International Food Research Journal 22(2): 476-481 (2015)
Journal homepage: http://www.ifrj.upm.edu.my

Modeling of drying kinetic of pretreated sour cherry

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Article history

Received: 9 February 2014
Received in revised form: 26 August 2014
Accepted: 30 August 2014

Keywords

Activation energy
Drying
Modeling
Sour cherryStorage

Abstract

The effects of pretreatment solution (dipping in boiling water, salty boiling water, ethil oleat) were studied on drying kinetic of sour cherry. The thin-layer drying of sour cherries were carried out at three air temperatures of 50, 60 and 70°C and airflow velocity of 1 m/s. The experimental data were fitted to several thin-layer drying models such as Newton, Henderson and Pabis, Page, Logarithmic, Approximate Diffusion, Two-term exponential, and Midilli *et al*.. Three statistical tools coefficient of determination (R^2), reduced chi-square (x^2) and root means square error (RMSE) were used to quantify the goodness of fit. According to the results, drying time of sour cherry samples dipped in salty boiling water solution was shorter than the pretreated samples and control treatments. Besids, The Midilli et al. and Logarithmic models were found to be most suitable in describing the drying characteristics of sour cherry respectively. The effective moisture diffusivity of sour cherries based on the analytical solution of Fick's second law ranged from 2.07×10^{-11} to 2.33×10^{-10} m²/s. Using of pretreated solutions caused to decreasing activation energy in sour cherry drying process. Activation energy values varied from 23.74 to 83.05 kJ/mol.

Introduction

Sour cherries (*Prunus cerasus* L.) production broadly distributed around the world. It being found in Asia, Europe, and North America. Iran is one of the ten prior countries in sour cherry production the world (FAO, 2010). In Iran, about half of the total quantity is consumed as fresh state for processing purposes such as juice, jam and confectionery. Fresh cherries such as sweet and sour cherry are very sensitive to microbial spoilage, even at refrigerated conditions. Thus, they must be preserved in some form. Drying, which is the oldest food preservation technique practiced by humankind, is the most important process to preserve sour cherry since it has a great effect on the quality of the dried products (Abdelhaq and Labuza, 1987; Vagenas and Marinos-Kouris, 1991; Doymaz and Ismail, 2011). The objective in drying sour cherry is to reduce the moisture content to a level that allows safe storage over an extended period. In many Middle East countries such as Iran, Iraq, Pakistan and Turkey, the most common and traditional drying method for horticultural fruits is open-air sun drying. In order to reduce time and improve the quality of fruits, traditional drying methods should be replaced by industrial dryers. The main disadvantages of solar dryers are the limited time of solar radiation and the short season of ripening of many agricultural products. Industrial Hot-air dryers, which are far more rapid, providing uniformity and hygiene are inevitable for industrial food drying processes (Karathanos and Belessiotis, 1997; Demir *et al*., 2004). Literature review showed that using of pretreatment solutions or methods greatly reduces drying time and improve water permeability of grape, apricot, mulberry, and plum. Dipping waxy fruits for several seconds in solutions of ethyl oleate or other suitable compounds (usually fatty acid derivatives used as wetting agents and emulsifiers) greatly reduces drying time and improved many quality parameters (Ponting and McBean, 1970; Bolin *et al*., 1975; Saravacos *et al.*, 1988; Dincer, 1996; Pala *et al*., 1996; Doymaz and Pala, 2002b; Doymaz and Pala, 2003).

Drying time of pretreated samples in alkali ethyl oleate solution, was about 26–30% shorter than that of untreated samples (Doymaz, 2007). Although using of alkali ethyl oleate solution investigated on sour cherry drying, but it is no study were found in the literature which compared the effect of many pretreatment solutions in comparison with control treatment (no pretreatment sample) on sour cherry drying process. The objective of this study was to investigate the effect of dipping in pretreatment solutions ethyl oleate, boiling water, boiling salty water in comparison with no pretreatment sample (control treatment) in 50-70°C on the drying rates of sour cherry to evaluate alternative thin-layer drying models and to determine diffusion coefficients and

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effective moisture diffusivity.

Materials and Methods

Sample preparation

Ripe sour cherries (*Prunus cerasus* L.) of proper maturity, uniform size, red color, and firm texture were prepared from a local garden of Karaj city, Iran. The overripe and bruised fruits were separated manually. After washing in cold water to remove all foreign material such as dust, dirt, and leaves, the fruits were kept in refrigerator at 4◦C before pretreatment and drying. Generally, samples of uniform size selected. The average diameter of samples was 13.40 ± 0.20 cm. Initial moisture content of the fresh sour cherries found about 75.0 ± 2.0 % (w.b.), and was determined by drying in an air convection oven at 105°C for 7-10 h, performed in five replications (Doymaz,, 2007; Ghaderi *et al*., 2011). Chemicals materials used for dipping sample were of laboratory grade. Using three units lab scale precision dryer. Effects of drying temperature in three levels 50, 60 and 70°C were investigated on drying time of sour cherry for below treatments: 1. Fresh sour cherry without pre treatment (Control), 2. Dipping fresh sour cherry in 2% ethyl oleate for 1 minute, 3.Dipping fresh sour cherry in boiling water for 1 minute and 4. Dipping fresh sour cherry in salty boiling water (sodium chloride 20%) for 1 minute

Drying procedure

In each experiment, about 1000 g of fresh sour cherry was used. All treatments were dried to 17.0 ± 3.0 % (w.b.). The product was cooled and packed in low-density polyethylene (LDPE) bags that were heat-sealed. The runs were performed in three replicates (Doymaz, 2007). The temperature and air velocity were measured by a digital thermometer (Atbin, AT400K.) with 1°C accuracy and Hot wire anemometer (Testo 425) with 0.1 m/s accuracy, respectively. Air velocity was adjusted about 1 m/s in the outlet air gate. Sample weights were determined automatically each 15 minutes using an electronic weighting system connected to the computer. Temperatures and relative humidity of the lab was 24±2°C and 39±8 % respectively.

Mathematical modeling

Drying curves were fitted with seven different moisture ratio models (Table1). In these models, the moisture ratio MR of sour cherries during the drying experiments was expressed by the following equation:

$$MR = \frac{M_t - M_e}{M_o - M_e} \quad (1)$$

Table 1. Selected thin layers drying models

Model	Equation#	References
Newton (**NM**)	$MR = exp(-kt)$	(Westerman *et al*., 1973)
Page (**PM**)	$MR = exp(-kt^n)$	(Page, 1949)
Henderson and Pabis (**HPM**)	$MR = a\,exp(-kt)$	(Henderson and Pabis, 1961)
Two term exponential (**TEM**)	$MR = a\,exp(-kt) + (1-a)\,exp(-kat)$	(Akpinar *et al*., 2003).
Approximate Diffusion (**ADM**)	$MR = a\,exp(-kt) + (1-a)\,exp(-kbt)$	(Doymaz, 2007).
Logarithmic (**LM**)	$MR = a\,exp(-kt)+b$	(Togrul and Pehlivan, 2002)
Midili et al. (**MDM**)	$MR = a exp(-kt^n)+bt$	(Midili *et al*., 2002)

MR: moisture Rate t: time (min) a, b, n and k are constants

Where M_t is the moisture content at any time (kg water/kg dry basis), M_o is the initial moisture content (kg water/kg dry basis), and M_e is the equilibrium moisture content of the sample (kg water/kg dry basis). The values of M_e are relatively small compared to M_t or M_o, hence the error involved in the simplification is negligible (Diamante and Munro, 1993; Akpinar *et al*., 2003; Doymaz, 2004).

The regression analysis performed using the STATISTICA 6.0 software. Non-linear regression was used to evaluate the goodness of fit mathematical models to the experimental data. Using Non-linear regression, three criteria coefficient of determination (R^2), the reduced chi-square (X^2) and root mean square error (RMSE) were used to evaluate the fit of each model. parameters and RMSE calculated as follows:

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

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{n}(MR_{pre,i} - MR_{exp,i})^2\right]^{1/2} \quad (3)$$

Where $MR_{exp,i}$ and $MR_{pre,i}$ are experimental and predicted dimensionless moisture ratios, respectively; N is the number of observations; and n is number of drying constants. The best model describing the thin-layer drying characteristics of sour cherry was chosen as the one with the highest coefficient of determination and the least reduced chi-square and root means square error (Akpinar *et al*., 2003; Doymaz, 2007).

Calculation of effective diffusivity and activation energy

After selection better model, the analytical solution of Fick's second law in spherical geometry by Crank (1975) is applicable, assuming that the effective moisture diffusivity is constant and is of the form:

$$MR = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{\pi^2}\exp\left(\frac{n^2\pi^2 D_{eff}t}{r^2}\right) \quad (4)$$

Where Deff is the effective moisture diffusivity (m^2/s), r is the radius of sour cherries (m), and n is a positive integer. For long drying times (setting n=1), Eq. (4) can be further simplified to a straight-line equation as (Pala *et al.*, 1996).

$$Ln(MR) = Ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}\, t}{r^2}\right) \quad (5)$$

The effective moisture diffusivity was calculated using the method of slopes. Effective diffusivities are typically determined by plotting experimental drying data in terms of ln(MR) versus time (Tutuncu and Labuza, 1996). From Eq. (5), a plot of ln(MR) versus time gives a straight line with a slope k_2 .

$$K_2 = \frac{\pi^2 D_{eff}}{r^2} \quad (6)$$

The dependence of the effective diffusivity on temperature is generally described by the Arrhenius equation (Simal *et al.*, 2005):

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{R(T+273.15)}\right) \quad (7)$$

Where D_0 is the pre-exponential factor of Arrhenius equation in m^2/s, is the activation energy in kJ/mol, is the universal gas constant in kJ/(mol K), and is temperature in °C.

Results and Discussion

Drying characteristics

The drying times of the differently treated, dried sour cherry are given in Table 2.

Table 2. Drying time of sour cherry for experimental treatments

Temperature (°C)	Pre treatment solution	Drying time (h)
50	No Treatment (Control)	119.7
	Ethyl Oleate	24.2
	Boiling Water	26.7
	NaCl+ Boiling Water	20.2
60	No Treatment (Control)	42.7
	Ethyl Oleate	13.2
	Boiling Water	13.7
	NaCl+ Boiling Water	10.5
70	No Treatment (Control)	17.3
	Ethyl Oleate	9.0
	Boiling Water	9.8
	NaCl+ Boiling Water	7.7

The initial moisture content of the sour cherry was about 75.0 ± 2.0 % (w.b.). Drying time of all treatments calculated when the samples moisture content reached to 17.0 ± 3.0 % (w.b.). Curves of moisture ratio versus drying time for pre/untreated sour cherry are shown in Figures 1, 2 and 3. It is apparent that

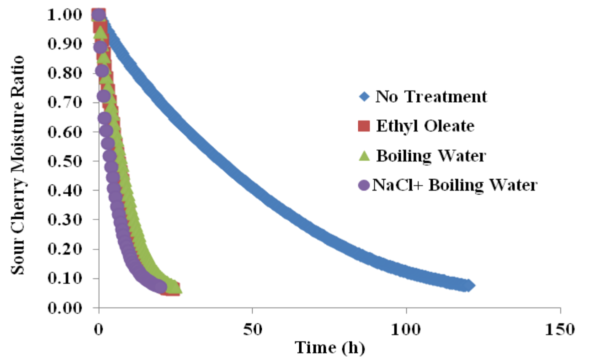

Figure 1. Effect of different dipping pre-treatments on sour cherry drying at temperature of 60◦C

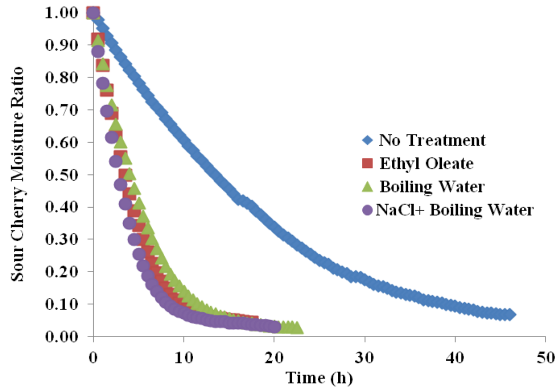

Figure 2. Comparison of experimental and predicted moisture ratios with the MDM and LM models versus drying time for dried salty boiling water sour cherry at 50 ◦C

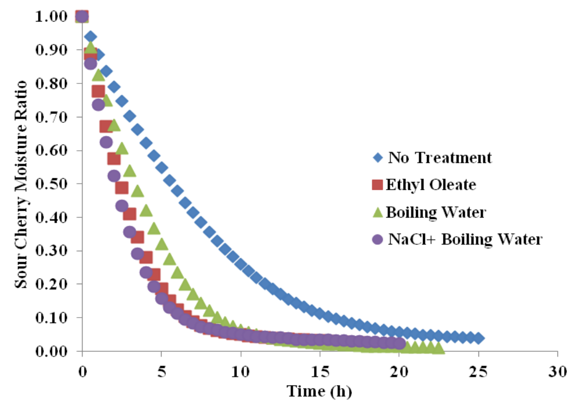

Figure 3. Comparison of experimental and predicted moisture ratios with the MDM and LM models versus drying time for dried salty boiling water sour cherry at 60 ◦C

at all drying temperatures, moisture ratio decreases continuously with drying time. In these curves, there was no constant-rate period, but falling-rate period was seen to occur. The difference between moisture curves trends of treatments was more in 50 and 60°C respectively than 70°C. It is indicated that the effect of pretreatment solutions on sour cherry drying were higher in lower temperatures. Similar results were obtained on drying of various fruits such as grapes, apricots, and mulberries (Raouzeos and Saravacos,

Table 3. Statistical results from various thin-layer drying models of experimental treatments

Model	No Treatment (Nature)			Ethyl Oleate			Boiling Water			Boiling Water + Nacl		
	R^2	X^2	RMSE	R^2	X^2	RMSE	R^2	X^2	RMSE	R^2	X^2	RMSE
Newton (NM)	0.99473	0.00039	0.01382	0.99303	0.00054	0.00944	0.99501	0.00039	0.00838	0.99196	0.00036	0.00692
Page (PM)	0.99883	0.00009	0.00657	0.99701	0.00023	0.00582	0.99879	0.00009	0.00421	0.99520	0.00031	0.00682
Henderson and Pabis(HPM)	0.99621	0.00028	0.01184	0.99516	0.00039	0.00781	0.99630	0.00013	0.00434	0.99358	0.00041	0.00818
Two Term Exponential (TEM)	0.99412	0.00042	0.01340	0.99709	0.00023	0.00570	0.99900	0.00008	0.00384	0.99544	0.00030	0.00668
Approximate Diffusion (ADM)	0.99774	0.00017	0.00864	0.99521	0.00040	0.00764	0.99768	0.00019	0.00548	0.99684	0.00022	0.00561
Logarithmic (LM)	0.99873	0.00010	0.00578	0.99593	0.00033	0.00715	0.99704	0.00023	0.00643	0.99803	0.00013	0.00448
Midili et al. (MDM)	0.99964	0.00003	0.00381	0.99955	0.00004	0.00239	0.99937	0.00005	0.00303	0.99912	0.00006	0.00299

1986; Vagenas and Marinos-Kouris, 1991; Doymaz and Pala, 2003).

Generally, drying times for sour cherry samples, which were dipped in pretreatment solutions, are shorter than control samples, at experimental temperatures (Table 2). The effect pretreatment solutions were higher on reduction time of sour cherry in 50°C. Dipping in salty boiling water was better than the other solutions. It reduced drying time of sour cherry more than 80%. In previous research results, the effect of ethyl oleate has been found a good pretreatment solution in drying of some fruits (Saravacos *et al*., 1988; Doymaz and Pala, 2002a; Doymaz and Pala, 2003; Doymaz, 2007), but there were no comparison between other solutions.

Modeling of drying curves

Moisture ratio data obtained at air temperatures of 50, 60 and 70°C were fitted in to the selected the thin-layer drying models. , and RMSE values obtained for sour cherries are summarized in Table 3. The best model describing the thin-layer drying characteristics of sour cherry was chosen as the one with the highest values and the lowest and RMSE values. In all cases, the values for the models were greater than 0.99, indicating a good fit. Generally, , and RMSE values varied between 0.99473–0.99964, 0.00003–0.00054 and 0.00239–0.01382, respectively. As expected, the Midili *et al*. (MDM) model gives the highest values of and the lowest values of and RMSE. Thus, MDM model assumed to represent the air-drying behavior of sour cherry. In addition, according of experimental results, Logarithmic (LM) model selected as the second model for estimation of the sour cherry drying process. This result is similar to pervious researches (Doymaz, 2007; Ghaderi *et al*., 2011). The constants of MDM and LM models were presented in Table 4 for different drying conditions. For the example figure 4 compares experimental and predicted moisture ratio with MDM and LM models versus drying time for dried pre/ untreated sour cherries at 60°C. Similar results were reported on drying of various fruits (Togrul and Pehlivan, 2002; Midilli, *et al*., 2002; Doymaz, 2007).

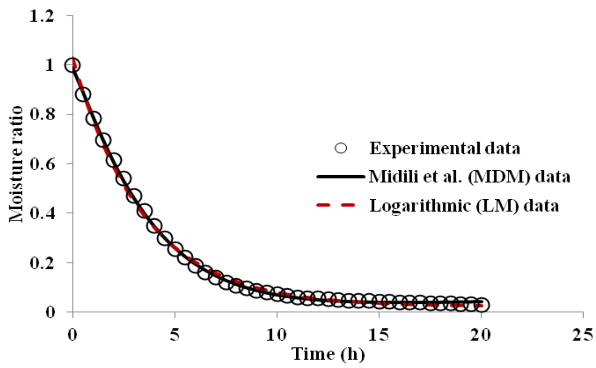

Figure 4. Comparison of experimental and predicted moisture ratios with the MDM and LM models versus drying time for dried salty boiling water sour cherry at 70 ◦C

Calculation of effective diffusivity and Activation energy

The results of effective moisture diffusivity are shown in Figure 5. The effective moisture diffusivities of sour cherries during drying, were found between 2.07×10^{-11} to 2.33×10^{-10} m^2/s among pretreated and control (No treatment) samples. According to these results, effective diffusivity increased with increasing temperature. The effective diffusivity was also affected by the pretreatment solution. As a result, pretreated of the sour cherries in resulted in higher effective moisture diffusivity than untreated samples. Pretreated sour cherry in salty boiling water caused to higher effective moisture diffusivity in comparing to other solutions. A similar effect of pretreatment solutions has been found in the air-drying of apricots, sour cherry, sweet cherry and grapes (Raouzeos and

Table 4. Coefficients of MDM and LM models for sour cherry drying

Per Treatment	Temprearure (oC)	Midili *et al.* (MDM)				Logarithmic (LM)		
		a	b	n	k	a	b	k
No Treatment (Nature)	50	0.978522	-0.000470	1.066967	0.012761	1.121364	-0.130444	0.014799
No Treatment (Nature)	60	0.983910	0.000087	1.151198	0.034534	1.075538	-0.057862	0.049904
No Treatment (Nature)	70	0.977261	0.000664	1.191010	0.087347	1.050309	-0.025806	0.127702
Ethyl Oleate	50	0.981194	0.001315	1.254698	0.068623	1.075237	-0.037090	0.113362
Ethyl Oleate	60	0.985760	0.002345	1.231268	0.153159	1.038869	0.004220	0.227213
Ethyl Oleate	70	0.995337	0.002053	1.204391	0.243891	1.035117	0.014287	0.335751
NaCl+ Boiling Water	50	1.012556	0.000719	0.859821	0.236486	0.922340	0.052442	0.196038
NaCl+ Boiling Water	60	0.990785	0.002002	1.124225	0.225791	1.005817	0.022956	0.286464
NaCl+ Boiling Water	70	1.001131	0.001921	1.099115	0.313298	1.008216	0.024800	0.376990
Boiling Water	50	0.967493	0.000578	1.191700	0.064933	1.063735	-0.056327	0.093179
Boiling Water	60	0.996210	0.000527	1.097282	0.155680	1.026060	-0.002260	0.187378
Boiling Water	70	0.980919	0.000598	1.247407	0.154695	1.056692	-0.008583	0.238656

Saravacos, 1986; Doymaz, 2004; Doymaz, 2007; Doymaz and Ismail , 2011). The activation energy was calculated by plotting versus the reciprocal of the temperature (1/(T + 273.15)). The activation energy values were found between 23.74 to 83.05 kJ/mol for the control and pre-treated samples. Generally, using of pre treated solutions caused to decreasing activation energy and drying time. These results were observed for other fruits (Vagenas and Marinos-Kouris, 1991; Tutuncu and Labuza 1996; Doymaz and Pala, 2002b).

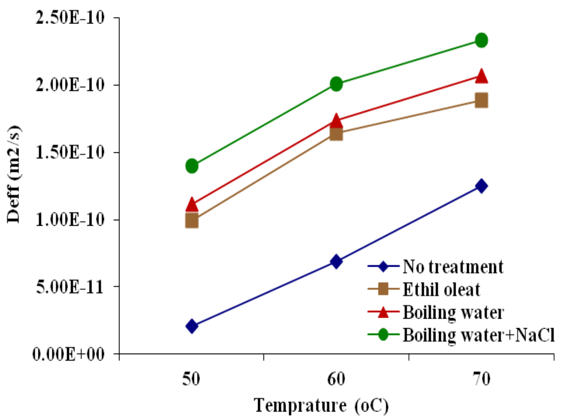

Figure 5. Air temperature effects on the effective diffusivity between 50- 70 ◦C for experimental samples

Conclusions

In this research concluded that using of pretreated solution is necessary for sour cherry drying process. It is reduced drying time up to 80 percent and more. According to the results, sour cherry samples dipped in salty boiling water solution before drying were found to have a shorter drying time in comparing with the samples dipped in ethyl oleate, boiling water, and control treatments. Midili *et al*. (MDM) model had best fitting with experimental data in range 50 to 70°C and represented the air-drying behavior of sour cherry. In addition, according of experimental results, Logarithmic (LM) model can be selected as the second model for estimation of sour cherry drying process. The activation energy values found from 23.74 to 83.05 kJ/mol for the control and pretreated samples. Besides, using of pretreated solutions caused to decreasing activation energy in sour cherry drying process.

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