

Research Article

Thin Layer Modeling of the Convective Drying of Barberry Fruit (*Berberis vulgaris*) "Influence of Drying Conditions on the Effective Moisture Diffusivity and Energy of Activation"

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Abstract: In this study, the drying kinetics of seedless barberry fruit was studied at 55, 65 and 75°C air temperatures and 1±0.2 m/s air velocity in a laboratory thin layer dryer with forced convection. Samples were subjected to two different pretreatments (citric acid and vapor). The drying of seedless barberry fruit took place in the falling rate drying period. Ten thin layer-drying models were fitted to the experimental moisture ratio. Compared with other models the Midilli *et al.* (2002) drying model was found to satisfactorily describe the drying curves of barberry with highest amounts of coefficient of determination (r^2) and lowest amounts of reduced chi-square (χ^2), Mean Bias Error (MBE) and Root Mean Square Error (RMSE). The effective moisture diffusivity (D_{eff}) of barberry increased as the drying air temperature increased. An Arrhenius relation with activation energy values of 45.577 kJ/mol (citric acid pretreatment) expressed the effect of temperature on the diffusivity.

Keywords: Activation energy, barberry, effective diffusivity, pretreatments, thin-layer drying

INTRODUCTION

In Iran, near about 10,000 ton of dried barberry is produced per annum, 97 percent of which is allocated to South Khorasan Province. The unique nutraceutical characteristics of barberry, such as having antimicrobial effects, decreasing blood sugar and cholesterol levels, lowering blood pressure, lessening inflammation, reducing Alzheimer progress, being anti-tumor and having heart booster effects, has led to a tendency for its consumption during all seasons. The most prominent by-product of it, manufactured and offered at present, is dried barberry (Aivaz *et al.*, 2011; Chahi *et al.*, 2000).

Drying operation is among the most important and fundamental steps in food industry which is employed to maintain properties of agricultural and medicinal products and also to cut down transport expenses and facilitate their consumption. The aim of drying a food is removing water and consequently preventing microbial and chemical decay and improving its shelf-life. There is an effort to maximize the rate of drying through conveying heat and humidity. Because of fewer expenses, hot air drying is one of the key approaches in manufacturing of dried products. The majority of industrial dryers utilize hot air flow to dry stuffs. Usage of these dryers results in acceleration of drying process and allows for fulfillment of hygienic conditions (Kafi and Balandri, 2002; Akanbi *et al.*, 2006). Considering the probability of undesired qualitative changes of

foodstuffs via drying, control of this process is of crucial importance. Therefore, for safe preservation of foods, their moisture needs to drop to a specific level. For that purpose, it is essential to determine moisture absorption by the product which is being dried (Chahi *et al.*, 2000). In order to attain these goals, drying process of various crops must be modeled, so that the methodology of drying procedure could be estimated based upon the pattern of this model. The objective of specifying a model for drying crops is to predict drying method (Akanbi and Oludemi, 2003; Rafiee *et al.*, 2009).

Today in Iran, barberry is dried through fully conventional methods without any pretreatment whose most significant drawbacks are high costs and retarded process. The high risk of damage to product by autumn rains and the infection with different molds and yeasts lead to an approximate 30 to 35% loss of annual product (Minaei *et al.*, 2012). A means to diminish crop losses during drying is usage of appropriate pretreatment for decrement in drying time. The main goals in drying process are reducing drying time, obtaining a high-quality product with regards to flavor, taste and color and extending product shelf-life (Chahi *et al.*, 2000).

Doymaz and Ismail (2010) formerly used two pretreatment of alkaline emulsion and ethyl oleate for drying sweet cherry and observed their influences on

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drying manner of sweet cherry in three temperatures of 60, 70 and 75°C, led to recommendation of page model as the best model for describing drying behavior of sweet cherry. Goyal *et al.* (2007) studied six mathematical models for drying apple slices with different pretreatments and eventually concluded that logarithmic model can best estimate drying behavior of apple slices than other models. Ponkham *et al.* (2011), using mathematical modeling in a survey of drying pineapple by two methods of hot air convection and infrared irradiation, showed that Midilli *et al.* (2002) model was better than other models. Sacilik and Elicin (2006) studied the drying process of apples. They dried 5 mm-thick and 9 mm-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. Doymaz (2004b) 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 temperatures and air relative humidities. Their experimental findings best described by the Two Term Exponential model having $R^2 = 0.995$, $\chi^2 = 0.00057$, MBE = 0.0027 and RMSE = 0.0235. Ertekin 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.* (2002) model best described the data with the least errors.

The objective hereof was to propose the best fitting model for drying barberry with different pretreatments in hot air dryer, so that the drying behavior of this crop could be predicted on the basis of obtained model. For that purpose, dynamic models of drying agricultural products were simulated for barberry and finally, based on investigated parameters, the best model was determined.

MATERIALS AND METHODS

Raw material: Barberry (*Berberis vulgaris*) was purchased from Qaen, South Khorasan and Iran. After separation of sticks, leaves and litters, barberry fruits were kept at 4-5 degree centigrade for lowering respiration rate and physiological and chemical changes. This project was conducted in January of 2012 in Islamic Azad University, Sabzevar, Iran.

Drying procedure: Barberry fruit were dried with pretreatments namely control (untreated samples), blanching, dipping in 5%, citric acid and blanching with water vapor. Experiments were conducted at 55, 65 and

75°C. The relative humidity was in the range of 30-40% whereas room air temperature varies from 20-27°C. The initial moisture content of fruits was evaluated by AOAC (2000) method no. 934.06, for barberry without pretreatment (control sample), barberry with water vapor pretreatment and barberry with citric acid pretreatment as 331.03, 344.44 and 356.62 percentage, respectively. Then, the three samples were prepared again and placed in the dryer.

Thin layer on a 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; 55, 65 and 75°C which was controlled in automatic form, using a PID controller. The air velocity was kept constant at 1 ± 0.2 m/s which 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 min 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.

Mathematical modeling: Moisture ratio of the samples during drying was expressed by the following equation:

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

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. However, the moisture ratio 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 and Bhargava, 2008). All the statistical analyses, including linear and non-linear regression analysis, MBE, RSME and χ^2 factors, were performed on Sigma Plot computer program (Statistical Package, version 10.0). Correlation coefficient (R^2) was one of the primary criteria to select the best model. Other statistical parameters such as chi-square (χ^2), Mean Bias Error (MBE) and Root Mean Square Error (RMSE) were used to determine the quality of the fit. In general, for a quality fit, R^2 value should be higher and χ^2 , MBE and RMSE should be lower (Guarte, 1996; Goyal and Bhargava, 2008; Ertekin and Yaldiz, 2004). Ten of the 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

Table 1: Mathematical models applied to the drying curves

References	Model	Name of model	No
1	Newton	MR = exp (-kt)	Ayensu (1997) and Liu and Bakker-Arkema (1997)
2	Page	MR = exp (-ktn)	Doymaz (2004c) and Park <i>et al.</i> (2002)
3	Modified page	MR = exp (-(kt)n)	Overhults <i>et al.</i> (1973)
4	Henderson and Pabis	MR = a exp (-kt)	Henderson and Pabis (1961) and Chhinnan (1984)
5	Logarithmic	MR = a exp (-kt) +c	Yaldiz <i>et al.</i> (2001)
6	Two-term	MR = a exp (-kt) + b exp (-k1t)	Madamba <i>et al.</i> (1996)
7	Two-term exponential	MR = a exp (-kt) + (1 - a) exp (-kat)	Ertekin and Yaldiz (2004)
8	Wang and singh	MR = 1+ at + bt ²	Wang and Singh (1978)
9	Midilli <i>et al.</i>	MR = a exp (-ktn) + bt	Ertekin and Yaldiz (2004) and Midilli <i>et al.</i> (2002)
10	Diffision approximation	MR = a exp (-kt) + (1 - a) exp (-kbt)	Ertekin and Yaldiz (2004)

barberry. The results were compared to determine a suitable model for describing the drying process of barberry. These parameters were calculated using the following equations:

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

$$MBE = \frac{1}{N} \sum_{i=1}^N (MR_{pre,i} - MR_{exp,i}) \quad (3)$$

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

Moisture diffusivity and activation energy: To calculate the effective moisture diffusivity, Fick's diffusion equation was used:

$$MR = \frac{8}{\pi^2} \exp \left(- \pi^2 \frac{D_{eff} t}{L^2} \right) \quad (5)$$

By plotting Ln (MR) versus experimental drying time and evaluating the slope, the effective moisture diffusivity, D_{eff} , was obtained (Goyal and Bhargava, 2008; Maskan *et al.*, 2002; Maskan, 2001; Doymaz, 2004a). D_{eff} may be related to temperature through Arrhenius equation:

$$D_{eff} = D_0 \exp \left(- \frac{Ea}{RT} \right) \quad (6)$$

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 and Kim, 2008).

RESULTS AND DISCUSSION

Drying behavior of apple slices: Table 2 shows average drying rate in all treatments of our study. Drying rate has a descending gradient with time. This descent is more at the beginning of time and at the end

Table 2: Values of drying rate for barberry in different temperatures and conditions

Drying temperature (°C)	Pretreatments	Drying Rate (kg moisture/kg dry m)
	Control	0.1744
	Vapour	0.1781
	Citric acid	0.1910
	Control	0.2066
	Vapour	0.2087
	Citric acid	0.2115
	Control	0.2841
	Vapour	0.2412
	Citric acid	0.3011

of drying period the value of inclination is declined due to the phenomenon of "reduction in saturated moisture". This way, the rate of removing water is higher at the beginning because of high moisture content in fruit tissue; hence, the rate of moisture diminution in fruit tissue is high and this curve has a steep descending slope, but as time goes by, considering that moisture content of product has decreased, the rate of conveying water from the depth to surface of the product and its escape is reduced and consequently drying rate is decelerated. The maximum drying rate for barberry is seen at 75°C. Use of pretreatment also had a positive effect on increment of drying rate. Removing cuticle (waxy layer) and creating minute fissures, vapor and citric acid pretreatments lessen the resistance against moisture diffusivity in barberry per carp/hull and hasten drying (Goyal *et al.*, 2007; Minaei *et al.*, 2012). The greatest drying rate in the shortest time (0.3011 kg moisture/kg dry mater) was associated with the sample dried at 75°C with citric acid pretreatment Similar results were reported in drying of apricots (Pala *et al.*, 1996; Doymaz, 2004a), grapes (Doymaz and Pala, 2002) and mangoes (Goyal *et al.*, 2006)

Mathematical modeling of drying curves: Dynamic model of drying barberry were fitted in temperature ranged from 55 to 75°C for hot air drying with vapor and citric acid pretreatments. The values of R^2 , χ^2 , RMSE and EMD are presented in Table 3. In most of models the R^2 value was higher than 0.98 that indicates acceptable fitting of experimental data with models

Table 3: Results of statistical analyses on the thin layer drying of barberry

Model	Treatment	R ²	χ ²	EMD	RMSE
1	Control	0.9779	0.00248	35.320	0.0460
	Vapour	0.9766	0.00265	21.632	0.0311
	Citric acid	0.9822	0.00188	16.186	0.0250
2	Control	0.9978	0.00122	9.561	0.0284
	Vapour	0.9962	0.00142	17.985	0.0295
	Citric acid	0.9950	0.00025	11.068	0.0382
3	Control	0.9975	0.00022	9.345	0.0478
	Vapour	0.9962	0.00460	41.469	0.0280
	Citric acid	0.9950	0.00208	74.322	0.0378
4	Control	0.9876	0.00107	87.932	0.0273
	Vapour	0.9868	0.00989	16.431	0.0256
	Citric acid	0.9862	0.00102	11.721	0.0269
5	Control	0.9958	0.00239	53.931	0.0374
	Vapour	0.9966	0.00022	28.321	0.0360
	Citric acid	0.9969	0.00023	12.555	0.0366
6	Control	0.9966	0.00102	45.132	0.0230
	Vapour	0.9962	0.00010	60.259	0.0245
	Citric acid	0.9985	0.00440	72.806	0.0358
7	Control	0.9964	0.00196	13.935	0.0367
	Vapour	0.9955	0.00019	89.981	0.0369
	Citric acid	0.9952	0.00018	70.806	0.0358
8	Control	0.9940	0.00166	0.381	0.0866
	Vapour	0.9925	0.00014	30.765	0.0333
	Citric acid	0.9882	0.00167	31.677	0.0361
9	Control	0.9981	0.00085	7.007	0.0468
	Vapour	0.9982	0.00034	10.007	0.0381
	Citric acid	0.9987	0.00030	6.743	0.0366
10	Control	0.9976	0.00014	16.386	0.0513
	Vapour	0.9978	0.00791	55.306	0.0171
	Citric acid	0.9987	0.00187	18.123	0.0122

(Ertekin and Yaldiz, 2004; Sharifi and Hassani, 2012). Results of statistical analysis showed that Midilli *et al.* (2002) model with R² = 0.9981 – 0.9987, χ² = 3.05 × 10⁻⁴ – 8.5 × 10⁻⁴, EMD = 10.007 – 6.743 and RMSE = 0.0468 – 0.0336 was chosen as the best model for hot air-dried barberry which compared to other models, had maximum value of R² and minimum values of χ², MBE and RMSE. Therefore, this model can be used in order to study and estimate the drying process of barberry with hot air. Similar results were observed by other researchers for various vegetables (Minaei *et al.*, 2012; Mwithiga and Olwal, 2005; Sacilik *et al.*, 2006; Sacilik and Elicin, 2006). Sharifi and Hassani (2012) demonstrated that Midilli *et al.* (2002) model displayed the best estimation of drying process of rhubarb slices in hot air thin layer drying.

Drying curves based on laboratory data and data from Midilli *et al.* (2002) model, as the best model used for hot air dried-barberry with pretreatment at various temperatures, is shown in Fig. 1 to 3, respectively. Taking the curve of moisture variations during drying, one can find out that drying process for all samples has occurred in the falling rate drying period, signifying that diffusion is the main physical mechanism which controls moisture movement within samples (Goyal *et al.*, 2006; Kim *et al.*, 2007). According to Fig. 1 to 3,

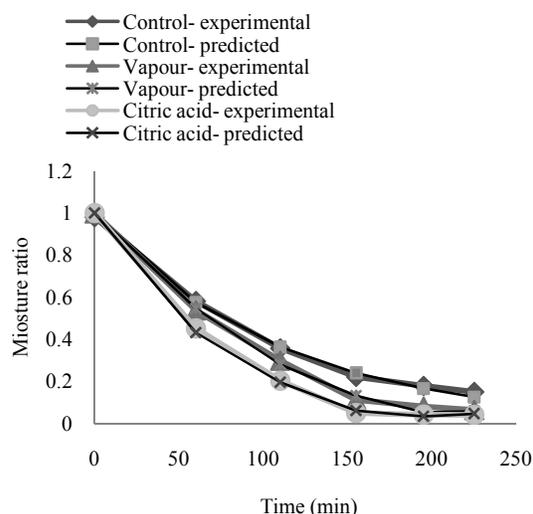


Fig. 1: Moisture variations during hot air drying with various pretreatments at 75°C, obtained from experimental data and data from Midilli *et al.* (2002) model

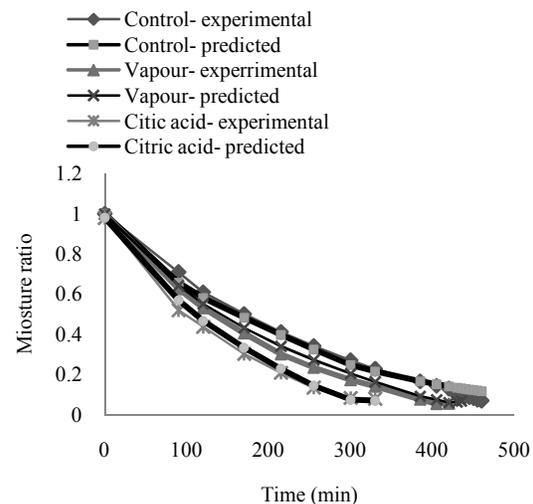


Fig. 2: Moisture variations during hot air drying with various pretreatments at 65 °C, obtained from experimental data and data from Midilli *et al.* (2002) model

experimental data and data obtained from the model are too close, so as the curve developed from experimental data and the curve from model data match on each other and this manifests justness of that model for fitting experimental data.

Calculation of effective moisture diffusivity: Values of D_{eff} (effective moisture diffusivity) and R², assessed for dried barberry, are given in Table 4. Results illustrated that with a rise in drying temperature and sample pretreatment, effective moisture diffusivity

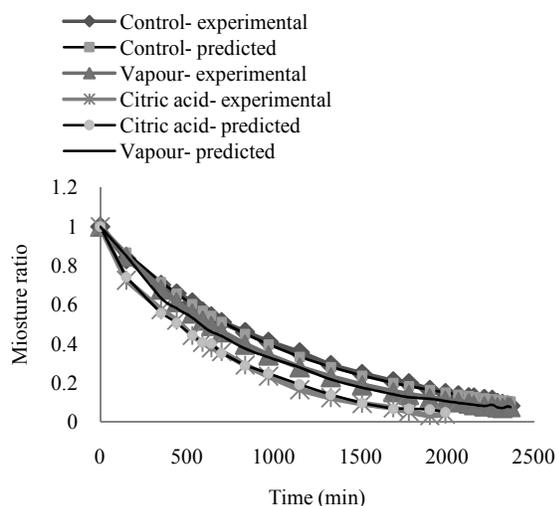


Fig. 3: Moisture variations during hot air drying with various pretreatments at 55 °C, obtained from experimental data and data from Midilli *et al.* (2002) model

Table 4: Effective moisture diffusivity for drying of barberry in different conditions and temperature

Drying temperature (°C)	Treatment	D_{eff} (m^2/s^1)	R^2
55 (°C)	Control	0.0454×10^{-10}	0.9921
	Vapour	0.0738×10^{-10}	0.9975
	Citric acid	0.1889×10^{-10}	0.9979
65 (°C)	Control	0.2282×10^{-10}	0.9735
	Vapour	0.2683×10^{-10}	0.9696
	Citric acid	0.3087×10^{-10}	0.9695
75 (°C)	Control	0.4564×10^{-10}	0.9686
	Vapour	0.4894×10^{-10}	0.9716
	Citric acid	0.4937×10^{-10}	0.9611

Table 5: The value of activation energy obtained for barberry in different temperatures and conditions

Treatment	E_a (kJ/mol)
Control	109.694
Vapour	90.946
Citric acid	45.577

increased (Goyal and Bhargava, 2008; Minaei *et al.*, 2012).

Amounts of effective moisture diffusivity for foodstuffs vary between 10^{-9} – 10^{-11} m^2/s (Akpinar *et al.*, 2003). Results proved that barberry samples with pretreatment had higher effective moisture diffusivity. Many researchers have calculated effective moisture diffusivity for foods; for example in apple slices dried at 50, 60 and 70°C, with and without pretreatment, it was found that $D_{eff} = 2.22 \times 10^{-10}$ – 4.69×10^{-10} (Goyal and Bhargava, 2008). In addition, for pomegranate arils dried by means of vacuum dryer at temperatures of 50, 60, 70, 80 and 90°C, the amount of D_{eff} was measured 0.74×10^{-10} – 5.25×10^{-10} (Minaei *et al.*, 2012). For

rhubarb slices dried at 50, 60 and 70°C, the obtained value of effective diffusivity was between 0.0456×10^{-9} and 0.1597×10^{-9} (Sharifi and Hassani, 2012).

Activation energy: Values of activation energy for dried barberry are presented in Table 5. The greatest activation energy was related to dried barberry sample without pretreatment. The value of activation energy for different crops has been reported by researchers; for example activation energy for pomegranate in a temperature range of 50-70°C in a vacuum dryer was 52.275 kJ/mol, compared to reported values for sweet pepper (51.42 kJ/mol) and sweet cherries dried with 2% alkaline ethyl oleate and control sample (43.05 and 49.17 kJ/mol, respectively) (Kaymak-Ertekin, 2002; Varadharaju *et al.*, 2001).

CONCLUSION

In this investigation, effects of different temperatures and pretreatments on time and rate of hot air drying for barberry was studied. Increase in drying temperature and pretreatment of samples led to decline of drying time and growth of drying rate. Following statistical analysis of model, results revealed that among fitted mathematical models, Midilli *et al.* (2002) model, for having maximum amount of R^2 and minimum values of χ^2 and RMSE, was the best one in hot air drying of barberry. Effective moisture diffusivity in a temperature range of 55°C to 75°C for barberry samples was estimated in the range of 0.4937×10^{-6} to 0.0454×10^{-10} (m^2/s), which for samples undergoing a pretreatment was higher. Activation energy in different temperatures during hot air drying for samples without pretreatment, samples experienced water vapor pretreatment and samples with citric acid pretreatment was 109.694, 90.946 and 45.577, respectively.

NOMENCLATURE

- X^2 : reduced chi-square
- a, b, c, n : empirical constants in drying models
- D_{eff} : effective moisture diffusivity, m^2/s^1
- K : drying constant
- L : thickness of slice, m
- M : moisture content at time t, kg moisture. kg dry matter
- MBE : mean bias error
- Me : equilibrium moisture content, kg moisture. kg dry matter
- Mo : initial moisture content, kg moisture. kg dry matter
- MR : dimensionless moisture ratio

MR_{exp} : expected moisture ratio
MR_{pre} : predicted moisture ratio
N : number of observations
R² : 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)
D₀ : pre-exponential factor of Arrhenius equation (m²/s)

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