

MATHEMATICAL MODELLING OF VACUUM DRYING CHARACTERISTICS FOR MAHLAB PUREE

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Abstract

Mahlab has bitter taste, strong aroma and high anthocyanin content and it might be used for producing different fruit snack bars which the drying step is very important for the manufacture. In this article, mathematical modelling of the drying of mahlab puree in vacuum dryer at different temperatures is investigated. Thin-layer drying processes were performed using a temperature controlled vacuum drying oven at 50, 60 and 70°C under 50 mbar absolute pressure and the weight data were collected at certain time intervals. The drying curves were fitted to eight different drying models. In this curve fitting, nonlinear regression analysis was used to evaluate the parameters of the selected models. Additionally, effective diffusion coefficient was obtained from diffusion model of Fick and the activation energy was determined using Arrhenius equation. According to statistical analysis results for three drying temperatures, Midilli et al. drying model has shown a better fit to the experimental drying data of mahlab puree. The effective diffusion coefficients were found as 1.71x10⁻¹⁰, 6.21x10⁻¹⁰ and 8.64x10⁻¹⁰ m²/s at 50, 60, and 70°C, respectively. The activation energy that expresses the temperature dependency of the diffusion coefficients was calculated as 75.2 kJ/mol.

Keywords: Mathematical modelling, mahlab, vacuum drying, activation energy, mass ratio

MAHLEP PÜRESİNİN VAKUM KURUTMA KARAKTERİSTİKLERİNİN MATEMATİKSEL MODELLENMESİ

Öz

Mahlep, acımsı tada, güçlü aromaya ve yüksek antosiyanin içeriğine sahiptir ve bu özellikleriyle, üretim aşamasında kurutmanın önem kazandığı aperatif tüketime yönelik meyve barlarının üretimi için kullanılabilmektedir. Bu çalışmada, farklı sıcaklıklarda gerçekleştirilen mahlep püresinin vakumlu kurutucudaki kurutma işleminin matematiksel modellenmesi incelenmiştir. İnce tabaka kurutma işlemi, sıcaklık kontrollü vakumlu kurutma fırını kullanılarak 50 mbar basınç altında, 50, 60 ve 70°C farklı kurutma sıcaklıklarında gerçekleştirilmiş olup, kütle kaybı belirli aralıklarla ölçülmüştür. Kurutma eğrileri sekiz farklı kurutma modeline göre elde edilmiştir. Matematiksel modellemede, seçilen modellerin parametrelerini değerlendirmek için doğrusal olmayan regresyon analizi kullanılmıştır. Ayrıca Fick'in difüzyon modelinden etkin difüzyon katsayısı elde edilmiş ve aktivasyon enerjisi Arrhenius denklemi kullanılarak belirlenmiştir. Üç farklı kurutma sıcaklığı için istatistiksel analiz sonuçlarına göre Midilli ve ark. kurutma modeli, mahlab püresinin deneysel kurutma verilerine en iyi uyum gösteren model olmuştur. Kurutma sıcaklıkları olan 50, 60 ve 70°C için etkin difüzyon katsayısı sırasıyla 1.71x10⁻¹⁰, 6.21x10⁻¹⁰ ve 8.64x10⁻¹⁰ m²/s olarak bulunmuştur. Difüzyon katsayılarının sıcaklığa olan bağlılığını ifade eden aktivasyon enerjisi ise 75.2 kJ/mol olarak hesaplanmıştır.

Anahtar Kelimeler: Matematiksel modelleme, mahlep, vakum kurutma, aktivasyon enerjisi, kütle oranı

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1. Introduction

Healthy eating has been an important factor in the choice of food among conscious consumers. Fruit and vegetable consumption is considered to be the most important part of healthy eating. But it is known that fruit bars have a greater nutritional value than fresh fruits. This is due to the fact that fruit bars contain concentrated nutrients [1]. However, it can be seen that a decrease in the flavour and nutritional value during the drying process used in the production of the fruit bar [2, 3].

Mahaleb cherry or Mahlab (*Prunus mahaleb L.*) from Rosaceae family is a tree which grows mostly in Turkey,

West Asia, Greece, Mediterranean, Iran, Sudan and Armenia. In the food industry, mahlab fruit, which has bitter taste, strong aroma and high anthocyanin content, is used in the production of wine, vinegar and liqueur [4]. It is thought that the potential use of mahlab fruit that has high antioxidant capacity in the composition of fruit bars which are frequently used in healthy nutrition.

In Turkey, the drying process is usually performed by spreading out the product to be dried on the ground. This method has many disadvantages such as poor quality products and hygienic problems. Losses in the quality of the dried product reduce the trade potential and economic value. Different drying methods have been developed to obtain high-quality dried products. In the drying process using the vacuum method, high antioxidant values were obtained while at the same time it showed good texture, colour and rehydration properties. On the other hand, commonly used dryers are not economical due to their high energy consumption. For this reason, vacuum dryers have a good opportunity to improve product quality and system efficiency [5]. In this purpose, this study was carried out in order to investigate the drying characteristics of mahlab in a vacuum dryer. The experimental drying data obtained is adapted to the mathematical models found in the literature.

2. Material and Method

2.1. Material

A commercial mahlab (*Prunus mahaleb* L.) puree composed of only fruit was used for the drying processes. The initial moisture content of mahlap puree was identified as 3.55±0.05 kg water/kg dry matter.

2.2. Vacuum drying process

Vacuum drying was carried out in a vacuum oven (Nuve EV 018, Turkey) with a 15 L internal chamber. A vacuum pump was used for lowering the pressure to 50 mbar inside the oven. The samples at room temperature were distributed homogeneously as a thin layer (thickness of 3 mm) over the aluminium drying pan having 80 mm diameter. The vacuum dryer was run idle until the desired temperature was achieved and the drying pan with sample was placed. The vacuum pump was switched on to initiate the dehydration. The data was recorded with a digital balance in certain time intervals. The drying temperatures were 50, 60 and 70°C and all drying tests were performed duplicate.

2.3. Mathematical modelling

The most examined mathematical model in the drying of foods is given by the solution of Fick's law [6-9]. Fick's law is generally used to describe the process of moisture distribution,

$$\frac{\partial M}{\partial t} = D_{eff} \frac{\partial^2 M}{\partial x^2} \tag{1}$$

where, D_{eff} is the effective diffusivity in m²/s, M is the moisture content on a dry basis, t is the time, and x is the spatial coordinate. In order to implement Fick's law, it is

assumed that the product is one-dimensional, having a uniform initial moisture content and the main resistance is the internal moisture movement [10];

$$\frac{M_{t} - M_{e}}{M_{0} - M_{e}} = \frac{8}{\pi^{2}} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^{2}} \exp\left(-(2n+1)^{2} \pi^{2} \frac{D_{eff}t}{4H^{2}}\right)$$
(2)

where, M_t , M_o , M_e , are the moisture content at time t, the initial moisture content and the equilibrium moisture content, respectively, H is the thickness of the mahlab puree. For long drying times (setting n = 1), the equation can be simplified;

$$\ln\left(\frac{M_t - M_e}{M_0 - M_e}\right) = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff} t}{4H^2}\right)$$
(3)

The effective diffusion coefficients are typically determined by plotting experimental drying data in terms of ln (M_t/M_0) versus time [11-14]. Effective diffusivity values in the range of $10^{-9}-10^{-11}$ m²/s are found in literature.

The Arrhenius equation shows the temperature dependence of the effective diffusion coefficient.

$$D_{eff} = D_0 \exp\left(\frac{-E_a}{R_g T_{abs}}\right) \tag{4}$$

where, E_a is the activation energy (kJ/mol), D_0 is the constant (m²/s) equivalent to the diffusion coefficient at infinite temperature, T_{abs} is the drying temperature (K) and R_g is the universal gas constant (kJ/mol K).

The obtained drying curves were applied to eight different drying models given in Table 1.

Table 1. Mathematical models for the drying curves

| Model No. | Model equation | Model name | Reference | |
|--------------|---|---------------------|-----------|--|
| 1 | $(M_t/M_o) = aexp(-k_1t) + bexp(-k_2t)$ | Two-Term | [15] | |
| 2 | $(M_t/M_o) = aexp(-kt)$ | Henderson and Pabis | [16] | |
| 3 | $(M_t/M_o) = \exp(-kt)$ | Newton | [17] | |
| 4 | $(M_t/M_o) = \exp(-kt^n)$ | Page | [18] | |
| 5 | $(M_t/M_o) = a \exp(-kt) + c$ | Logarithmic | [19] | |
| 6 | $(M_t / M_o) = 1 + at + bt^2$ | Wang and Singh | [20] | |
| 7 | $(M_t/M_o) = a \exp(-kt)+(1-a) \exp(-gt)$ | Verma et al. | [21] | |
| 8 | $(M_t/M_o) = a \exp(-k(t^n))+bt$ | Midilli et al. | [22] | |

Experimental drying data for the mahlab puree were fitted to eight different drying models given in Table 1. Curve fitting studies were performed using statistical computer program. The coefficient of determination (R²) was one of the important criteria for choosing the best equation in the vacuum drying curves of the mahlab puree. In addition to R², the various statistical parameters such as; mean bias error (MBE), reduced Chisquare (χ^2), the root mean square error (RMSE) and the modelling efficiency (EF) were used to determine the quality of the fit. The RMSE gives the deviation between the experimental and predicted values and this value is expected to converge to zero. The lower the values of the χ^2 , the better the goodness of the fit. The EF also gives the ability of the model and it is desirable to approach to 1 [23]. These parameters can be calculated as;

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

$$MBE = \frac{1}{N} \sum_{i=1}^{N} \left(MR_{pre,i} - MR_{\exp,i} \right)$$
(6)

$$RMSE = \sqrt{\frac{\sum_{l=1}^{N} \left(MR_{pre,i} - MR_{\exp,i}\right)^2}{N}}$$
(7)

$$EF = \frac{\sum_{i=1}^{N} (MR_{\exp,i} - MR_{i,\exp mean})^2 - \sum_{i=1}^{N} (MR_{pre,i} - MR_{\exp,i})^2}{\sum_{i=1}^{N} (MR_{\exp,i} - MR_{i,\exp mean})^2}$$
(8)

where, $MR_{exp,i}$ is the moisture value obtained in any experimental measurement and $MR_{pre,i}$ is the estimated moisture value for these experimental measurements. $MR_{exp,mean}$ is the mean value of the experimental MR, n is the number of constants and, N is the number of observations [24, 25].

3. Results and Discussion

In this study, thin-layer drying processes were performed using a temperature controlled vacuum drying oven at 50, 60 and 70°C under 50 mbar absolute pressure and the weight data were collected at certain time intervals. The drying curves were fitted to eight different drying models. Nonlinear regression analysis was used to evaluate the results.

The change in the moisture ratio of the mahlab puree depending on the drying time is shown in Figure 1. Experimental data were obtained at varying temperatures ranging from 50°C to 70°C. During the tests performed, depending on the temperature the time to reach the final moisture content was 34, 11 and 8 hours, respectively and all the drying processes were seen to occur in the falling rate period.



Figure 1. Time dependent variation of the moisture ratio for the mahlab puree

Regression analysis was performed by Matlab statistical computer program to investigate the effect of moisture ratio on time. Using eight drying models, the variation of the time-dependent moisture content was formulated as best as possible. Table 2, 3, and 4 show drying model coefficients of drying of mahlab puree at three different temperatures and the comparison criteria used to evaluate goodness of fit, namely the coefficient of determination (R²), the modelling efficiency (EF), the reduced Chi-square (χ^2), the root mean square error (RMSE) and mean bias error (MBE).

Table 2. Mathematical modelling results for 50°C drying temperature

| | 5 5 1 | | | | | |
|---------------------|--------------------------------|-----------------------|---------|----------|----------------|---------|
| Model name | Coefficients | R ² | RMSE | MBE | χ ² | EF |
| Two-Term | k1=0.1093;k2=0.1093; | 0.9814 | 0.05895 | 0.0775 | 0.01275 | 0.89259 |
| | a=-2847;b=2848 | | | | | |
| Henderson and Pabis | a= 1.063 k=0.1701 | 0.9768 | 0.05806 | 0.00676 | 0.00275 | 0.97678 |
| Newton | k=0.1601 | 0.9727 | 0.05975 | -0.00014 | 0.00324 | 0.97268 |
| Page | k =0.05833 n=1.537 | 0.9972 | 0.02004 | -0.00017 | 0.00032 | 0.99723 |
| Logarithmic | a=1.079; c =-0.01954; k=0.1634 | 0.9779 | 0.06013 | -0.00011 | 0.00262 | 0.97786 |
| Wang and Singh | a =-0.1026; b =0.00226 | 0.9415 | 0.09220 | 0.01018 | 0.00695 | 0.94143 |
| Verma et al. | a =11.43;g =0.3521; k = 0.3223 | 0.9955 | 0.02700 | 0.00079 | 0.00053 | 0.99553 |
| Midilli et al. | a =0.9841;b = 0.000203 | 0.9975 | 0.02141 | 0.00028 | 0.00029 | 0.99754 |
| | k = 0.05244; n = 1.586 | | | | | |

Table 3. Mathematical modeling results for 60°C drying temperature

| Model name | Coefficients | R ² | RMSE | MBE | χ ² | EF |
|---------------------|-----------------------------------|-----------------------|---------|----------|----------------|---------|
| Two-Term | k1=0.2372;k2=0.2355; | 0.9705 | 0.07266 | 0.00744 | 0.00353 | 0.97040 |
| | a=43.34;b =-42.25 | | | | | |
| Henderson and Pabis | a= 1.088 ;k=0.3051 | 0.9643 | 0.07146 | 0.01859 | 0.00425 | 0.96434 |
| Newton | k = 0.2839 | 0.9561 | 0.07562 | 0.00864 | 0.00524 | 0.95607 |
| Page | k =0.1231;n = 1.576 | 0.9967 | 0.02182 | 0.00689 | 0.00039 | 0.99668 |
| Logarithmic | a = 1.226; c = -0.1746 ;k =0.2127 | 0.9855 | 0.04804 | -0.00026 | 0.00173 | 0.98549 |
| Wang and Singh | a = -0.2029;b = 0.01014 | 0.9944 | 0.02834 | -0.00572 | 0.00066 | 0.99438 |
| Verma et al. | a = -8.744;g = 0.1312 ;k = 0.1196 | 0.9845 | 0.04971 | -0.00655 | 0.00185 | 0.98445 |
| Midilli et al. | a = 0.9821;b =-0.001886 | 0.9977 | 0.02031 | 0.00020 | 0.00027 | 0.99770 |
| | k = 0.117;n =1.574 | | | | | |

Hilal İsleroğlu, Gökhan Gürlek Mathematical Modelling of Vacuum Drying Characteristics For Mahlab Puree

| Model name | Coefficients | R ² | RMSE | MBE | χ ² | EF |
|---------------------|---|-----------------------|---------|----------|----------------|---------|
| Two-Term | a = 2.046;b = -1; | 0.9849 | 0.05871 | -0.00045 | 0.00191 | 0.98494 |
| | k ₁ =0.2394; k ₂ = 0.1308 | | | | | |
| Henderson and Pabis | a =1.073; k = 0.4251 | 0.9633 | 0.07745 | 0.019320 | 0.00466 | 0.96332 |
| Newton | k =0.4012 | 0.9572 | 0.07822 | 0.009667 | 0.00543 | 0.95725 |
| Page | k =0.2009;n = 1.627 | 0.9979 | 0.0184 | 0.005129 | 0.00026 | 0.99793 |
| Logarithmic | a =1.208; c = -0.1613;k = 0.3039 | 0.983 | 0.05702 | 0.000185 | 0.00216 | 0.98296 |
| Wang and Singh | a = -0.2861;b = 0.02011 | 0.9935 | 0.03272 | -0.00602 | 0.00083 | 0.99345 |
| Verma et al. | a =6.31; g = 0.1637;k =0.1897 | 0.9828 | 0.05727 | -0.00757 | 0.00218 | 0.98281 |
| Midilli et al. | a =0.9901; b = -0.001836 | 0.9984 | 0.01912 | 0.000313 | 0.00020 | 0.99840 |
| | k = 0.1961;n = 1.617 | | | | | |

Table 4. Mathematical modeling results for 70°C drying temperature

Figure 2 shows the comparison of the predicted and experimental moisture ratios for the Midilli et al. model for vacuum drying for 50°C, 60°C and 70°C drying temperature respectively.

According to three different drying temperatures, the Midilli model showed good conformity between experimental and predicted moisture ratios. The predicted data is usually banded around the flat line, indicating the suitability of this model for describing the vacuum drying behavior of the mahlab puree.



Figure 2. Comparison of predicted and experimental moisture ratios for 50°C, 60°C and 70°C drying temperature

The effective diffusivity values generally are in the range of $10^{-9}-10^{-11}$ m²/s [26]. The results found in studies done in the literature are also in this direction. Values like $1.383x10^{-9}$ to $4.145x10^{-9}$ m²/s for pumpkin, $1.31x10^{-9}$ to $1.07x10^{-9}$ m²/s for organic tomato, $5.42x10^{-11}$ to $9.29x10^{-10}$ m²/s for pistachio nuts can be given as examples [9, 27]. Doymaz [28] presented that the effective diffusivity values change from $5.65x10^{-10}$ to $7.53x10^{-10}$ m²/s for different temperatures. In this study, the effective diffusion coefficients were found as $1.71x10^{-10}$, $6.21x10^{-10}$ and $8.64x10^{-10}$ m²/s at 50°C, 60°C and 70°C respectively.

Activation energy can vary depending on the structure of the dried product and the thickness of the product. The activation energy can be calculated from the slope of Arrhenius plot and expresses the sensitiveness of the food material to temperature changes during the drying process. Figure 3 shows the ln (D_{eff}) values as a function of absolute temperature.



Figure 3. Temperature dependence of effective diffusion coefficient

The activation energy was calculated as 74.79 kJ/mol. The values of activation energy in food generally vary between 12.32-83.93 kJ/mol according to the drying process applied and the structure of food [29]. The value of activation energy obtained in the current study was found to be in accordance with the literature. In different studies activation energy values were determined as 41.6-49.5 kJ/mol for tarhana dough, 24.512 kJ/mol for apple pulp, 21.30 kJ/mol for olive pulp and 10.3-21.7 kJ/mol for grape pulp [16, 30, 31, 32].

4. Conclusion

The mahlab pure was dried as a thin layer in a vacuum drier and the drying process was explained by different mathematical models. It has been determined that the model which expressed the process best in all drying conditions is the Midilli et al. model. Diffusion coefficient and activation energy values obtained for the drying of mahlab pure were in accordance with studies done with different products in the literature. The results obtained from this study would be useful for drying applications concerning mahlab which has potential use in fruit bars.

5. References

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