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

1Akram Sharifi and 2Bahram Hassani
1Department of Food Science and Technology, Sabzevar Branch, Islamic Azad University, Sabzevar, Iran
2Member of National Club of Coordination Knowledge and Industry of Barberry and Jujube in Iran

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 $0.0228 \times 10^{-410}$ and $0.2538 \times 10^{-410} \text{m}^2/\text{s}$, 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 rcondite 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...
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 pards 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:

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

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 \(M/Me\) instead of \((M - Me)/(M0 - Me)\) as the value of \(Me\) is relatively small compared to \(M\) or \(M0\) (Goyal and Bhargava, 2008). All the statistical analyses, including linear and non-linear regression analysis, MBE, RSME and \(\chi^2\) factors, were performed on Sigma Plot computer program (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 a quality fit, R² 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 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:

| No | Name of model       | Model                                                                 | References                          |
|----|---------------------|----------------------------------------------------------------------|-------------------------------------|
| 1  | Newton              | \(MR = \exp (-kt)\)                                                  | Ayensu (1997) and Liu and Bakker-Arkema (1997) |
| 2  | Page                | \(MR = \exp (-kt^2)\)                                                | Doymaz (2004c) and Park et al. (2002) |
| 3  | Modified page       | \(MR = \exp (-kt^3)\)                                                | Overhults et al. (1973)             |
| 4  | Henderson and Pabis | \(MR = \exp (-kt)\)                                                  | Henderson and Pabis (1961) and Chinnan (1984) |
| 5  | Logarithmic         | \(MR = \exp (-kt) + c\)                                              | Yaldiz et al. (2001)                |
| 6  | Two-term            | \(MR = \exp (-kt) + b \exp (-kt + t)\)                              | Madamba et al. (1996)               |
| 7  | Two-term exponential| \(MR = \exp (-kt) + (1 - a) \exp (-kat)\)                           | Ertekin and Yaldiz (2004)           |
| 8  | Wang and Singh      | \(MR = 1 + at + bt^2\)                                               | Wang and Singh (1978)               |
| 9  | Midilli et al.      | \(MR = \exp (-kt^3) + bt\)                                           | Ertekin and Yaldiz (2004) and Midilli et al. (2002) |
| 10 | Approximation of Diffusion | \(MR = \exp (-kt) + (1 - a) \exp (-ktb)\) | Ertekin and Yaldiz (2004) |
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).

**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 $R^2$, $\chi^2$, 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 (Ertekin and Yaldiz, 2004; Sharifi et al., 2008). 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) | Treatment | Drying rate (kg moisture/kg dry mater) |
|--------------------------|-----------|--------------------------------------|
| 35                       | Control   | 0.0953                               |
|                          | Vapour    | 0.0994                               |
|                          | Citric acid | 0.1332                             |
| 45                       | Control   | 0.0735                               |
|                          | Vapour    | 0.0932                               |
|                          | Citric acid | 0.0778                             |
| 55                       | Control   | 0.0707                               |
|                          | Vapour    | 0.0778                               |
|                          | Citric acid | 0.0727                             |

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).
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

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

| Drying temperature (°C) (vacuum) | Treatment | D eff (m²/s) | R² |
|---------------------------------|-----------|-------------|----|
| 55                              | Control   | 0.1825×10^{-4} | 0.8826 |
|                                 | Vapour    | 0.2282×10^{-4} | 0.8918 |
|                                 | Citric acid | 0.2538×10^{-4} | 0.9116 |
| 45                              | Control   | 0.0912×10^{-4} | 0.8765 |
|                                 | Vapour    | 0.0963×10^{-4} | 0.9527 |
|                                 | Citric acid | 0.1037×10^{-4} | 0.9187 |
| 35                              | Control   | 0.0228×10^{-4} | 0.9687 |
|                                 | Vapour    | 0.0251×10^{-4} | 0.9667 |
|                                 | Citric acid | 0.0273×10^{-4} | 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      |
| Vapour       | 82.493      |
| Citric acid  | 27.618      |

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 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 $D_{\text{eff}}$ (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 $10^{-9}$-$10^{-11}$ m²/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 $D_{\text{eff}} = 2.22×10^{-10}$-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 $D_{\text{eff}}$ 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 $0.0456 \times 10^{-9}$ and $0.1597 \times 10^{-9}$ (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 was 97.662, 82.493 and 27.618, 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} to 0.2538×10^{-10} (m²/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**

\[ \chi^2 : \text{Reduced chi-square} \]
\[ a, b, c, n : \text{Empirical constants in drying models} \]
\[ D_{eff} : \text{Effective moisture diffusivity, m}^2/\text{s} \]
\[ K : \text{Drying constant} \]
\[ L : \text{Thickness of slice, m} \]
\[ M : \text{Moisture content at time t, kg moisture, kg dry matter} \]
\[ MBE : \text{Mean bias error} \]
\[ Me : \text{Equilibrium moisture content, kg moisture, kg dry matter} \]
\[ Mo : \text{Initial moisture content, kg moisture, kg dry matter} \]
\[ MR : \text{Dimensionless moisture ratio} \]
\[ MR_{exp} : \text{Expected moisture ratio} \]
\[ N : \text{Number of observations} \]
\[ R^2 : \text{Coefficient of determination} \]
\[ RMSE : \text{Root mean square error} \]
\[ T : \text{Drying time, min} \]
\[ Z : \text{Number of drying constants} \]
\[ T : \text{Absolute temperature (K)} \]
\[ R : \text{Universal gas constant (8.314 kJ/kmol k)} \]
\[ Ea : \text{Activation energy (kJ/mol)} \]
\[ D_0 : \text{Pre-exponential factor of Arrhenius equation (m}^2/\text{s}) \]

**REFERENCES**

Aivaz, M., B. Hasani, A. Sharifi and M. Hasani, 2011. Study and Comparison of Different Conventional and Industrial Methods of Drying Barberry. National Congress of Food Industries, Qouchan.

Akpinar, E.K., A. Midilli and Y. Bicer, 2003. Single layer drying behaviour of potato slices in a convective cyclone dryer and mathematical modeling. Energ. Convers. Manage., 44(10): 1689-1705.

Ayensus, A., 1997. Dehydration of food crops using a solar dryer with convective heat flow. Sol. Energy, 59(4-6): 121-126.

Chahi, J., H. Qasem-Zadeh and A. Ranjbar, 2000. Influence of ethyl oleate, powdery potassium carbonate and warm water pre-treatments on the drying kinetics of barberry. 5th National Congress of Agricultural Machines and Mechanization, Ferdowsi University of Mashhad.

Chinnan, M.S., 1984. Evaluation of selected mathematical models for describing thin-layer drying of in-shell pecans. T. ASAE, 27: 610-615.

Doymaz, I., 2004a. Effect of pre-treatments using potassium metabisulphite and alkaline ethyl oleate on the drying kinetics of apricots. Biosyst. Eng., 89(3): 281-287.

Doymaz, I., 2004b. Convective air drying characteristics of thin layer carrots. J. Food Eng., 61(3): 359-364.

Doymaz, I., 2004c. Drying kinetics of white mulberry. J. Food Eng., 61(3): 41-426.

Doymaz, I. and M. Pala, 2002. The effect of dipping pre-treatments on air drying rates of the seedless grapes. J. Food Eng., 52: 413-417.

Doymaz, I. and O. Ismail, 2010. Drying characteristics of sweet cherry. J. Food Inst. Chem. E., 89(1): 31-38.

Ertckin, C. and O. Yaldiz, 2004. Drying of eggplant and selection of a suitable thin layer drying model. J. Food Eng., 63: 349-359.

Goyal, R.K. and O.M. Bhargava, 2008. Mathematical modeling of thin layer drying kinetics of apple in tunnel dryer. Int. J. Food Eng., 4(8), DOI: 10.2202/1556-3758.1233.

Goyal, R.K., A.R.P. Kingsly, M.R. Manikantan and S.M. Iyas, 2006. Thin layer drying kinetics of row mango slice. Biosyst. Eng., 95(1): 43-49.
Goyal, R.K., A.R.P. Kingsly, M.R. Manikantan and S.M. Iyas, 2007. Mathematical modeling of thin layer kinetics of plum in a tunnel dryer. J. Food Eng., 79(1): 176-180.

Guarte, R.C., 1996. Modeling the drying behaviour of copra and development of a natural convection dryer for production of high quality copra in the Philippines. Ph.D. Thesis, Hohenheim, Stuttgart, Germany.

Henderson, S.M. and S. Pabis, 1961. Grain drying theory I: Temperature effect on drying coefficient. J. Agr. Eng. Res., 6(3): 169-174.

Jaya, S. and H. Das, 2003. A vacuum drying model for Mango pulp. Dry. Technol., 21(7): 1215-1234.

Kaymak-Ertekin, F., 2002. Drying and rehydration kinetics of green and red pepper. J. Food Sci., 67: 168-175.

Kim, K.R., L. Lee, S. Paek, S.P. Yim, D.H. Ahn and H. Chung, 2007. Adsorption tests of water vapor on synthetic zeolites for an atmospheric detritiation dryer. Radiat. Phys. Chem., 76(8-9): 1493-1496.

Lee, J.H. and H.J. Kim, 2008. Vacuum drying kinetics of Asian white radish slices. J. Food Sci. Tech., 42: 180-186.

Liu, Q. and F.W. Bakker-Arkema, 1997. Stochastic modeling of grain drying, part 2: Model development. J. Agr. Eng. Res., 66: 275-280.

Madamba, P.S., R.H. Driscoll and K.A. Buckle, 1996. The thin layer drying characteristics of garlic slices. J. Food Eng., 29: 75-97.

Maskan, M., 2001. Kinetics of colour change of kiwifruits during hot air and microwave drying. J. Eng., 48(2): 169-175.

Maskan, A., S. Kaya and M. Maskan, 2002. Hot air and sun drying of grape leather (pestil). J. Food Eng., 54: 81-88.

Midilli, A., H. Kucuk and Z. Yapid, 2002. A new model for single layer drying. Dry. Technol., 20(7): 1503-1513.

Minaei, S., A. Motevali, E. Ahmadi and M.H. Azizi, 2012. Mathematical models of drying pomegranate arils in vacuum and microwave dryer. J. Agri. Sci. Tech., 14: 311-325.

Overhults, D.G., H.E. White, H.E. Hamilton and I.J. Ross, 1973. Drying soybeans with heated air. T. ASAE, 16: 112-113.

Pala, M., T. Mahmutoğlu and B. Saygi, 1996. Effects of pretreatments on the quality of open-air and solar dried products. Nehru Food, 40: 137-141.

Park, K.S., Z. Vohnikova and F.P.R. Brod, 2002. Evaluation of drying parameters and desorption isotherms of garden mint leaves (Mentha crispa L). J. Food Eng., 51: 193-199.

Ponkham, K., N. Meeso, S. Soponronnarit and S. Siriamornpun, 2012. Modeling of combined far-infrared radiation and air drying of a ring shaped-pineapple with/without shrinkage. Food Bioprod. Process., 90(2): 155-164.

Sharifi, A., B. Hassani and M. Niakousari, 2012. Experimental study and mathematical modeling on thin layer drying of rhubarb (Rheum Ribesl). Sci. Series Data Report J., 4(4).

Varadharaju, N., C. Karunanidhi and R. Kailappan, 2001. Coffee cherry drying: A two-layer model. Dry. Technol., 19: 709-715.

Wang, C.Y. and R.P. Singh, 1978. Use of variable equilibrium moisture content in modeling rice drying. T. ASAE, 78: 6505.

Yaldiz, O., C. Ertekin and H.I. Uzun, 2001. Mathematical modeling of thin layer solar drying kinetics of sultana grapes. Energy Int. J., 26: 457-465.