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 aim of drying a food is to maintain properties of agricultural and medicinal products and also to cut down transport expenses and facilitate their consumption. The focus of drying is to remove 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., 2000). 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...
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 Qazen, 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 \( \pm 0.2 \) 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:

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

(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 \( (M - Me)/(M_0 - Me) \) 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, RMSSE and \( \chi^2 \) 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 (\( \chi^2 \)), 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 \( \chi^2 \), 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 (-ktm)     | Doymaz (2004c) and Park et al. (2002) |
| 3 Modified page | MR = exp (-0ktm) | Overhults et al. (1973) |
| 4 Henderson and Pabis | MR = a exp (-kt) | Henderson and Pabis (1961) and Chhinnan (1984) |
| 5 Logarithmic | MR = a exp (-kt + c) | Yaldiz et al. (2001) |
| 6 Two-term | MR = a exp (-kt) + b exp (-kt1) | 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 | Wang and Singh (1978) |
| 9 Midilli et al. | MR = a exp (-ktm) + bt | Ertekin and Yaldiz (2004) and Midilli et al. (2002) |
| 10 Diffusion approximation | MR = a exp (-kt) + (1 - a) exp (-ktb) | 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:

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

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

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

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:

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

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 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).

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                           |

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 \( R^2 \), \( \chi^2 \), 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 | $R^2$ | $\chi^2$ | EMD | RMSE |
|-------|-----------|-------|---------|-----|------|
| 1     | Control   | 0.9779| 0.00248 | 35.320 | 0.0460 |
|       | Vapour    | 0.9766| 0.00265 | 21.632 | 0.0311 |
|       | Citric acid | 0.9922| 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| 0.00046 | 41.469 | 0.0280 |
|       | Citric acid | 0.9950| 0.00028 | 74.322 | 0.0295 |
| 4     | Control   | 0.9975| 0.00022 | 9.345  | 0.0478 |
|       | Vapour    | 0.9962| 0.00107 | 87.932 | 0.0273 |
|       | Citric acid | 0.9968| 0.00089 | 16.431 | 0.0256 |
| 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| 0.00079 | 55.306 | 0.0171 |
|       | Citric acid | 0.9987| 0.00187 | 18.123 | 0.0122 |

(Ertekin and Yaldiz, 2004; Sharifi and Hassan, 2012). Results of statistical analysis showed that Midilli et al. (2002) model with $R^2 = 0.9981 – 0.9987$, $\chi^2 = 3.05 \times 10^{-4} – 8.5 \times 10^{-4}$, 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 $R^2$ and minimum values of $\chi^2$, 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 Hassan (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, 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 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) | $R^2$  |
|-------------------------|-------------|----------------------|--------|
| 55 (°C)                 | Control     | $0.0454 \times 10^{-10}$ | 0.9921 |
|                         | Vapour      | $0.0738 \times 10^{-10}$ | 0.9975 |
|                         | Citric acid | $0.1889 \times 10^{-10}$ | 0.9979 |
| 65 (°C)                 | Control     | $0.2282 \times 10^{-10}$ | 0.9735 |
|                         | Vapour      | $0.2683 \times 10^{-10}$ | 0.9696 |
|                         | Citric acid | $0.3087 \times 10^{-10}$ | 0.9695 |
| 75 (°C)                 | Control     | $0.4564 \times 10^{-10}$ | 0.9686 |
|                         | Vapour      | $0.4894 \times 10^{-10}$ | 0.9716 |
|                         | Citric acid | $0.4937 \times 10^{-10}$ | 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   |

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 $D_{eff} = 2.22 \times 10^{-10}$ – $4.69 \times 10^{-10}$ (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 $0.74 \times 10^{-10}$ – $5.25 \times 10^{-10}$ (Minaei et al., 2012). For rhubarb slices dried at 50, 60 and 70°C, the obtained value of effective diffusivity was between $0.0456 \times 10^{-9}$ and $0.1597 \times 10^{-9}$ (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 $\chi^2$ 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 $0.4937 \times 10^{-6}$ to $0.0454 \times 10^{-10}$ (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
- $K$: drying constant
- $L$: thickness of slice, m
- $M$: moisture content at time $t$, kg moisture/ kg dry matter
- $M_{eq}$: equilibrium moisture content, kg moisture/ kg dry matter
- $M_0$: 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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