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Research Article

Vacuum Drying of Barberry Fruit (*Berberis vulgaris*) and Selection of a Suitable Thin Layer Drying Model

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Abstract: In an investigation on kinetics of seedless barberry drying at 35, 45 and 55°C in vacuum and with water vapor and citric acid pre-treatments, the value of effective moisture Diffusivity (D_{eff}) was calculated using the second Fick's diffusion equation, activation energy was determined and drying process was simulated by 10 common mathematical equations of thin layer-drying models. Results which were obtained from regression analysis of studied models showed that approximation of diffusion model had the best fitting for vacuum-drying of barberries through available data. Drying barberry took place in the falling rate drying period and pre-treated samples had higher drying rate. The effective diffusivity coefficient for vacuum-drying of barberry fruits was evaluated between 0.0228×10^{-10} and 0.2538×10^{-10} m^2/s, which increased along with temperature rise. An Arrhenius equation for drying of seedless barberry with activation energy values ranged from 27.618 to 92.493 kJ/mol expressed the effect of temperature on moisture diffusivity.

Keywords: Activation energy, barberry, effective diffusivity, pretreatments, vacuum drying

INTRODUCTION

Barberries are a substantial group of evergreen spiny shrubs that due to its multiple applications and utilizations, including nutritional uses of fruits, is of great importance. It's most significant product now manufactured and offered in Iran is dried barberry. In Iran, the fruits are presented freshly and finitely in harvest season and in other seasons dried barberry are utilized as an additive or for decorating foods or desserts. In other countries, barberry mostly possesses ornamental or medicinal application (Aivaz *et al*., 2011; Chahi *et al*., 2000).

The most vital step in barberry processing is its drying. This is performed in order to extend the product's shelf-life, prevent deterioration, decrease the volume, improve packaging efficiency and facilitate transport and preservation. Most of drying methods used for foods take advantage of heat, so it is not possible to design drying systems without understanding recondite changes happening throughout extracting moisture from food. Cognizing factors that affect drying process helps you choose and apply the best drying method in order for being cost effective, as well as conserving color and visual characteristics of produce (Aivaz *et al*., 2011).

Today in Iran, barberry is dried through fully traditional methods without any pre-treatment, the most significant drawback of which is increased costs and retarded process, which in turn causes increased risk of damage on product by autumn rains and infection with different molds and yeasts and so an approximate of 30 to 35% loss of annual product (Chahi *et al*., 2000). Hence mechanical approaches such as hot air drying, besides accelerating drying operation, can provide satisfactory hygiene conditions. However, this method could have unfavorable consequences in color and quality of product, or may lead to wrinkling or superficial scald of product (Minaei *et al*., 2012). In recent years, utilization of vacuum drying has been considered as a potential means for manufacturing high quality dried foods. In this method the required heat flux for drying process decreases and therefore, injuries developed on product are alleviated and less structural destruction happens. Another alternative to minimize crop loss while drying is applying proper pre-treatment in order to lessen drying time (Jaya and Das, 2003).

Doymaz and Ismail (2010) used two pre-treatments of alkaline emulsion and ethyl elevate for drying sweet cherry and observed their influences on 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) examined six mathematical models

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for drying thin apple slices with different pre-treatments and eventually concluded that logarithmic model can best estimate drying behavior of apple samples than other models. Ponkham *et al.* (2012), using mathematical modeling in a survey of drying pineapple by two methods of hot air convection and infrared irradiation, showed that Midilli model was better than other models. Minaei *et al*. (2012) surveyed the best model for vacuum drying of pomegranate arils. Experiments were performed at temperature range of 50 to 90°C and 250 kPa atmospheric pressure. It is concluded that the best model with the minor error was of Midilli *et al.* (2002).

The objective of this study was to propose the best fitting model for drying barberry with different pre-treatments in vacuum dryer, so that the drying behavior of this crop could be predicted on the basis of pattern obtained from that 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

This project was conducted in September of 2011 in pardis top toes company located in ferdows, Iran. Barberry (*Berberis vulgaris*) was purchased from Qaen, South Khorasan and Iran. After separation of sticks, leaves and litters, barberry fruits were kept, until onset of drying, at 4-5°C for lowering respiration rate and physiological and chemical changes. For launching the process, pre-treatments, involving a solution of 5% citric acid and water vapor, were carried out for 10 min on barberries. The initial moisture content of fruits was evaluated by AOAC method no. 93406. The initial moisture content of fruits for barberry without pre-treatment (control sample), barberry with water vapor pre-treatment and barberry with citric acid pre-treatment was 331.03, 344.44 and 356.62, respectively. Then, these samples were prepared again and placed in an experimental vacuum dryer (LAB TECH 40 L) at 35, 45 and 55°C and 250 kpa of vacuum.

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 (Sharifi *et al*., 2012).

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

$$MR = \frac{M - M_e}{M_0 - M_e} \tag{1}$$

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 $(M - M_e)/(M0 - M_e)$ as the value of Me 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 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:

Table 1: Mathematical models applied to the drying curves

No	Name of model	Model	References
1	Newton	MR = exp (-kt)	Ayensu (1997) and Liu and Bakker-Arkema (1997)
2	Page	MR = exp ($-kt^n$)	Doymaz (2004c) and Park *et al*. (2002)
3	Modified page	MR = exp ($-(kt)^n$)	Overhults *et al*. (1973)
4	Henderson and Pabis	MR = a exp (-kt)	Henderson and Pabis (1961) and Chinnan (1984)
5	Logarithmic	MR = a exp (-kt) + c	Yaldiz *et al*. (2001)
6	Two-term	MR = a exp (-kt) + b exp ($-k_1t$)	Madamba *et al*. (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 *et al.*	MR = a exp ($-kt^n$) + bt	Ertekin and Yaldiz (2004) and Midilli *et al*. (2002)
10	Approximation of Diffision	MR = a exp (-kt) + (1 - a) exp (-kbt)	Ertekin and Yaldiz (2004)

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

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

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

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

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

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; Maskan, 2001; Doymaz, 2004a). D_{eff} may be related to temperature through Arrhenius equation:

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

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

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 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 55°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 (0.1332 kg moisture/kg dry mater) was associated with the sample dried at 55°C with citric acid pretreatment. Similar results were reported in drying of apricots (Pala *et al*., 1996; Doymaz, 2004b), grapes (Doymaz and Pala, 2002) and mangoes (Goyal *et al*., 2006).

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

Drying temperature (°C) (vacuum)	Treatment	Drying rait (kg moisture/kg dry mater)
55	Control	0.0953
	Vapour	0.0994
	Citric acid	0.1332
45	Control	0.0735
	Vapour	0.0932
	Citric acid	0.0778
35	Control	0.0707
	Vapour	0.0778
	Citric acid	0.0727

Table 3: Results of statistical analyses on the vacuum drying of barberry

Model	Treatment	R^2	χ^2	EMD	RMSE
1	Control	0.9702	0.00213	22.143	0.0427
	Vapour	0.9726	0.00224	23.272	0.0178
	Citric acid	0.9702	0.00249	22.521	0.0180
2	Control	0.9821	0.00030	40.561	0.0147
	Vapour	0.9807	0.00641	45.523	0.0208
	Citric acid	0.9826	0.00268	33.945	0.0147
3	Control	0.9821	0.00207	57.261	0.0397
	Vapour	0.9802	0.00185	77.591	0.0321
	Citric acid	0.9820	0.00198	73.474	0.0392
4	Control	0.9725	0.00130	81.971	0.0313
	Vapour	0.9695	0.00012	70.466	0.0308
	Citric acid	0.9742	0.00011	73.902	0.0302
5	Control	0.9883	0.00719	78.291	0.0454
	Vapour	0.9845	0.00280	44.621	0.0193
	Citric acid	0.9908	0.00040	27.623	0.0257
6	Control	0.9919	0.00501	23.561	0.0498
	Vapour	0.9849	0.00446	170.271	0.0491
	Citric acid	0.9909	0.00045	34.981	0.0502
7	Control	0.9876	0.00180	84.561	0.0344
	Vapour	0.9849	0.00446	70.271	0.0491
	Citric acid	0.9816	0.00146	60.851	0.0286
8	Control	0.9761	0.00266	91.271	0.0448
	Vapour	0.9690	0.00243	183.316	0.0437
	Citric acid	0.9836	0.00246	77.014	0.0439
9	Control	0.9921	0.00110	58.132	0.0412
	Vapour	0.9919	0.00034	27.871	0.0442
	Citric acid	0.9907	0.00270	50.555	0.0399
10	Contro	0.9932	0.00039	14.831	0.0955
	Vapour	0.9925	0.00056	6.5960	0.0438
	Citric acid	0.9938	0.00048	10.231	0.0523

Mathematical modeling of drying curves: Dynamic model of drying barberry were fitted in temperature ranged from 35 to 55°C for vacuum 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 (Ertekin and Yaldiz, 2004; Sharifi *et al*., 2012). Results of statistical analysis showed that approximation of diffusion model with R^2 = 0.9925-0.9938, $\chi^2 = 3.9\times10^{-4}$ -5.6×10^{-4}, EMD = 6.59-14.83 and RMSE = 0.0438-0.0959 was chosen as the best model for vacuum dried barberry which compared to other models, had maximum value of R^2 and minimum values of χ^2, MBE and RMSE. Similar results were observed by

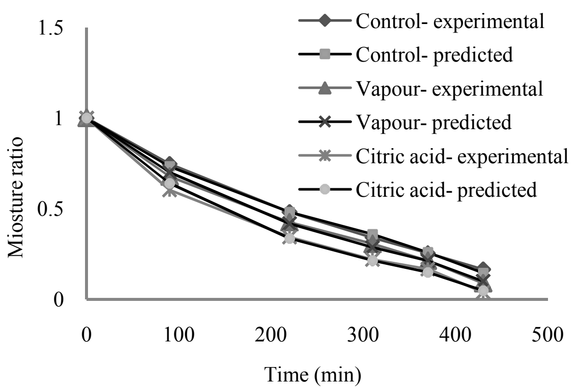

Fig. 1: Moisture variations during vacuum drying with various pretreatments at 55°C, obtained from experimental data and data from approximation of diffusion model

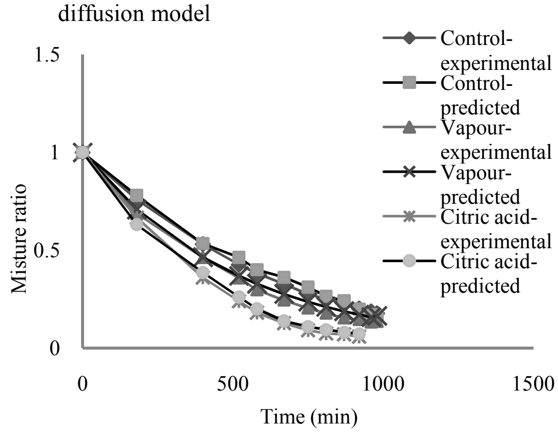

Fig. 2: Moisture variations during vacuum drying with various pretreatments at 45°C, obtained from experimental data and data from approximation of diffusion model

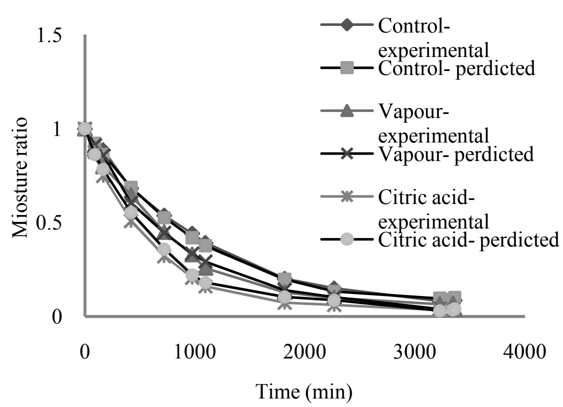

Fig. 3: Moisture variations during vacuum drying with various pretreatments at 35°C, obtained from experimental data and data from approximation of diffusion model

other researchers for various vegetables (Minaei *et al*., 2012; Doymaz, 2004c). Sharifi *et al*. (2012) demonstrated that Midilli *et al*. (2002) model displayed the best estimation of drying process of rhubarb slices in hot air thin layer drying.

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

Drying temperature (°C) (vacuum)	Treatment	D_{eff} (m^2/s)	R^2
55	Control	0.1825×10^{-10}	0.8826
	Vapour	0.2282×10^{-10}	0.8918
	Citric acid	0.2538×10^{-10}	0.9116
45	Control	0.0912×10^{-10}	0.8765
	Vapour	0.0963×10^{-10}	0.9527
	Citric acid	0.1037×10^{-10}	0.9187
35	Control	0.0228×10^{-10}	0.9687
	Vapour	0.0251×10^{-10}	0.9667
	Citric acid	0.0273×10^{-10}	0.9403

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

Pretreatment	Ea (kj/mol)
Control	97.662
Vapor	82.493
Citric acid	27.618

Drying curves based on laboratory data and data from approximation of diffusion model, as the best model used for vacuum 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, 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 R^2, assessed for vacuum dried barberry, are given in Table 4. Results illustrated that with a rise in drying temperature and sample pretreatment, effective moisture diffusivity 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 $D_{eff} = 2.22\times10^{-10}$-$4.69\times10^{-10}$ (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 *et al*., 2012).

Activation energy: Values of activation energy for vacuum 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, kinetics of seedless barberry drying at 35, 45 and 55°C in vacuum and with water vapor and citric acid pre-treatments, was studied. Constant drying rate period was not observed, the drying of barberry under vacuum 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 approximation of diffusion model was considered most adequate to describe the vacuum drying behavior of barberry. The values of calculated effective diffusivity varied from about 0.0228×10^{-10}-0.2538×10^{-10} (m^2/s), over the temperature range. The effective diffusivity increases as temperature increases. 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 97.662, 82.493 and 27.618, respectively.

NOMENCLATURE

χ^2	:	Reduced chi-square
a, b, c, n	:	Empirical constants in drying models
D_{eff}	:	Effective moisture diffusivity, m^2/s
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
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)
Ea	:	Activation energy (kJ/mol)
D_0	:	Pre-exponential factor of Arrhenius equation (m^2/s)

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