

Study on Effective moisture diffusivity, activation energy and mathematical modeling of thin layer drying kinetics of bell pepper

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Abstract

Thin-layer drying kinetics of bell pepper was experimentally investigated in a laboratory scale convective dryer. Experiments were performed at air temperatures of 40, 50, 60, 70, and 80°C and constant air velocity of 2 m/s. In order to select a suitable form of the drying curve, 12 different thin layer drying models were fitted to experimental data. The high values of coefficient of determination and the low values of reduced chi-square and root mean square error indicated that the Logarithmic model could satisfactorily illustrate the drying curve of bell pepper. The Logarithmic model had the highest value of R^2 (0.9929), the lowest χ^2 (0.00003497) and RMSE (0.00481743). The Logarithmic model was found to satisfactorily describe the drying behavior of bell pepper. Fick's second law was used to calculate the Effective moisture diffusivity. The moisture diffusion coefficient varied between 1.7×10^{-9} and 11.9×10^{-9} m²/s for the given temperature range and corresponding activation energy was 44.49 kJ/mol.

Introduction

The bell pepper is utilized world-wide either as a food or as a flavor. There are high losses due to storage problems, marketing and the lack of suitable processing technologies. According to the USDA National Nutrient Database (2006), the nutritional composition of green sweet peppers in raw state, per 100g of edible portion is 93.89g of water, 0.86g of protein, 0.17g total lipids, 6.64g of carbohydrate, 2.40g total sugars, 1.70g total dietary fiber and 0.43g of ash. The potassium (175mg/ 100g) was the most abundant element in this vegetable, followed by potassium (277-296 mg 100g-1), phosphorous (20mg/ 100g), calcium (10mg/ 100g) and iron (0.34mg/100g). The amounts of total ascorbic acid (vitamin C) is 80.4mg/100g and vitamin A is 370 IU/100g of edible portion (Faustino et al., 2007). Therefore, the bell-pepper is used to prepare soaps and stews due to high amounts of vitamins, minerals and energy. The reduction of moisture is one of the oldest techniques for food preservation. Mechanical and thermal methods are two basic methods to remove the moisture in a solid material (Karimi, 2010). Raw foods have high amount of moisture and thus perishable. Many applications of drying have been successfully applied to decrease physical, biochemical and microbiological deterioration of food products due to the reduction of the moisture content to the level, which allows safe storage over a long period and brings substantial reduction in weight and volume, minimizing packaging, storage and transportation costs (Zielinska and Markowski, 2010).

The principle of modelling is based on having a set of mathematical equations which can satisfactorily explain the system. The solution of these equations must allow calculation of the process parameters as a function of time at any point in the dryer based only on the primary condition (Kaleta and Górnicki, 2010). Hence, the use of a simulation model is an important tool for prediction of performance of drying systems.

The objective of this research was the evaluation and the modeling of the drying kinetics of mass transfer during the hot-air drying process of bell pepper, and the analysis of the influence of temperature on the kinetic constants of the proposed models. Also, the Effective moisture diffusivity and

activation energy of bell pepper cultivated in Iran were determined.

Materials and methods

Samples preparation and drying unit

Drying experiment was performed using laboratory scale dryer which was designed and developed in the Department of Agricultural Machinery at University of Tehran. A portable, 0-10 m/s range digital anemometer (TESTO, 405-V1) was used to measure passing air flow velocity through the system. The airflow was adjusted by a variable speed blower. The heating structure was consisted of four heating elements placed inside the canal. Moreover, a simple control algorithm was used to control and adjust the drying chamber temperature. The used measuring instruments with their specifications are given in (Table 1). The airflow control unit was regulated the velocity of the drying air flowing through the 30 cm diameter drying chamber. The dryer is capable of providing any desired drying air temperature in the range of 20 to 120 °C and air velocity in the range of 0.1 to 3.0 m/s with high accuracy. After turning on the computer, fan, scale, elements and data acquisition system, the essential velocity for the fan was set. A manual sensor (TESTO 405-V1) was used to measure the velocity. The control software was implemented and the required temperature for the experiment was adjusted. Experiments were carried out 20 minutes after the system was turned on to reach to its steady state condition. After that, the tray holding the samples is carefully put in the dryer. Prior to drying, samples were taken out of storage, bell pepper were washed and sliced in thickness of 3mm using a cutting machine (Faustino et al., 2007). About 100 g of bell pepper slices were weighed and uniformly spread in a tray and kept inside the dryer. Three replications of each experiment were performed according to a pre-set air temperature and time schedule. The reproducibility of the experiments was within the range of $\pm 5\%$. The hot air drying was applied until the weight of the sample reduced to a level corresponding to moisture content of about 0.5% d.b. The drying experiment was conducted at five air temperatures of 40, 50, 60, 70 and 80°C and constant air velocity of 2.0 m/s.

Table 1. Specifications of measurement instruments including their rated accuracy

| Instrument | Model | Accuracy | Make |
|-----------------|------------|----------|-------------|
| Digital balance | GF3000 | ±0.02 | A&D, Japan |
| T-sensor | LM35 | ±1°C | NSC, USA |
| RH-sensor | Capacitive | ±3% | PHILIPS, UK |
| V-sensor | 405-V1 | ±3% | TESTO, UK |

Table 2. Thin layer drying curve models considered.

| Mode no. | Model name | Model | References |
|----------|------------------------------|---|------------------------------|
| 1 | Newton | $MR = \exp(-kt)$ | (Henderson, 1974) |
| 2 | Page | $MR = \exp(-kt^n)$ | (Guarte, 1996) |
| 3 | Henderson and Pabis | $MR = a \exp(-kt)$ | (Zhang and Litchfield, 1991) |
| 4 | Aghbashlo et al | $MR = \exp(-k_1t/1+k_2t)$ | (Aghbashlo et al., 2009) |
| 5 | Logarithmic | $MR = a \exp(-kt) + c$ | (Karathanos, 1999) |
| 6 | Tow term | $MR = a \exp(-k_0t) + b \exp(-k_1t)$ | (Yaldiz et al., 2001) |
| 7 | Tow- term exponential | $MR = a \exp(-kt) + (1 - a) \exp(-kat)$ | (Yaldiz et al., 2001) |
| 8 | Wang and Singh | $MR = 1 + at + bt^2$ | (Wang and Singh, 1978) |
| 9 | Diffusion approach | $MR = a \exp(-kt) + (1 - a) \exp(-kbt)$ | (Karathanos, 1999) |
| 10 | Modified Henderson and Pabis | $MR = a \exp(kt) + b \exp(gt) + c \exp(ht)$ | (Karathanos, 1999) |
| 11 | Verma et al. | $MR = a \exp(-kt) + (1 - a) \exp(-gt)$ | (Verma et al., 1985) |
| 12 | Midilli et al. | $MR = a \exp(-kt^n) + bt$ | (Midilli et al., 2002) |

The moisture content of the dried materials at the end of the drying cycles was found by vacuum drying at 70 °C for 24 h. Weight reduction due to longer temperatures and times of drying is not only due to water evaporation but also, partial sugar decomposition to water vapor and carbon dioxide (Tunde-Akintunde et al., 2005).

Mathematical modeling of drying curves

The moisture ratio (MR) of bell pepper during drying experiments was calculated using the following Equation:

$$MR = \frac{M_d - M_e}{M_0 - M_e} \quad (1)$$

Where M , M_0 , and M_e are moisture content at any drying time, initial and equilibrium moisture content (kg water/kg dry matter), respectively. The values of M_e are relatively little compared to those of M or M_0 , the error involved in the simplification is negligible (Aghbashlo et al., 2008), thus moisture ratio was calculated as:

$$MR = \frac{M_d}{M_0} \quad (2)$$

For drying model selection, drying curves were fitted to 12 well known thin layer drying models which are given in (Table 2). The best of fit was determined using three parameters: higher values for coefficient of determination (R^2), reduced chi-square (χ^2) and root mean square error (RMSE) using Equations (3-5), respectively. The statistical analyses were carried out using SPSS 15 software.

$$R^2 = 1 - \frac{\sum_{i=1}^N (MR_{per,i} - MR_{exp,i})^2}{\sum_{i=1}^N (MR_{per,i} - MR_{exp,i})^2} \quad (3)$$

$$\chi^2 = \frac{\sum_{i=1}^n (MR_{exp,i} - MR_{pre,i})^2}{n - N} \quad (4)$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^n (M_{exp,i} - M_{pre,i})^2 \right]^{1/2} \quad (5)$$

In the above Equations $MR_{pre,i}$ is the i th predicted moisture ratio, $MR_{exp,i}$ is the i th experimental moisture ratio, N is number of observations and m is number of constants.

Calculation of Effective moisture diffusivity and activation energy

Drying process of food materials generally occurs in the falling rate period. To predict the moisture transfer during this period, several mathematical models have been proposed using Fick's second law. Crank proposed Eq. (6) using Fick's second law and considering following assumptions, for the effective Effective moisture diffusivity of an infinite slab (Crank, 1975):

- (1) Moisture is initially distributed uniformly throughout the mass of a sample.
- (2) Mass transfer is symmetric with respect to the center.
- (3) Surface moisture content of the sample instantaneously reaches equilibrium with the condition of surrounding air.
- (4) Resistance to the mass transfer at the surface is negligible compared to internal resistance of the sample.
- (5) Mass transfer is by diffusion only.
- (6) Diffusion coefficient is constant and shrinkage is negligible.

$$MR = \frac{M}{M_0} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left(-\frac{(2n-1)^2 \pi^2 Dt}{4L^2}\right) \quad (6)$$

Where M_0 is the initial moisture content (kg water/kg dry solid), MR is moisture ratio, M is the moisture content at any time (kg water/kg dry matter), $n = 1, 2, 3, \dots$ the number of terms taken into consideration, t is the time of drying in second, D is effective Effective moisture diffusivity in m^2/s and L is the thickness of slice (m).

Only the first term of Eq. (4) is used for long drying times (Lopez et al., 2000), hence:

$$MR = \frac{8}{\pi^2} \exp\left(-\frac{\pi^2 Dt}{4L^2}\right) \quad (7)$$

The slope (k_0) is calculated by plotting $\ln(MR)$ versus time according to Eq. (3):

$$k_0 = \frac{\pi^2 D}{4L^2} \quad (8)$$

The energy of activation was calculated by using an Arrhenius type equation (Lopez et al., 2000):

$$D = D_0 \exp\left(-\frac{E_a}{RT_a}\right) \quad (9)$$

Where E_a is the energy of activation (kJ/mol), R is universal gas constant (8.3143 kJ/mol), T_a is absolute air temperature (K), and D_0 is the pre-exponential factor of the Arrhenius equation (m^2/s).

The activation energy can be calculated from the slope of the Arrhenius plot, $\ln(D)$ versus $1/T_a$.

From Eq. (4), a plot of $\ln(D)$ versus $1/T_a$ gives a straight slope of K_1

$$K_1 = E_a/R \quad (10)$$

The drying process was stopped after no further change in weights was observed. At this point moisture content decreased from 91.49 % to 10 % (w.b.). Moisture content data were converted to moisture ratio and then fitted to the 12 thin layer drying models Table 3 showed that the results of fitting the experimental data to the thin layer drying models listed in Table 2 (R^2 , RMSE and χ^2). The best-fitting model for air velocity 2 m/s was bolded in Table 3. criterion for selection of the best model describing the thin layer drying kinetics was according to the highest R^2 average values, and the lowest RMSE and χ^2 average values.

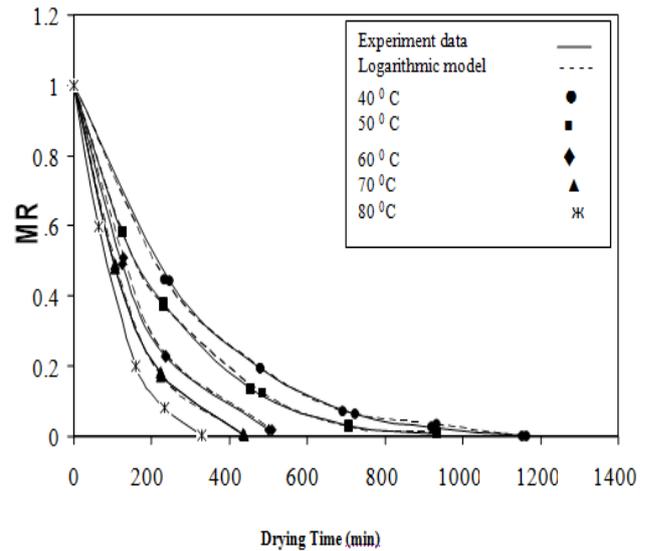


Fig 1. Experimental and predicted moisture ratio by the logarithmic model versus drying time for air velocity of 2m/s.

Table 3. Statistical results obtained from the selected models

| Model name | R^2 | χ^2 | RMSE |
|------------------------------|--------|------------|------------|
| Newton | 0.9353 | 0.0040997 | 0.015932 |
| Page | 0.9405 | 0.00023023 | 0.0097473 |
| Henderson and Pabis | 0.9368 | 0.007643 | 0.01399406 |
| Modified Henderson and Pabis | 0.9368 | 0.00077321 | 0.1396621 |
| Logarithmic | 0.9929 | 0.00003497 | 0.00481743 |
| Tow term | 0.9369 | 0.00028082 | 0.0275882 |
| Tow- term exponential | 0.9413 | 0.00045338 | 0.0443283 |
| Diffusion approach | 0.9407 | 0.0008964 | 0.00681063 |
| Midilli et al. | 0.9912 | 0.00049553 | 0.00656423 |
| Werma et al | 0.9411 | 0.00069483 | 0.00846807 |
| Wang and Singh | 0.9634 | 0.00033568 | 0.00496631 |
| Aghbashlo et al | 0.9443 | 0.00067329 | 0.00553321 |

Table 4. Values of the drying constant and coefficients of the best model (logarithmic model)

| Temperature (°C) | R^2 | a | k(min^{-1}) | c |
|------------------|--------|-------------|-----------------|--------------|
| 40 | 0.9994 | 1.016281177 | 0.00395397 | -0.024216629 |
| 50 | 0.9926 | 1.003662826 | 0.004777381 | -0.02500799 |
| 60 | 0.9872 | 1.063656664 | 0.00761588 | -0.028768061 |
| 70 | 0.9952 | 1.112475033 | 0.007515769 | -0.101449538 |
| 80 | 0.9902 | 1.106159964 | 0.009382973 | -0.086065374 |

$$MR = a \exp(-kt) + c$$

Table 5. Estimated effective moisture diffusivity

| Temperature (°C) | $D_{we}(m^2s^{-1})$ | R^2 |
|------------------|--|--------|
| 40 | $1.7 \times 10^{-9} \pm 0.4 \times 10^{-9}$ | 0.9949 |
| 50 | $3.5 \times 10^{-9} \pm 0.8 \times 10^{-9}$ | 0.9923 |
| 60 | $7.1 \times 10^{-9} \pm 1.1 \times 10^{-9}$ | 0.9911 |
| 70 | $10.7 \times 10^{-9} \pm 0.9 \times 10^{-9}$ | 0.9933 |
| 80 | $11.9 \times 10^{-9} \pm 0.7 \times 10^{-9}$ | 0.9959 |

Therefore, the best model for this quantity of air velocity are Logarithmic with 0.9929, 0.00481743 and 0.00003497; values for R^2 , RMSE and χ^2 , respectively. The constants of Logarithmic model are presented in Table 4 for different drying conditions. Figure 1 present the variation of experimental and predicted moisture ratio using the best

models with drying time for dried bell pepper. the Logarithmic. Model gives a good estimation for the drying process. As can be seen from Figure 1, by increasing air temperature, a decrease in drying time was observed. Also Figure 1 exhibits the variation of moisture ratio as a function of time. The moisture ratio of the samples decreased

continually with drying time. As expected, increase in the temperature of drying air reduces the time required to reach any given level of moisture ratio since the heat transfer increases. In other words, at high temperatures the transfer of heat and mass is high and water loss is excessive. This can be explained by increasing temperature difference between the drying air and the product and the resultant water migration. These results are in agreement with other findings reported for drying of bell pepper (Vega et al., 2007).

This figure showed that the experimental and calculated moisture ratio of the best model, where a good fit can be graphically observed when using these equations. In addition, other authors have obtained good results when applying this model in drying kinetics of food (Arumuganathan et al., 2009; Simal et al., 2005; Meisami-asl et al., 2010).

Effective moisture diffusivity increases with increase in drying air temperature and constant air humidity. The effective diffusivity coefficient was estimated to be between 1.7×10^{-9} and 11.9×10^{-9} m²/s for the given temperature range, (Table 6). The effect of temperature on the diffusivity was expressed by the Arrhenius equation, where the logarithm of the diffusivity exhibited a linear relationship against the reciprocal of the absolute temperature ($R^2 = 0.90$). In addition, E_a of 44.49 kJ/mol and D_0 of 9.37×10^{-3} m²/s were obtained. Similar values of E_a are reported for other varieties of red bell pepper, such as: 44 kJ/mol in the Jaranda variety of red pepper, (Sanjua'n et al., 2003), 42.8 kJ/mol in the Bursa variety of red pepper (Kaymak-Ertekin, 2002) and 39.70 kJ/mol in the variety Lamuyo red bell pepper (Vega et al., 2007).

Conclusions

The drying behavior of bell pepper slices in a laboratory dryer was investigated at five different drying air temperatures. The times to reach equilibrium moisture (10%) from the initial moisture content at five temperatures were found to be between 320 and 1150 min. In order to explain the drying behavior of bell pepper cultivated in Iran, 12 models in the literature were applied and fitted to the experimental data. According to the statistical analysis applied to all models, it can be concluded that among these models, Logarithmic gave the best results. In addition to, these results showed good agreement with the experiment data. It can be concluded that the influence of air temperature on drying time cause to with increase in air temperature a decrease in drying time during falling rate period is observed. According to the results, it can be stated that Logarithmic model could describe the drying characteristics of bell pepper in the drying process at a temperature range 40-80 °C and air velocity of 2 ms⁻¹. The effect of temperature on the diffusivity was expressed by the Arrhenius equation, where the logarithm of the diffusivity exhibited a linear behavior against the reciprocal of the absolute temperature.

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