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FREEZE DRYING KINETICS OF PERSIMMON PUREE

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Abstract

This study was intended to determine the drying kinetics of persimmon puree in a freeze drier. Experimental drying data were fitted to theoretical (Fick's Law of Diffusion) and ten well-known empirical thin layer drying models. In addition, the effective moisture diffusivity and color changes depending on the drying time were determined. The criteria considered for selecting the most suitable model were to obtain the highest R^2 and lowest RMSE, and χ^2 values. Depending on these criteria, Logarithmic model (R^2=0.994, RMSE=0.0250 and χ^2 =0.0009) was chosen to estimate the moisture ratio of persimmon puree during the drying process with a great accuracy. The effective moisture diffusivity (D_{eff}) of freeze dried persimmon puree was calculated by using the Fick's Law of diffusion model, and it was found to be as 7.302 x10^{-10} m^2/s. During the drying operation L* values increased and a* and b* values of persimmon puree decreased with a total amount of color change (ΔE) of 32.20

Keywords: Persimmon, freeze drying, thin layer modelling, effective moisture diffusivity, color changes

CENNET ELMASI PÜRESİNİN DONDURARAK KURUTMA KİNETİĞİNİN BELİRLENMESİ

Özet

Bu çalışmada dondurarak kurutulmuş cennet elması püresinin kuruma kinetiğinin belirlenmesi hedeflenmiştir. Deneysel veriler teorik (Fick'in Difüzyon Yasası) ve on farklı ince tabaka kurutma modeli kullanılarak modellenmiştir. Bunlara ek olarak, etkin difüzyon katsayısı ve kuruma zamanına bağlı olarak meydana gelen renk değişimi belirlenmiştir. Uygun modelin seçilmesinde en yüksek R^2 değeri ve en düşük RMSE ve χ^2 değerleri kriter olarak seçilmiştir. Bu kriterlere bağlı olarak, kuruma işlemi boyunca cennet elması püresinin nem oranı değerlerini en iyi Logaritmik modelin (R^2=0.994, RMSE=0.0250 ve χ^2 =0.0009) temsil ettiği belirlenmiştir. Cennet elması püresinin etkin difüzyon katsayısı (D_{eff}) Fick' in Difüzyon Yasası ile belirlenmiş ve 7.302 x10^{-10} m^2/s olarak bulunmuştur. Kurutma işlemi boyunca kuruma zamanına bağlı olarak L* değerinin arttığı; a* ve b* değerlerinin ise azaldığı gözlenmiş ve toplam renk değişimi 32.20 olarak hesaplanmıştır.

Anahtar kelimeler: Cennet elması, dondurarak kurutma, ince tabaka modelleme, etkin difüzyon katsayısı, renk değişimi

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INTRODUCTION

Persimmon (*Diospyros kaki* L.) is rich in bioactive compounds, such as ascorbic acid, condensed tannins, and carotenoids, which contribute its antioxidant properties. In addition, it is also a good source of dietary fibers, phenolics and mineral compounds (1-3). Persimmon is cultivated in warm regions in the world (4, 5). It is an important fruit in China, Japan and Korea and is also gaining popularity in the Mediterranean countries such as Turkey (6). The persimmon fruits, harvested generally are two types being astringent and non-astringent. The heart-shaped Hachiya is the most common variety of astringent persimmon. The non-astringent persimmon can be consumed still very firm and remain edible when very soft. Astringent persimmons contain high levels of soluble tannins and they are unpalatably astringent if eaten before completely softened (6). Although, the persimmon is quite susceptible after their harvest, it can be stored for up to 6 months in modified or controlled atmospheres (7). In order to prolong the shelf life of persimmons and improve new consumption areas; canning, freezing and drying might be suitable techniques. Among these techniques drying constitutes an alternative way to increase the shelf life and consumption of persimmon by reducing physiological, microbial, and enzymatic degradation. With conventional hot-air drying, higher drying rate at the initial stage may cause case hardening of the product's surface, considerable shrinkage and formation of dense structure, color changes and totally significant quality losses. In order to protect foods from the above mentioned drying effects, freeze drying can be used. Although freeze drying is an expensive method, the obtained product with superior properties especially in texture, nutritional quality and color makes this process advantageous for drying of sensitive foods. Dried foods in form of slices or certain shapes need a rehydration stage before consumption and in most of the cases rehydration may lead to further undesirable quality changes. For this reason, if the end use of the dried food is suitable, production of the dried material in powdered form can be an alternative. Powdered foods have advantages in storage, transportation, dosing and mixing into food systems.

Describing dehydration kinetic is important for the design and optimization of drying processes and to determine the effect of the processing variables on the drying process (8). Thin layer drying equations are important in mathematical modeling of drying. They are practical and provide sufficiently good results (9) where theoretical model and experimental data are not in a good correlation. Thin layer drying generally means to dry as one layer of sample which provide uniform temperature and physical properties assumption and suitable for lumped parameter models (9, 10). This work aimed at studying the freeze drying behavior of persimmon puree. Further, color changes during drying and effective moisture diffusivity value of persimmon puree were determined.

MATERIAL and METHODS

The fresh, mature and non-damaged persimmon fruits were obtained from a local supermarket in Izmir, Turkey. They were peeled; seeds were removed and ground into puree by using a home type blender (Tefal Smart, MB450141, Turkey).

Freeze Drying

Experiments were performed in a pilot scale freeze dryer (Armfield, FT 33 Vacuum Freeze Drier, England). The persimmon puree were frozen in a layer of 3 mm in the petri dishes at - 40 °C in an air blast freezer for two hours, then freeze dried under vacuum (13.33 Pa absolute pressure), at - 48 °C condenser temperature. For this process, each experiment for increasing time periods was carried out with new samples of equal mass. The moisture loss was determined by weighing the petri dishes using a digital balance with 0.01 precision (Ohaus AR2140, USA). The powder was obtained by grinding the dried material in a blender (Tefal Smart, MB450141, Turkey). Moisture content of the persimmon puree was determined by using AOAC methods (11). Water activity was measured by using Testo-AG 400, Germany, water activity measurement device.

Evaluation Modeling of Drying Data

In order to determine drying characteristics of persimmon puree during freeze drying, the obtained data was converted to moisture ratio which is given in Equation (1).

$$MR = \frac{M_t - M_e}{M_0 - M_e} \qquad \text{(Eq. 1)}$$

Where the M_t, M_0 and M_e are the moisture content at any time, initial, and equilibrium moisture content (kg H_2O/ kg dry matter (DM)), respectively.

Theoretical (Fick's Law of diffusion) and empirical model equations were used to determine the drying kinetics of persimmon puree. Theoretical equation is given in Equation (2);

$$MR = \frac{M_t - M_e}{M_0 - M_e} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\pi^2\frac{D_{eff}}{4L^2}t\right] \qquad \text{(Eq. 2)}$$

Where t is the time (s), D_{eff} is the effective diffusivity (m^2/s) and L is the thickness of samples (m).

For empirical modeling; drying data was fitted to ten well-known thin layer drying models (Lewis, Page, Henderson and Pabis, Logarithmic, Midilli, Modified Midilli, Two-term, Two-term Exponential, Modified Two-term Exponential and Wang and Singh) (9).

Nonlinear regression analysis was used to evaluate the parameters of the selected model by using statistical software SPSS 16.0 (SPSS Inc., USA). The goodness of fit was determined using the coefficient of determination (R^2), root mean square error (RMSE), and the reduced chi-square (χ^2) that can be described in Equations (3), (4) and (5) as;

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

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}(MR_{\exp,i} - MR_{pre,i})^2\right]^{1/2} \qquad \text{(Eq. 4)}$$

$$\chi^2 = \frac{\sum_{i=1}^{N}(MR_{\exp,i} - MR_{pre,i})^2}{N-n} \qquad \text{(Eq. 5)}$$

Where $MR_{exp,i}$ and $MR_{pre,i}$ is the experimental, and predicted moisture ratio at observation i; N is number of the experimental data points, and n is number of constants in model.

The effective moisture diffusivity (D_{eff}) of freeze dried persimmon puree powder was calculated by using the Fick's Law of diffusion model which is given in Equation (2).

For long drying times, a limiting case of Equation (2) is obtained, and expressed in a logarithmic form;

$$\ln MR = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{4L^2}\right)t \qquad \text{(Eq. 6)}$$

The effective diffusivity was calculated by plotting experimental moisture ratio in logarithmic form versus drying time. From Equation (6), a plot of ln MR versus drying time gives a straight line with a slope of $\left(\frac{\pi^2 D_{eff}}{4L^2}\right)$.

Determination of Color Changes of Persimmon Pure

The color values (L*, a*, and b* values) of fresh persimmon fruits, and the powders were measured with Minolta CR-400 Colorimeter, Japan, calibrated with white standard plate three times and results as the average of three measurements were expressed in accordance with the CIE Lab. System. The L* value, is a measure of lightness which ranges between 0 and 100. Increases in a* value in positive, and negative scales correspond to increases in red or green color, respectively. The b* value represents color ranging from yellow (+) to blue (-). Total color change (ΔE) of freeze dried persimmon puree with respect to fresh persimmon puree was calculated by using Equation (7);

$$\Delta E = \sqrt{(\Delta L^2 + \Delta a^2 + \Delta b^2)} \qquad \text{(Eq. 7)}$$

RESULTS and DISCUSSION

Drying Characteristic and Evaluation of the Models

In this study, it was observed that freeze drying can satisfactorily be applied for drying of persimmon puree. During the drying process, total time was determined to be as 9 hours by following the changes in the weight of the samples. For each drying experiment only a small volume of the drying chamber was loaded. The temperature of the heating plate was set to +30 °C which accelerated the sublimation process, not leading to melting of the product under working conditions and kept as constant during the drying process. According to the results, moisture content (5.97±0.55 %, wet basis (wb)) and water activity values (0.253±0.001) of the persimmon powders were in acceptable limits for safe storage of products.

Moisture content data were used in the form of the moisture ratio in curve fitting computations with respect to the drying time by using theoretical and thin layer drying models. The summary of models parameters of drying models that were used for expressing drying characteristics and the statistical evaluation of models using three different criteria (R^2, RMSE and χ^2) are presented in Table 1.

used six thin-layer drying models (Lewis, Henderson and Pabis, Logarithmic, Page, Midilli et al., and Weibull) in order to evaluate the hot air drying (50, 60 and 70°C) kinetics of blanched and unblanced persimmon slices (5 mm thickness) and the research reported that Midilli et al., Page and Weibull models showed a better fit to experimental drying data compared to the other models.

It can be seen from Figure 1 and 2 that Logarithmic model showed a high level of concordance with the experimental results for persimmon puree.

Table 1. The model equations and statistical results (R^2, RMSE and χ^2).

Models	Equations	R^2	RMSE	χ^2
Fick's Law of Diffusion	$MR = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\pi^2\frac{7.302\text{x}10^{-10}}{4L^2}t\right]$	0.900	0.0227	0.1506
Lewis	$MR = e^{-0.404t}$	0.986	0.0399	0.0014
Page	$MR = e^{-0.325t^{1.187}}$	0.992	0.0285	0.0010
Henderson and Pabis	$MR = 1.019e^{-0.410t}$	0.987	0.0372	0.0017
Logarithmic	$MR = 1.076e^{-0.338t} - 0.076$	0.994	0.0250	0.0009
Midilli	$MR = 1.003e^{-0.366t} - 0.007t$	0.993	0.0265	0.0010
Modified Midilli	$MR = e^{-0.364t} - 0.007t$	0.993	0.0265	0.0009
Two Term	$MR = 0.51e^{-0.410t} + 0.509e^{-0.410t}$	0.987	0.0372	0.0023
Two-Term Exponential	$MR = 1.681e^{-0.523t} - 0.681e^{-0.523*1.681t}$	0.992	0.0287	0.0010
Modified Two-Term Exponential	$MR = 822.229e^{-0.221t} - 860.229e^{-0.221t}$	0.995	0.0440	0.1756
Wang and Singh	$MR = 1 - 0.276t + 0.019t^2$	0.991	0.0318	0.0013

In different studies, drying models in which (R^2) value is highest and RMSE, and χ^2 values are smallest was chosen to be the most suitable models (10,12-14). In this study, R^2 values of the models changed between 0.900 and 0.995. The highest R^2 (0.995) value was obtained from Modified Two-term Exponential model and the lowest R^2 value was obtained from theoretical model (Table 1 and Figure 1). In evaluation of the drying data with theoretical model the first three terms of the equation were used since the remaining terms were negligible on the calculation. Although the coefficient of correlation (R^2=0.995) of Modified Two-Term Exponential model RMSE= 0.0440 and χ^2=0.1756 is higher compared with other models, the lowest values of RMSE (0.025) and χ^2 (0.0009) was obtained from Logarithmic model (R^2=0.994). For this reason, Logarithmic model was chosen to estimate the moisture ratio of persimmon puree during the drying process with great accuracy (Figure 1 and 2). Doymaz (15),

Figure 2 shows the experimental and predicted moisture ratio values of Logarithmic Model for pure freeze dried persimmon.

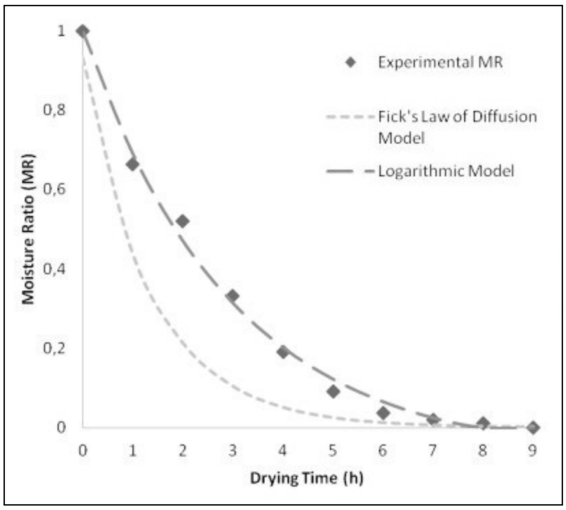

Figure 1. Experimental and computed moisture ratio values for freeze dried persimmon puree.

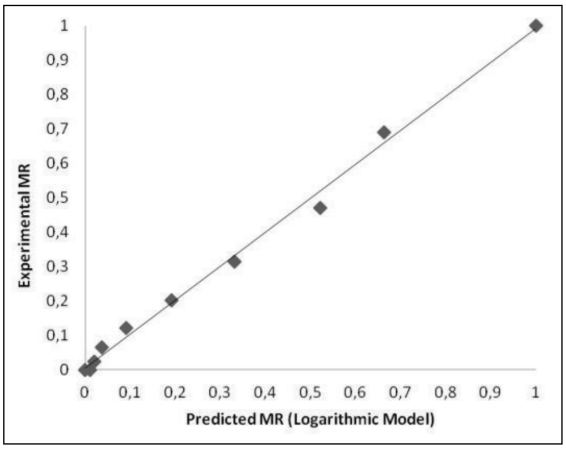

Figure 2. Experimental and predicted moisture ratio values of Logarithmic Model for freeze dried persimmon puree.

The effective moisture diffusivity (D_{eff}) of freeze dried persimmon puree was calculated by using the Fick's Law of diffusion model, and it was found to be as 7.302 x10^{-10} m^2/s. Depending on the modeling part of this study, it was observed Fick's Law of Diffusion is not satisfactory for defining the drying behavior. However, the estimation of diffusion coefficient is important in drying studies to see the rate of drying. For this reason, to estimate the diffusion coefficient on an order of magnitude level the calculation was performed. In their review, Erbay and Icier (9) reported that the effective moisture diffusivity values in foods were in the range of 10^{-12} to 10^{-6} m^2/s and 75% of these values were accumulated in the region 10^{-10} to 10^{-8} m^2/s, similar to this study. In addition, Doymaz, (15) studied on the effect of blanching and drying temperature (50, 60 and 70°C) on drying kinetics of persimmons under hot-air drying and reported that the effective moisture diffusivity values of persimmon slices ranged from 7.05 x 10^{-11} to 2.34 x 10^{-10} m^2/s.

Color Changes of Persimmon Pure

The color values (L*, a*, and b*) of fresh persimmon puree were measured as 50.20±3.21; 7.98±1.66 and 22.37±2.58. Karaman et. al. (16) measured the color values of fresh and freeze dried persimmon powders as 22.7±0.05 (L), 7.1±0.02 (a), 18.6±0.08 (b) and 75.1±0.01 (L), 19.5±0.03 (a), 52.5±0.35 (b), respectively. Total color change of persimmon pure after freeze drying process was calculated as 32.20. In the study of Karaman et. al. (16) total color change of persimmon puree was found to be as 63.63. The differences between the results may cause the differences between process conditions. In addition, the operations before drying such as peeling, blending and freezing may cause some enzymatic reactions which cause the change of color of vegetables and fruits. The physical and chemical properties of vegetables and fruits changes depending on harvest time, cultivar, maturation stage, geography and climate. For this reason the differences between color values of fresh persimmon and persimmon powder were explained as color change (ΔE) values, by this way the effect of drying conditions were observed independent of the mentioned differences. The variation of the color values of samples depending on the drying time was shown in Figure 3. It can be seen that L* values increased, a* and b* values of persimmon puree decreased depending on drying time. The increase in the brightness value and decrease in the redness value of persimmon after freeze drying operation was also observed by Karaman et. al. (16). On the contrary of the obtained results of this study, the researcher reported that yellowness value of the sample increased after freeze drying application.

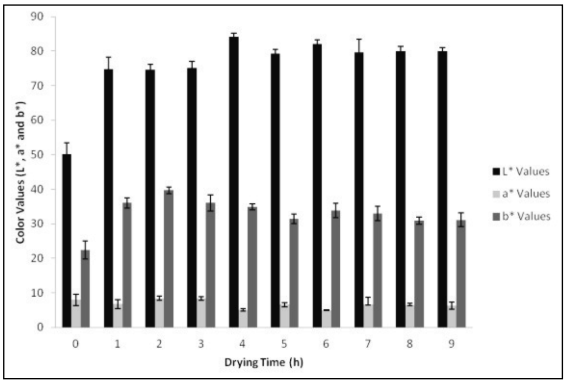

Figure 3. The variation of the color values of samples depending on the drying time.

CONCLUSION

In this study, it was observed that freeze drying can satisfactorily be applied for drying of persimmon puree. Logarithmic model was chosen to estimate the moisture ratio of persimmon puree during the drying process with great accuracy. The effective moisture diffusivity (D_{eff}) of freeze dried persimmon puree was found to be as 7.302 x10^{-10}

m^2/s which is in the same range (10^{-12} to 10^{-6}) with most of the foods. According to the measurement of color values, L* values increased, a* and b* values of persimmon puree decreased depending on drying time.

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