective moisture diffusion coefficients (D_{eff}) were calculated as 1.20x10⁻¹¹ m²/s. Approximately 51.1% of the vitamin C in the fruit was degraded during the drying.

Nomenclature

| a, , b, k, n | model constants | | |
|------------------------------|---|--|--|
| $D_{e\!f\!f}$ | effective diffusivity coefficient | | |
| | (m ² /s) | | |
| \mathbf{M}_{t} | moisture content of material at | | |
| | time t (g H_2O/g dry matter) | | |
| \mathbf{M}_{e} | equilibrium moisture content | | |
| | of material (g $H_2O/$ g dry | | |
| | matter) | | |
| M_{o} | initial moisture content of | | |
| | material (g H ₂ O/ g dry matter) | | |
| MR | moisture ratio | | |
| MR _{exp} | experimental moisture ratio | | |
| $\mathbf{MR}_{\mathrm{pre}}$ | predicted moisture ratio | | |
| Ν | number of observations | | |
| R ² | regression coefficient | | |
| R | rate of drying (g H_2O /g dry | | |
| | matter.h) | | |
| ro | radius (m) | | |
| RMSE | root mean square error | | |
| t | time (h) | | |
| Z | number of constants in the | | |
| | model | | |
| χ^2 | reduced khi-kare | | |

X

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