Sun drying of seedless and seeded grapes

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Abstract In this study, sun drying behaviour of seedless and seeded grapes was investigated. The drying study showed that the times taken for drying of seedless and seeded grapes of berry size of 1.72 cm and 2.20 cm thicknesses from the initial moisture contents of 78.2% and 79.5% (w.b.) to final moisture content of around 22% (w.b.) were 176 and 228 h in open sun drying, respectively. The drying data were fitted to 12 thin-layer drying models. The performance of these models were compared using the determination of coefficient (R^2), mean relative percent error (P), reduced chi-square (χ^2) and root mean square error (RMSE) between the observed and predicted moisture ratios. The results showed that Midilli et al. model was found to satisfactorily describe the sun drying curves of seedless and seeded grapes. The effective moisture diffusivity values were estimated from Fick's diffusion model by 1.02×10^{-11} and 1.66×10^{-11} m²/s for seeded and seedless grapes.

Keywords Sun drying · Seedless and seeded grapes · Thin-layer drying models · Non-linear regression · Effective moisture diffusivity

Nomenclature

a, b, c, g, h	Empirical constants in drying models
D_{eff}	Effective diffusivity (m ² /s)
K, k_0 , k_1	Empirical coefficients in the drying models (1/h)
K	Slope

$MR_{\text{exp},i}$	Experimental moisture ratio
$MR_{\text{pre},i}$	Predicted moisture ratio
M	Moisture content at time t (kg water/kg dry matter)
M_e	Equilibrium moisture content (kg water/kg dry matter)
M_0	Initial moisture content (kg water/kg dry matter)
N	Number of observations
n	Constant, positive integer
P	Mean relative percent error
R^2	Determination of coefficient
RMSE	Root mean square error
r	Radius (m)
t	Drying time (h)
χ^2	Reduced chi-square
z	Number of constants

Introduction

Drying of fruit and vegetable is one of the oldest forms of food preservation methods known to man and is the most important process to preserve food since it has a great effect on the quality of the dried products. The major objective in drying agricultural products is the reduction of the moisture content to a level, which allows safe storage over an extended period. Also, it brings about substantial reduction in weight and volume, minimising packaging, storage and transportation costs (Okos et al. 1992; Zomorodian and Dadashzadeh 2009). In spite of many disadvantages such as long drying times, contamination of the product and product losses, sun drying is still practised in many places throughout the world. Solar energy is an important

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alternative source of energy and preferred to other energy sources because it is abundant, inexhaustible, renewable, cheap and non-pollutant (Basunia and Abe 2001; Akbulut and Durmus 2009; Chong et al. 2009).

Grape is one of the world's largest fruit crops. According to FAO data for 2007, grape production all over the world was about 67,221 million tones. The major producer countries include Italy, China, United States of America, France, Spain, Turkey, and Iran (FAO 2008). Turkey exported 240 600 tones dried grapes (raisin) in 2007 and income was about 240 599 000 US\$ (IGEME 2007). Most of the grapes in Turkey are produced in the Aegean region. In general, the fresh grapes are untreated or pre-treated with traditional solution (5% K_2CO_3 + 1.5% olive oil) and left for sun drying. Drying process usually takes 15 to 20 days for untreated grapes and 7 to 12 days for pre-treated grapes, depending on the relative humidity and temperature of ambient air (Pala et al. 1993). Grapes are covered naturally with a thin-layer of wax; hence, it is necessary to increase water transport from grape berries during drying process. Dipping in hot water or the use of chemicals such as sulphur, potassium meta bisulphide (KMS), potassium hydroxide (KOH), sodium hydroxide (NaOH), potassium carbonate (K_2CO_3), and ethyl or methyl oleate emulsions are some of pretreatments widely used for fruit drying to increase drying rate and improve the colour quality of products (Mahmutoglu et al. 1996; Di Matteo et al. 2000; Kingsly et al. 2007; Serratos et al. 2008; Bingol et al. 2008; Shi et al. 2008).

Drying is a complex thermal process in which unsteady heat and moisture transfer occur simultaneously (Sahin and Dincer 2005). From an engineering point of view, it is important to develop a better understanding of the controlling parameters of this complex process. Mathematical

models of the drying processes are used for designing new or improving existing drying systems or even for the control of the drying process. Many mathematical models have been proposed to describe the drying process, of them thin-layer drying models have been widely in use. These models can be categorized as theoretical, semi-theoretical, and empirical (Ozdemir and Devres 1999; McMinn 2006). Recently, there have been many research on the mathematical modelling and experimental studies of the drying behaviour of various fruits, such as grapes (Kostaropoulos and Saravacos 1995; Sawhney et al. 2009), apricots (Togrul and Pehlivan 2004), figs (Babalıs and Belessiotis 2004; Doymaz 2005), plum (Sabarez and Price 1999), and mulberry (Akpınar 2008; Akbulut and Durmus 2009). Studies on the sun drying of seedless and seeded grapes are scarce in the literature. Therefore, the present study was undertaken to study the drying kinetics of seedless and seeded grapes in direct exposure to the sun, to calculate the effective diffusivity of the samples, and to fit the drying curves with 12 thin-layer drying models.

Material and methods

Materials

Fresh ripe hand harvested grapes (seedless and seeded) from Iskenderun region, Hatay, were used for the drying tests. Hatay is a province of southern Turkey, situated between the Mediterranean Sea to the west and Syria to the South-East. Its geographic coordinates are $35^\circ 52'$ to $37^\circ 04'$ North, $35^\circ 40'$ to $36^\circ 35'$ West and is hot and dry in summer. For ensuring the uniformity of the physical characteristics of the grapes dried. The average berry

Table 1 Proposed thin-layer drying models for seedless and seeded grapes

Model no	Model name	Model equation	References
1	Lewis	$MR = \exp(-kt)$	Ayensu (1997)
2	Henderson and Pabis	$MR = a \exp(-kt)$	Henderson and Pabis (1961)
3	Modified Henderson and Pabis	$MR = a \exp(-kt) + b \exp(-gt) + c \exp(-ht)$	Karathanos (1999)
4	Logarithmic	$MR = a \exp(-kt) + c$	Kingsly et al. (2007), Akpınar (2008), Vega-Gálvez et al. (2009).
5	Two-term	$MR = a \exp(-k_0t) + b \exp(-k_1t)$	Yaldiz et al. (2001), Togrul and Pehlivan (2004)
6	Two-term exponential	$MR = a \exp(-kt) + (1 - a) \exp(-kat)$	Midilli and Kucuk (2003)
7	Verma et al.	$MR = a \exp(-kt) + (1 - a) \exp(-gt)$	Verma et al. (1985)
8	Approximation of diffusion	$MR = a \exp(-kt) + (1 - a) \exp(-kbt)$	Yaldiz and Ertekin (2001)
9	Page	$MR = \exp(-kt^n)$	Rajkumar et al. (2007), Sawhney et al. (2009).
10	Midilli et al.	$MR = a \exp(-kt^n) + bt$	Midilli et al. (2002), Bingol et al. (2008), Boughali et al. (2009).
11	Parabolic	$MR = a + bt + ct^2$	Sharma and Prasad (2004)
12	Wang and Singh	$MR = 1 + at + bt^2$	Wang and Singh (1978)

diameters of seedless and seeded grapes were kept at 1.72 ± 0.1 and 2.20 ± 0.1 cm, respectively.

Drying procedure

The selected samples were cleaned with tap water to make samples free from dust and foreign materials. The grapes were then subjected to dipping in order to remove wax layer on the grapes so as to increase drying rate. For this reason, seedless and seeded grapes are dipped for 1 min into the solution of potassium carbonate and olive oil (2.5% K_2CO_3 + 0.5% olive oil). Pre-treated samples, about 300 ± 0.5 g, were distributed uniformly in a single layer in the sample tray, and then sun dried by direct exposure to solar radiation in August 2007 in the Iskenderun, Hatay. The grapes were exposed to sunlight for 12 h daily. Moisture loss was measured at 4-h intervals during drying for determination of the drying curves by a Mettler balance (model BB3000), which has 0–3000 g measurement range with an accuracy of ± 0.1 g. No measurement was made during the night. Drying was continued until the sample reached the desired moisture level of $22 \pm 0.5\%$ (w.b). Dried samples were packed in Low Density Polyethylene (LDPE) bags. The experiments were conducted in triplicate and the average values were reported.

Initial moisture content

The average initial moisture contents of the seedless and seeded grape samples were found to be $78.2 \pm 0.2\%$ and $79.5 \pm 0.2\%$ (w.b.), respectively, as determined by using vacuum oven at 70°C for 24 h following the Association of Official Analytical Chemists (AOAC 1990).

Ambient air temperature

Ambient air temperature during drying was measured by an iron-constantan thermocouple, with a manually controlled 8-channel automatic digital thermometer, with reading accuracy of $\pm 0.1^\circ\text{C}$ (Meter Electronic, Turkey).

Mathematical modeling of drying curves

Moisture ratio (MR) of grapes was obtained using the equation below:

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

where M_t is the moisture content at anytime (kg water/kg dry matter), M_0 is the initial moisture content (kg water/kg dry matter) and M_e is the equilibrium moisture content of samples (kg water/kg dry matter). The moisture ratio (MR)

Fig. 1 Variation of ambient temperature during sun drying of seedless and seeded grapes on a typical day of August 2007 at Iskenderun, Hatay

was simplified to M_t/M_0 instead of $(M_t - M_e)/(M_0 - M_e)$ by some investigators (Diamante and Munro 1993; Yaldiz et al. 2001; Doymaz 2005; Kingsly et al. 2007; Akpınar 2008) because of the continuous fluctuation of relative humidity of the drying air during sun drying.

Drying curves were fitted to 12 thin-layer drying models, which are widely used in the scientific literature to describe the kinetics of the drying process. The selected thin-layer drying models are identified in Table 1. A nonlinear estimation package (Statistica 6.0) was used to estimate the coefficients of the given models. The four criteria of statistic analysis have been used to evaluate the fitting of

Fig. 2 Experimentally moisture contents of seedless and seeded grapes versus drying time

Table 2 Curve fitting criteria for the various models and parameters for drying of seedless grapes

Model no	Constants	R ²	P	χ ²	RMSE
1	k: 0.0105	0.9788	16.4944	0.00165	0.18409
2	a: 1.0269, k: 0.0108	0.9802	15.6052	0.00159	0.18392
3	a: −18.1370, k: 0.0290, b: 7.7622, g: 0.0359, c: 11.3748, h: 0.0230	0.9951	5.8843	0.00045	0.08916
4	a: 1.4712, k: 0.0054, c: −0.4945	0.9962	3.7993	0.00031	0.08037
5	a: −16.1182, k ₀ : 0.0192, b: 17.0797, k ₁ : 0.0184	0.9916	8.8371	0.00072	0.11677
6	a: 0.0017, k: 6.0812	0.9786	16.6194	0.00172	0.18403
7	a: −4.620, k: 0.0191, g: 0.0169	0.9900	9.5772	0.00083	0.12219
8	a: −5.6006, k: 0.0188, b: 0.9063	0.9900	9.5619	0.00083	0.12219
9	k: 0.0043, n: 1.1939	0.9888	9.7126	0.00089	0.12822
10	a: 0.9894, k: 0.0098, n: 0.9069, b: −0.0015	0.9964	3.4653	0.00031	0.07967
11	a: 0.9703, b: −0.0074, c: 0.0001	0.9959	3.7892	0.00033	0.08382
12	a: −0.0080, b: 0.0001	0.9943	4.4772	0.00045	0.08841

the experimental data to the different models; the coefficient of determination (R^2), mean relative percent error (P), reduced chi-square (χ^2) and root mean square error (RMSE). These parameters can be calculated as:

$$P = \frac{100}{N} \sum_{i=1}^N \frac{|MR_{exp,i} - MR_{pre,i}|}{MR_{exp,i}} \quad (2)$$

$$\chi^2 = \frac{\sum_{i=1}^N (MR_{exp,i} - MR_{pre,i})^2}{N - z} \quad (3)$$

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

where $MR_{exp,i}$ and $MR_{pre,i}$ are experimental and predicted dimensionless moisture ratios, respectively; N is number of

observations; z is number of constants. For quality fit, R^2 value should be higher and P, χ^2 and RMSE values should be lower (Kingsly et al. 2007; Vega-Gálvez et al. 2009).

Determination of effective moisture diffusivity

Fick's second law of diffusion equation was used to fit the experimental data for the determination of effective moisture diffusivity:

$$\frac{\partial M}{\partial t} = D_{eff} \nabla^2 M \quad (5)$$

The analytical solution of Fick's second law (Eq. 5) unsteady state diffusion in a spherical coordinates with the assumptions of moisture migration being by diffusion, negligible shrinkage, constant effective moisture diffusivity

Table 3 Curve fitting criteria for the various models and parameters for drying of seeded grapes

Model no	Constants	R ²	P	χ ²	RMSE
1	k: 0.0082	0.9687	20.9432	0.00258	0.27709
2	a: 1.0503, k: 0.0087	0.9731	18.5239	0.00227	0.25875
3	a: 9.5141, k: 0.0154, b: −3.4207, g: 0.0169, c: −5.1432, h: 0.0169	0.9931	7.6239	0.00064	0.12351
4	a: 1.6033, k: 0.0038, c: −0.6135	0.9956	6.1286	0.00037	0.10278
5	a: 25.2698, k ₀ : 0.0158, b: −24.3196, k ₁ : 0.0164	0.9931	7.5937	0.00061	0.12321
6	a: 0.0012, k: 6.4832	0.9684	21.1572	0.00267	0.27813
7	a: −4.2613, k: 0.0166, g: 0.0143	0.9910	8.7674	0.00078	0.14037
8	a: −5.8401, k: 0.0163, b: 0.8906	0.9910	8.7426	0.00078	0.14013
9	k: 0.0018, n: 1.3089	0.9908	7.6445	0.00078	0.13904
10	a: 0.9616, k: 0.0019, n: 1.2489, b: −0.0005	0.9963	4.3141	0.00032	0.08614
11	a: 0.9875, b: −0.0059, c: 0.0001	0.9962	4.9585	0.00033	0.09270
12	a: −0.0061, b: 0.0001	0.9960	4.4775	0.00033	0.09059

Fig. 3 Experimental vs. predicted moisture ratio (MR) values for seedless and seeded grapes drying

and temperature during the drying process is given as follows (Crank 1975):

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

where, D_{eff} is the effective moisture diffusivity in m^2/s , r is the radius of samples in m , and n is a positive integer. For long drying periods, Eq. (6) can be further simplified to only the first term of the series. Thus, Eq. (6) is written in a logarithmic form as follows:

$$\ln(MR) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff} t}{r^2}\right) \quad (7)$$

The effective moisture diffusivity is obtained by plotting the experimental drying data in terms of $\ln(MR)$ versus

time. From Eq. (7), a plot of $\ln MR$ versus time gives a straight line with a slope of (K) , in which:

$$K = \frac{\pi^2 D_{eff}}{r^2} \quad (8)$$

Results and discussion

Ambient temperature

The experiments were performed in August 2007, in Iskenderun, Hatay, Turkey. The variation of ambient air temperatures during sun drying of grape samples under natural convection in a typical day is shown in Fig. 1. During the drying experiments, the weather was generally sunny and no rain appeared. From Fig. 1, the temperature of ambient air ranged from 32 to 46 °C. The ambient air temperature increased to reach 46 °C at 13:00, which was considered the maximum ambient temperature during the day time.

Drying curves

The changes in moisture content with drying time of samples in open sun drying are presented in Fig. 2. The interruptions of the line in this figure represent the night periods of the drying process. The seedless and seeded grapes of average initial moisture content of around 78.2% and 79.5% (w.b.), respectively, were reduced to the final moisture content of 22% (w.b.). It is apparent that moisture ratio decreases continuously with drying time. It is seen from Fig. 2 that the time required to dry the seedless and seeded grapes was 176 and 228 h, respectively. As expected, drying time increased with increase in berry size when diameters increased from 1.72 to 2.20 cm. It observed that small grapes (1.72 cm) could be heated up more

Table 4 Effective moisture diffusivity values of seedless and seeded grapes and other products

Fruits	Drying type	Effective moisture diffusivity (m^2/s)	References
Seedless grapes	Sun drying	1.66×10^{-11}	Present work
Seeded grapes	Sun drying	1.02×10^{-11}	Present work
Seedless grapes	Solar drying	$0.95\text{--}1.05 \times 10^{-10}$	Raouzeos and Saravacos (1986)
Seedless grapes	Hot-air drying	$2.40\text{--}6.22 \times 10^{-10}$	Pahlavanzadeh et al. (2001)
Seedless grapes	Air-impingement drying	$1.82\text{--}5.84 \times 10^{-10}$	Xiao et al. (2010)
Seedless grapes	Hot-air drying	$7.91\text{--}24.5 \times 10^{-10}$	Ismail et al. (2008)
Fig	Sun drying	2.47×10^{-10}	Doymaz (2005)
Prune	Hot-air drying	$4.30 \times 10^{-10}\text{--}7.60 \times 10^{-10}$	Sabarez and Price (1999)
Ciku	Sun drying	$1.95 \times 10^{-10}\text{--}2.08 \times 10^{-10}$	Chong et al. (2009)
Chempedak	Hot-air drying	$3.29 \times 10^{-10}\text{--}4.53 \times 10^{-10}$	Chong et al. (2008)
Apple	Hot-air drying	$2.27 \times 10^{-10}\text{--}4.97 \times 10^{-10}$	Sacilik and Elicin (2006)

quickly than large ones (2.20 cm). Therefore, small fruits showed high drying rates. Similar results have been reported by Shi et al. (2008).

Evaluation of the models

Non-linear regression analyses were performed to thin-layer drying models (Table 1) regarding moisture ratio versus drying time data. The models were evaluated based on the determination of coefficient (R^2), mean relative percent error (P), reduced chi-square (χ^2) and root mean square error (RMSE). R^2 , P, χ^2 and RMSE values obtained are summarised in Tables 2 and 3. The best model describing the thin-layer drying characteristics of seedless and seeded grapes was chosen as the one with the highest R^2 values and the lowest P, χ^2 and RMSE values. In all cases, the R^2 values for the models were greater than 0.96, indicating a good fit. From Tables 2 and 3, the statistical parameter estimations showed that R^2 , P, χ^2 and RMSE values ranged from 0.9684 to 0.9964, 3.4653 to 21.1572, 0.00031 to 0.0026 and 0.07967 to 0.27813, respectively. As expected, the Midilli et al. model gives the highest value of R^2 and lowest of P, χ^2 and RMSE values (Tables 2 and 3). Thus, Midilli et al. model may be assumed to represent sun drying characteristics of seedless and seeded grapes in thin-layers. Figure 3 compares the experimental data with the predicted ones using Midilli et al. model for seedless and seeded grapes. The prediction using the model showed MR values banded along a straight line, which proved the suitability of these models in describing the drying characteristics of samples. This observation is in agreement with the result reported by Midilli et al. (2002), and Akbulut and Durmus (2009).

Effective moisture diffusivity

The values of effective moisture diffusivity were calculated using Eq. (8) and found as $1.02 \times 10^{-11} \text{ m}^2/\text{s}$ for seeded grapes and $1.66 \times 10^{-11} \text{ m}^2/\text{s}$ for seedless grapes. As expected, D_{eff} values increased with decrease in berry size from 2.20 to 1.72 cm. Table 4 shows the D_{eff} values of the present study as well as information available in the literature. Obviously, the effective moisture diffusivity values in sun drying are smaller, mainly because the daytime temperature was below 46 °C most of the time. The temperature is the most important factor affecting the drying process of grape samples. The D_{eff} values reported herein are within the general range of 10^{-11} to $10^{-9} \text{ m}^2/\text{s}$ for food materials (Madamba et al. 1996). The differences between the results could be due to the differences in fruits and varieties, pretreatments and drying equipments.

Conclusions

In this study, sun drying characteristics of seedless and seeded grapes were investigated under open sun. Results showed that the drying time increased with increased berry size. To explain the drying characteristics of grapes 12 thin-layer drying models were applied. The Midilli et al. model showed better fit with high R^2 , and low P, χ^2 and RMSE values. The resulting model gave values of parameters for samples in the thin layer sun drying process: R^2 : 0.9963–0.9964, P: 3.4653–4.3141, χ^2 : 0.00031–0.00032, and RMSE: 0.07967–0.08614. The effective moisture diffusivity values for seeded and seedless grapes estimated using Fick's diffusion model were 1.02×10^{-11} and $1.66 \times 10^{-11} \text{ m}^2/\text{s}$, respectively.

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