Experimental study and mathematical modeling of thin layer drying of rhubarb (Rheum ribes L.)

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**Abstract**

In this study rhubarb stem slices were dried as single layers with thickness of 3 mm in the inlet air temperature range of 50-70°C and air velocity of 1 ± 0.2 m/s in a laboratory scale cabinet dryer. The effect of drying air temperature on the drying characteristics was determined and the relationship between the drying parameters with temperature and moisture content was examined. Moisture transfer from rhubarb slices was described by applying the Fick's diffusion model. The effective diffusivity changes between 4.56×10\(^{-11}\) and 15.97×10\(^{-11}\) m\(^2\)/s within the given temperature range and as the temperature increased so did the effective moisture diffusivity. An Arrhenius relation with activation energy values of 57.4638 kJ/mol expressed the effect of temperature on the diffusivity. The experimental moisture loss data were fitted through 10 thin-layer drying models available in the literature. The models were compared based on the coefficient of determination, mean bias error, root mean square error, and the reduced chi-square between the observed and predicted moisture ratios. The Midilli et al. model has shown a better fit to the experimental drying data as compared to other models.

**Keywords:** Activation energy, Drying models, Effective diffusivity, Rhubarbs slices, Thin-layer drying

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1. Introduction

Although rhubarb is botanically a vegetable, it is used as a fruit. Except for its pink color, rhubarb is similar in appearance to celery. The acidity and intensity of flavors vary, and young stalks are more tender than older stalks. The roots and leaves of rhubarb are not eaten because they contain significant amounts of oxalic acid and are highly poisonous (Dole Food Company, 2002). Much of the history of cultivation of rhubarb is related to its use as a medicinal plant. The earliest recorded use of rhubarb for medicinal purposes appeared in 2700 B.C. Marco Polo was the first to introduce rhubarb to Europe. Although rhubarb stalks were eaten in Iran and Turkey as early as the 13th century, it was not until the 18th century that Europeans began to use rhubarb as a food. Rhubarb contains a good amount of antioxidant and various vitamins including A, B\(_1\), B\(_2\) and C. Additionally, rhubarb maintains various elements, such as potassium, magnesium, calcium and some organic acids like citric acid and malic acid (Ozturk, 2007). In Iran, it is mostly eaten fresh or is cooked with some sugar to be used in pie filling or jam, but, due to its antioxidant activity, could be consumed as functional seasoning, if dried and milled.

Over the years, many research studies have been made on the drying of different agricultural products. Sacilik and Elicin (2006) studied the drying process of apples. They dried 5- and 9 millimeter-thick layers of apple at 40 and 60°C with an air velocity of 1 m/s. The linear regression of the logarithmic model seemed to best describe their experimental results. Doyraz (2004c) studied the drying process of 0.5 cm thick layers of carrot at 50 to 70°C and drying air flow rate of between 0.5-1 m/s. The results were satisfactorily fitted by the page model. Zare et al. (2009) carried out thin layer drying of pomegranate kernels at various temperature and air relative humidity. Their experimental findings best described by the Two Term Exponential model. Ertek and Yaldiz (2004) applied thin layer drying to eggplant slices at temperatures between 30 and 70°C and air velocities ranging between 0.5 and 2 m/s. The Midilli et al model best described the data with the least errors. Simal et al. (2005) compared and evaluated the page, diffusion approximation and exponential models for the drying of layers of kiwi fruit. Goyal et al. (2008) used 6 well-known mathematical models to describe the thin layer drying of apple slices. In this case,
the logarithmic model best described the drying behavior. Several investigators have proposed numerous mathematical models for the thin layer drying of various vegetables or fruits; apricot (Togrul & Pehlivan, 2002), plum (Doyraz, 2004a), green pepper, stuffed pumpkin, green bean and onion (Yaldiz & Ertekin, 2001), carrot (Doyraz, 2004c), potato (Akpınar et al., 2003a), mulberry (Maskan & Gogus, 1998; Doyraz, 2004d), red pepper (Doyraz & Pala, 2002; Akpınar, Bicer, & Yildiz, 2003). However, a few published data is available on experimental drying of rhubarb stem. In the present study rhubarb slices from North Eastern region of Iran were thin layer dried at constant air velocity and varying air temperature. The drying kinetics was studied and the data was fitted to 10 well known drying models to determine the best fit and to compute effective moisture diffusivity and activation energy of samples.

2. Material and Methods

2.1. Raw material

The rhubarb stems were hand-picked from the hills surrounding Sabzevar, a city in the North East of Iran. The stems were cleaned off from mud and dirt. They were kept refrigerated at 4±1°C until their use for the drying experiment. Rhubarb stems were washed with cold water and then, cut manually into 3 mm thick slices using a sharp knife.

2.2. Drying procedure

The initial moisture content of rhubarb was 584.93% (dry basis) (AOAC, 2000). The slices were weighed and without applying any pretreatment were placed evenly as a thin layer on the tray of a cabinet dryer, equipped with flow and temperature control system (Hi Tech Dryer – FD-02, Iran). The drying process was carried out at three air temperatures; 50, 60 and 70°C which was controlled in automatically, using a PID controller. The air velocity was kept constant at 1± 0.2 m/s, which was measured by a digital hot wire anemometer (Lutron, Model AM4204, Taiwan). During each experimental run, the moisture reduction (by weight reduction of samples) was determined at 10 minutes intervals (for the first 2 h) and at 20 min intervals thereafter, till the end of the experiment. At the end of each experimental run, the dried samples were stored in desiccators for 10 min prior to final moisture content measurement. All experiments were carried out in triplicate.

2.3. Mathematical modeling

The Moisture ratio (MR) of the samples during drying was expressed by the following equation:

\[ MR = \frac{M - M_e}{M_0 - M_e} \]  

(1)

In this equation, the moisture content of samples compared to their initial moisture content, the equilibrium moisture content and the moisture content at a time are calculated at any time during the drying process (Goyal et al., 2008). However, the MR was simplified to \( M/M_0 \) instead of \( (M - M_e) / (M_0 - M_e) \) as the value of \( M_e \) is relatively small compare to \( M \) or \( M_0 \) (Goyal et al., 2008). All the statistical analyses, including linear and non-linear regression analysis, MBE, RMSE and \( \chi^2 \) factors, were performed using Sigma Plot software (Statistical Package, version 10.0). Correlation coefficient (R²) was one of the primary criteria to select the best model. Other statistical parameters such as chi-square (\( \chi^2 \)), mean bias error (MBE) and root mean square error (RMSE) were used to determine the quality of the fit. In general, for achieving a high quality fit, R² value should be higher, and \( \chi^2 \), MBE and RMSE should be lower (Guarte, 1996; Goyal et al. 2008; Ertekin & Yaldiz, 2004). Ten most widely used models of thin layer drying described in Table 1, were used to analyze the experimental data in order to find the most suitable drying model for the drying process of rhubarb slices. The results were compared to determine a suitable model for describing the drying process of rhubarb. \( a, b, c, n, k \) and \( k_i \) were empirical constants in drying models and \( Z \) was number of drying constants. These parameters were calculated using the following equations:

\[ X^2 = \frac{\sum_{i=1}^{N} (MR_{exp,i} - MR_{pre,i})^2}{N - z} \]  

(2)

\[ MBE = \frac{1}{N} \sum_{i=1}^{N} (MR_{pre,i} - MR_{exp,i}) \]  

(3)

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

(4)

2.4. Moisture diffusivity and activation energy

To calculate the effective moisture diffusivity, Fick’s diffusion equation was used.

\[ MR = \frac{8}{\pi^2} \exp\left(-\pi^2 \frac{D_{eff} t}{L^2}\right) \]  

(5)

By plotting Ln (MR) versus experimental drying time and evaluating the slope, the effective moisture diffusivity, \( D_{eff} \), was obtained (Goyal et al., 2008; Maskan et al., 2002; Doyraz, 2004a). \( D_{eff} \) may be related to temperature through Arrhenius equation.

\[ D_{eff} = D_0 \exp\left(-\frac{E_a}{RT}\right) \]  

(6)

In the same way, the activation energy can be determined from the slope of the line made by plotting data in terms of Ln (\( D_{eff} \)) versus 1/T (Lee & Kim, 2008).

3. Results and Discussion

3.1. Drying behavior of rhubarb slices

The rhubarb slices with initial moisture content of 584.93% (dry basis) was dried to a final moisture content of about 19% d. b. The drying time required to reach the final moisture content were 240, 180 and 130 min at the drying air temperatures of 50, 60 and 70°C respectively. The samples dried at 70°C enjoyed the shortest drying time and the fastest drying rate (Fig. 1). The drying air temperature had an important effect on the drying of the rhubarb slices. This is due to the fact that at higher drying air temperatures the water vapor pressure within the rhubarb slices increases initiating easier moisture movement. Similar observations have been reported for drying of apple slices (Goyal et al., 2008) and onion slices (Sarsavadia et al., 1999).
Table 1. Mathematical models applied to the drying curves.

<table>
<thead>
<tr>
<th>No</th>
<th>Name of model</th>
<th>Model</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Newton</td>
<td>$\text{MR} = \exp(-kt)$</td>
<td>Ayensu (1997), Liu and Bakker-Arkema (1997)</td>
</tr>
<tr>
<td>2</td>
<td>Page</td>
<td>$\text{MR} = \exp(-kt^n)$</td>
<td>Page (1949), Doymaz (2004d), Park et al., (2002)</td>
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<tr>
<td>3</td>
<td>Modified Page</td>
<td>$\text{MR} = \exp(-(kt)^n)$</td>
<td>Overhults et al. (1973)</td>
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<td>4</td>
<td>Henderson and Pabis</td>
<td>$\text{MR} = a \exp(-kt)$</td>
<td>Henderson and Pabis (1961), Chhinnan (1984)</td>
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<td>5</td>
<td>Logarithmic</td>
<td>$\text{MR} = a \exp(-kt)+c$</td>
<td>Yaldiz et al. (2001)</td>
</tr>
<tr>
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<td>Two-term exponential</td>
<td>$\text{MR} = a \exp(-kt) + b \exp(-kt_1)$</td>
<td>Dandamrongrak et al. (2002), Madamba et al. (1996)</td>
</tr>
<tr>
<td>7</td>
<td>Two-term exponential</td>
<td>$\text{MR} = a \exp(-kt) + (1 - a)\exp(-kt_1)$</td>
<td>Ertekin and Yaldiz (2004)</td>
</tr>
<tr>
<td>8</td>
<td>Wang and Singh</td>
<td>$\text{MR} = 1+ at + bt^2$</td>
<td>Wang and Singh (1978)</td>
</tr>
<tr>
<td>9</td>
<td>Midilli et al.</td>
<td>$\text{MR} = a \exp(-kt^2) + bt$</td>
<td>Ertekin and Yaldiz (2004), Midilli et al. (2002)</td>
</tr>
<tr>
<td>10</td>
<td>Diffusion approximation</td>
<td>$\text{MR} = a \exp(-kt) + (1 - a)\exp(-kbt)$</td>
<td>Ertekin and Yaldiz (2004)</td>
</tr>
</tbody>
</table>

Fig. 1. Experimental and predicted moisture ratio changes with drying time at different drying temperatures for Midilli model.

Fig. 2. Experimental and predicted moisture ratio at different drying temperatures for Midilli model.

3.2. Mathematical modeling of drying curves

Once the experimental drying data for drying of rhubarb slices at 50, 60 and 70°C were obtained (Fig. 1), the moisture ratio data were fitted into the 10 thin layer drying models previously introduced in Table 1. The constants in drying models which were tabulated were in Table 1 were determined and correlated with drying air temperature. The coefficients of correlation and results of statistical analysis are listed in Table 2. In all cases, the $R^2$ values for the models were greater than 0.95, indicating a good fit (Goyal et al., 2008). Furthermore, $R^2$ of greater than 0.99 in Page, Modified Page, Newton, Logarithmic, Two Term, Two Term
Exponential and Midilli et al give them some edge over other models which examined in this study. Nevertheless, the results show that the highest values of $R^2$ and lowest values of $\chi^2$, MBE and RMSE at all drying temperatures were achieved for Midilli et al model. On these accounts, it is believed that the Midilli et al model represents and successfully predicts the drying process for thin layer drying of rhubarb slices for the process conditions stated in the Materials and Methods section. A similar conclusion was drawn by Menges and Ertekin (2005) for drying apricots. Fig. 1 shows the experimental data and predicted data based on Midilli et al model for drying of rhubarb slices versus drying time. The predicted data band around the experimental data indicating the suitability of the model in describing the thin layer drying of rhubarb slices in temperature ranges of 50 to 70°C.

The results indicate that in the first 15 min of the drying process, the changes in the moisture ratio for all the three temperatures investigated were almost similar, most likely because the product temperature was being adjusted to the temperature of drying chamber in this period (settle down period). However, further into the drying, e.g. at 50 min, the moisture ratio at 70°C was almost 3 times lower than those at 50°C indicating the faster dehydration rate at higher temperature. This finding is similar to those reported by Yaldiz et al. (2001) for drying sultana grapes. Fig. 2 emphasizes the applicability of the Midilli et al model for these data sets, as the predicted moisture ratio lied around the experimental values for all three temperatures. Ertekin and Yaldiz (2004) found the same results for drying of eggplant in a thin layer drying experiment.

3.3. Calculation of effective moisture diffusivity

Once the effective moisture diffusivity for three temperatures was determined through calculating the slope of the line formed by plotting experimental drying data in terms of Ln (MR) versus drying time (Lee & Kim, 2008). Table 3 summarizes the data related to $R^2$ and effective moisture diffusivity. The results of the study showed that as the temperature increased so did the effective moisture diffusivity. These results are closely compatible with those reported by Goyal et al. (2008) in thin layer drying of apple slices at 50 to 70°C range with or without pretreatment. Maskan et al. (2002) tabulated effective moisture diffusivity of between $10^{-8}$ to $10^{-11}$ m$^2$/s for variety of foodstuffs.

The effect of temperature on the effective moisture diffusivity is shown by Eq. 6 (Arrhenius equation). Equ. (7) represents equation of a line which obtained by plotting Ln (D$_{eff}$) versus reciprocal of drying temperature (1/T) in the temperature range 50-70°C.

This line had an $R^2$ value of 0.9532, the slope of which shows the activation energy. The activation energy for the drying conditions stated previously in drying of a 3 mm thick rhubarb slices was found to be 57.4638 kJ/mol. The value was close to those reported by Gogus and Maskan (1999) for okra (51.26 kJ/mol), Lee and Kim (2008) reported values of 16.49 and 20.26 kJ/mol respectively. When drying 4 and 6 mm thick layer of radish. Other investigators reported values for different fruit and vegetables; Kaya et al. (2007) for apple slices (19.96-22.62 kJ/mol), and Kaymak-Ertekin (2002) for green pepper (51.4 kJ/mol).

Table 2. Results of statistical analyses on the thin layer drying of Rhubarb (DT is drying temperature (°C)).

<table>
<thead>
<tr>
<th>no</th>
<th>DT</th>
<th>Model Constants</th>
<th>$R^2$</th>
<th>$x^2$</th>
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<tr>
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<tr>
<td>50</td>
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<td>0.00021</td>
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<td>0.0138</td>
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<td>2</td>
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<td>0.00238</td>
<td>13.420</td>
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<td>7.6968</td>
<td>0.0185</td>
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<tr>
<td>50</td>
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<td>0.00021</td>
<td>5.1455</td>
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4. Conclusion

The drying kinetics of rhubarb slices were investigated in a thin layer of 3 mm at the drying air temperatures of 50, 60 and 70°C in a cabinet dryer. Constant drying rate period was not observed, the rhubarb drying occurring in the falling rate period. The moisture content and drying rate were influenced by the drying air temperature. An increase in the drying air temperature caused a decrease in the drying time and an increase in the drying rate. The effective diffusivity increased with the increase in the drying air temperature. Based on the analysis carried out among 10 mathematical models, the Midilli et al model was considered most adequate to describe the thin-layer drying behavior of rhubarb slices. The values of calculated effective diffusivity varied from about 4.56 ×10^{-9} to 15.97 ×10^{-9} m²/s over the temperature range. The effective diffusivity increases as temperature increases. Temperature dependence of the diffusivity values was described by an Arrhenius-type relationship. The activation energy for moisture diffusion was found as 57,4638 kJ/mol.

Acknowledgment

The authors would like to thank Dr. K. Lessan for editing the manuscript.

Nomenclature

\[ \chi^2 \] reduced chi-square
\[ a, b, c, n, k \] empirical constants in drying models
\[ D_{eff} \] effective moisture diffusivity, m²/s
\[ K \] drying constant
\[ L \] thickness of slice, m
\[ M \] moisture content at time t, kg moisture.kg⁻¹ dry matter
\[ MBE \] mean bias error
\[ M_e \] equilibrium moisture content, kg moisture.kg⁻¹ dry matter
\[ M_i \] initial moisture content, kg moisture.kg⁻¹ dry matter
\[ MR \] dimensionless moisture ratio
\[ MRexp \] expected moisture ratio
\[ MRpre \] predicted moisture ratio
\[ N \] number of observations
\[ R^2 \] coefficient of determination
\[ RMSE \] root mean square error
t drying time, min
\[ Z \] number of drying constants
\[ T \] absolute temperature (K)
\[ R \] universal gas constant (8.314 kJ/kmol -K)
\[ E_a \] activation energy (kJ/mol)
\[ D_0 \] pre-exponential factor of Arrhenius equation (m²/s)
\[ Y \] Ln (D_{eff})
\[ X \] 1/T

Table 3. Effective moisture diffusivity for drying of Rhubarb slices.

<table>
<thead>
<tr>
<th>Drying temperature (°C)</th>
<th>D_{eff} (m²/s)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0456 ×10⁻⁹</td>
<td>0.9838</td>
</tr>
<tr>
<td>60</td>
<td>0.0684 ×10⁻⁹</td>
<td>0.9868</td>
</tr>
<tr>
<td>70</td>
<td>0.1597 ×10⁻⁹</td>
<td>0.9874</td>
</tr>
</tbody>
</table>

References


Page, GE. (1949). Factors influencing the maximum of air drying shelled corn in thin layer. Indiana: Purdue University.


