Convective Drying Kinetics and Phenolic Contents of Olive Leaves

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Abstract. Olive leaves have considerable amount of "oleuropein" which is a kind of polyphenol. This compound could lower blood pressure, cancer risk and oxidative damage of cells. Because of the health benefits of this excellent antioxidant material, olive leaves are the subject of this study. Results of the research will contribute to information about drying behaviour of and drying impact on olive leaves.
Leaves were collected from *Olea europaea* trees from the garden located in Osmaniye Korkut Ata University, Turkey. After collection, they were washed, waited in room temperature to evaporate residual water and pulverized in a commercial blender. Leaf powders were dried in a conventional oven at 50, 60 and 70°C and the weight changes of samples were recorded manually in every 10 minutes for 50 and 60°C and 5 minutes for 70°C. Moisture ratio values were fitted into 13 different thin layer drying models and Parabolic and Cubic models were the best and had the highest R^2 value. On the other hand, total phenolic contents of dried powders were determined with Folin-Ciocalteu method and the highest phenolic amount (633.85 mg / kg gallic acid equivalent) belonged to the 60°C. Colour is accepted as one of the major quality characteristic of leaves and L^*, a^* and b^* values of leaf powders were determined. Temperature had an important effect on a* and b* values of samples ($P < 0.05$).

Keywords:
Olive leave, Drying, Mathematical modelling, Phenolich compound, Color

INTRODUCTION

The specific tree of Mediterrenean region and Asia is *Olea europaea* and known as its therapeutic effects dated from ancient times (Satish and Ansari 2013; Ben Salem et al. 2014). The products of this tree like extracts, teas, fruits and powder are attributed to biophenolic compounds such as secoiridoid oleuropein, tyrosol and hydroxytyrosol and some of these components inhibit microbial activity (Renis 1969; Hirschaman 1972). Several researches have indicated that especially olive leaf extract prevents muscle spasms, reduces blood pressure, stimulates blood flow (Bahloul et al. 2009) and demonstrates antidiabetic, hypolipidemic and anti-inflammatory activity (Ben Salem et al. 2014).

Infusion or decoction are main methods for preparation of olive leaves. Leaves are usually dried because of making easier of extraction procedure and lowering moisture content consequently. Drying is an oldest method for preservation of food stuffs and plays an important role in food processing (Ertekin and Heybeli, 2013). Mathematical modelling of drying kinetics is also significant and required for process optimization and product quality (Karathanos and Belessiotis 1999).

The aims of this study are (i) to determine the temperature effect on drying kinetics of olive leaves, (ii) to fit experimental data to various semi-empirical mathematical models, (iii) to evaluate total phenolic contents of olive leaves.

MATERIAL AND METHOD

Material

Olive leaves which were used for conventional drying experiments were collected from Fakiusagi region (37° 2'44.47"N;36°13'25.40"E) in Osmaniye, Turkey and harvesting of olive leaves was conducted in May, 2016 at nearly temperature of 27 ºC.

Method

50, 60 and 70 ºC were selected temperatures for convective drying of leaves and drying was conducted at a constant air velocity (1.5 m/s) with a laboratory type dryer (Memmert, Germany). Firstly, olive leaves were milled using a commercial blender (Waring, Germany) into 4 mm diameter, then 6-7 grams of powdered olive leaf were put into a petri dish and dehydration was started. Weight of samples were collected in every 10 minutes for 50-60 ºC and every 5 minutes for 70 ºC manually using a 4-digit balance (Ohaus Pioneer, USA) until no weight changes were observed.

Mathematical modelling of drying curves

13 thin layer drying models were used for fitting experimental data and shown in Table 1. The calculation of moisture ratio (MR) was made with the help of Equation (1)

$$MR = \frac{M}{M_0} \quad (1)$$

where M is the moisture content at time t (g water / g sample) and M_0 is the initial moisture content (g water / g sample). Equilibrium moisture content was negligible (Doymaz, 2004).

OriginPro 2016 (OriginLab, USA) software was used for regression analysis. Correlation coefficient (R^2), root mean square error (RMSE) (Equation 2) and reduced chi square (χ^2) (Equation 3) were important parameters to choose superior model. The highest R^2 and the lowest RMSE and χ^2 demonstrated the goodness of the fit.

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

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

where, N is the number of experimental data, y is the number of constant in model, $MR_{exp,i}$ is experimental moisture ratio at *i*, $MR_{pre,i}$ is the predicted moisture ratio at *i* (Doymaz, 2007).

Table 1: Semi-emphirical models for convective drying available in literature

Model Name	Equation	Reference
Lewis	MR = exp (-kt)	Bruce (1985)
Page	MR = exp ($-kt^n$)	Page (1949)
Modified Page	MR = exp $(-kt)^n$	White et al. (1981)
Henderson and Pabis	MR = a exp (-kt)	Henderson and Pabis (1961)
Logarithmic	MR = a exp (-kt) + c	Togrul and Pehlivan (2002)
Two-term	MR = a exp ($-k_0t$) + b exp ($-k_1t$)	Henderson (1974)
Midilli et al.	MR = a exp ($-kt^n$) + bt	Sharma and Prasad (2004)
Wang and Singh	MR = 1 + at + bt^2	Wang and Singh (1978)
Weibull	MR = exp (-(t/b) ^{a})	Corzo et al. (2008)
Parabolic	MR = a + bt + ct^2	Sharma and Prasad (2004)
Cubic	MR = a + bt + ct^2 + dt^3	Dalvand et al. (2012)
Sigmoid	MR = a + $\frac{b}{1+e^{k(t-c)}}$	Figiel (2009)
Thompson	t = a ln(MR) + b [ln $(MR)^2$]	Thompson et al. (1968)

Effective moisture diffusivity and activation energy

Hashemi et al. (2009) and Bahloul et al. (2009) reported that the effective moisture diffusivity should be considered for optimization of dehydration process. Also, activation energy (Equation 4) could be defined as the amount of heating energy required for moving water from food (Aghbashlo et al. 2009) and stated an Arrhenius type equation.

$$D_{eff} = D_0 \exp(-E_{\downarrow}a/RT) \qquad (4)$$

where, D_{eff} is the effective moisture diffusivity (m^2/s), E_a is the activation energy (kJ/mol), R is the universal gas constant (8.3143 J/mol K), T is medium temperature (K) and D_0 is the exponential factor (m^2/s).

Total phenolic content (TPC)

Total phenolic contents (TPC) of dried leaves were confirmed according to the Folin-Ciocalteu (FC) method. 0.5 ml aliquot of the sample was put into a tube and 0.5 ml of FC reagent was added after adding 2 ml of Na_2CO_3 solution (200 g/L). The solution was mixed and the reaction proceeded for 15 min. at medium temperature. Then, 10 ml of distilled water was added and the formed precipitate was removed by centrifugation for 5 min at 4000 g. Finally, absorbance was measured at 725 nm (Huang and Prior, 2005).

Colour determination

In order to calculate total colour change (ΔE); L*, a*, b* values of leave powders were measured from top, center and bottom regions by Minolta Chroma meter CR 400 color meter and ΔE was calculated with the aid of equation (6). Unprocessed leave powders were accepted as reference.

$$\Delta E = \sqrt{\left(\left[\left(L^* - L_{ref}^*\right)^2 + \left(a^* - a_{ref}^*\right)^2 + \left(b^* - b_{ref}^*\right)\right)^2\right]} \qquad (5)$$

Statistical analysis

The statistical differences of total phenolic content and colour were evaluated by Duncan test using SPSS software version 18.0 at 5 % confidence interval.

RESULTS AND DISCUSSION

Drying kinetics and mathematical modelling of drying curves

The initial and final moisture content of leaves were determined as 52.6 % and 6.0 % respectively according to method of AOAC, 1990. On dry basis, 1.109 kg water was found in leaves at the beginning. Drying temperature had a positive effect on drying kinetics. When temperature rose, drying rate increased, hence drying time reduced. Figure 1 demonstrates moisture ratio (MR) versus time during dehydration process. No constant rate period was observed in studied temperature range. Falling rate period was actively seen in whole process.

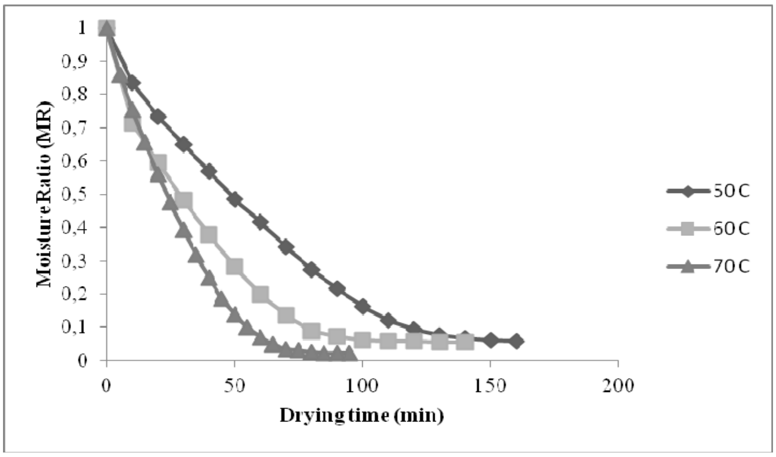

Figure 1
Moisture ratio values versus drying time at different temperatures

Experimental moisture ratio data provided a basis for mathematical modelling. Thirteen thin-layer drying models were analogised in terms of statistical results containing R^2, RMSE and reduced χ^2. In convective drying of olive leaves in temperature range of 50-70 ºC, R^2 was changed between 0.977 and 0.999; RMSE between 0.008 and 0.044; reduced χ^2 0.00007 and 0.00214 for applied all models. Parabolic and Cubic models were the best models describing dehydration of olive leaves and their statistical results and model constants were shown in Table 2.

The experimental moisture diffusivities of leave powders were found as directly proportional with temperature. 1.321×10^{-10}, 1.650×10^{-09} and 3.2×10^{-09} m^2/s were calculated moisture diffusivities for 50, 60, 70 ºC respectively. These results were compatible with literature (Zang et al. 2010; Bahloul et al. 2009). Activation energy of samples was estimated as 147.736 kJ/mol and this value was higher than statements by Aghbashlo et al. (2008). They indicated that E_a values of agricultural products were in the intervals of 12 and 110 kJ/mol. This could be originated from powder form of leaves. Because powder forms have extra surface area when compared to other products.

Table 2: Parabolic and cubic model parameters of olive leaves

	Temperature (ºC)	***R^2***	***RMSE***	***χ^2***
Parabolic Model	50	0.998	0.01195	1.734×10^{-4}
	60	0.988	0.03102	0.0012
	70	0.999	0.00925	1.006×10^{-4}
Cubic Model	50	0.998	0.01185	1.842×10^{-4}
	60	0.995	0.01992	5.410×10^{-4}
	70	0.999	0.00758	7.191×10^{-5}

	Temperature (ºC)	***a***	***b***	***c***	***d***
Parabolic Model	50	0.975	0.012	3.816×10^{-5}	-
	60	0.921	0.016	7.515×10^{-5}	-
	70	0.987	0.024	1.521×10^{-4}	-
Cubic Model	50	0.972	0.012	3.445×10^{-5}	1.545×10^{-8}
	60	0.963	0.021	1.560×10^{-4}	-3.848×10^{-7}
	70	0.997	0.026	1.927×10^{-4}	-2.849×10^{-7}

Total phenolic content (TPC) and colour

2385.5 mg/kg gallic acid (GA) equivalent was the initial phenolic content of olive leaves. The maximum phenolic amount was observed in samples dried at 60 ºC (633.85 mg / kg GA equivalent). Phenolic levels were recorded as 303.61 mg / kg GA eqv. for 50 ºC and 447.05 mg / kg GA eqv. for 70 ºC. Duncan test results also showed that the temperature had an important effect on TPC ($P<0.05$). Similar results were found by Gamli et al. (2016) that the highest phenolics were found in olive leaves dried at 360 W rather than 90, 180, 600 and 900 W power levels.

L^*, a^*, b^* values of olive leaves were expressed in Table 3. Drying temperature had a significiant effect on only a^* and b^* levels ($P<0.05$). a^* and b^* levels were increased with increasing dehydration temperature. L value was not affected from temperature importantly ($P>0.05$). ΔE values were calculated as 7.989; 5.122; 10.014 for 50, 60, 70 ºC respectively.

Table 3: Colour parameters of dried olive leaves

Temperature (ºC)	L^*	a^*	b^*
50	48.35 ± 0.96^a	-4.40 ± 0.33^a	24.66 ± 0.56^a
60	46.31 ± 0.72^a	-3.70 ± 0.11^b	24.04 ± 0.51^a
70	48.16 ± 1.57^a	-2.07 ± 0.23^c	22.72 ± 0.20^b

Different superscript letters in the same column indicate significant difference at $P<0.05$.

CONCLUSION

In this research, convective drying kinetics of *Olea europaea* leaves were studied. Increasing of dehydration temperature had a shortened effect on drying time. Thirteen thin layer drying models were applied to drying data and parabolic and cubic models were chosen as the best. Diffusion coefficients were affected from temperature strongly and the highest moisture diffusivity pertained to 70 ºC. Activation energy of leaf powders was seemed to be higher according to researches available in literature. TPC values of samples showed the maximum level at 60 ºC. There were no significiant differences and correlation between L (brightness) of dried olive leaf powders ($P<0.05$).

REFERENCES

Aghbaslo, M., Kianmehr, M.H. & Samimi-Akhijayani, H. (2008). Influence of drying conditions on the effective moisture diffusivity, energy of activation and energy consumption during the thin layer drying of beriberi fruit (*Berberidaceae*). *Energy Conversion And Management*, 49: 2865–2871.

AOAC. (1990). Official method of analysis. Association of official analytical chemists (No. 934.06), Arlington, VA.

Bahloul, N., Boudhrioua, N., Kouhila, M., & Kechaou, N. (2011). Convective solar drying of olive leaves. *Journal of Food Process Engineering*, 34(4): 1338–1362.

Ben Salem, M., Affes, H., Ksouda, K., Sahnoun, Z., Zeghal, K. M., & Hammami, S. (2015). Pharmacological Activities of *Olea europaea* Leaves. *Journal of Food Processing and Preservation*, 39(6):3128–3136.

Bruce, D. M. (1985). Exposed-layer barley drying, three methods fitted to new data up to 150 ºC. *Journal of Agricultural Engineering Research*, 32(4): 337-347.

Corzo, O., Bracho, N., Pereira, A. & Vásquez, A. (2008). Weibull distribution for modelling air drying of coroba slices, *LWT - Food Science and Technology*, 41:2023-2028.

Dalvand, M.J., Mohtasebi, S.S. & Rafiee, S. (2012). Determining the influence of drying conditions on EHD drying process. *Journal of Agriculture and Biological Sciences*. 7:396–401.

Doymaz, I. (2004). Effect of pre-treatments using potassium metabisul-phide and alkaline ethyl oleate on the drying kinetics of apricots. *Biosystems Engineering,* 89:281–287.

Doymaz, I. (2007). Air drying characteristics of tomatoes. *Journal of Food Engineering*, 78: 1291–1297.

Ertekin, C., & Heybeli, N. (2014). Thin-layer infrared drying of mint leaves.

Journal of Food Processing and Preservation, 38(4): 1480–1490.

Figiel, A. (2009). Drying kinetics and quality of vacuum-microwave dehydrated garlic cloves and slices. *Journal of Food Engineering*, 94: 98–104.

Gamli, Ö.F., Süfer, Ö. & Eker, T. (2016). Microwave drying kinetics and infusion characteristics of olive leaves. 3rd Global Congress on Microwave Energy Applications, 25-29 July 2016, Cartagena, Spain (*Accepted as oral presentation and full paper is in press*).

Karathanos, V.T. & Belessiotis, V.G. (1999). Application of a thin layer equation to drying data fresh and semi-dried fruits. *Journal of Agricultural Engineering Research*, 74: 355–361.

Hashemi, G., Mowla, D. & Kazemeini, M. (2009). Moisture diffusivity and shrinkage of broad beans during bulk drying in an inert medium fluidized bed dryer assisted by dielectric heating. *Journal of Food Engineering*, 92: 331–338.

Henderson, S. M. (1974). Progress in developing the thin layer drying equation. *Transactions of the ASAE*, 17(6): 1167-1172.

Henderson, S. M. & Pabis, S. (1961). Grain drying theory. 1. Temperature effects on drying coefficients. *Journal of Agricultural Engineering Research*, 6(3*)*:169-174.

Hirschaman, S.A. (1972). Inactivation of DNA polymerases of murine leukaemia viruses by calcium elenolate. *Nature: New biology,* 238:277–279.

Huang, D.,Ou, B. & Prior, R.L. (2005). The chemistry behind antioxidant capacity assays. *Journal of Agriculture and Food Chemistry*, 53:1841-1856.

Page, G. E. (1949). Factors influencing the maximum rates of air drying shelled corn in thin layers. M. S. Thesis. Purdue, *Department of Mechanical Engineering, Purdue University*. USA.

Renis, H.E. (1969). In vitro antiviral activity of calcium elenolate. *Antimicrob Agents Chemother,* 9:167–172.

Satish, T. & Ansari, Z. (2013). Ethanobotanical medicinal importance of *Olea europeae* (zaytun). *International Journal of Pure & Applied Bioscience,* 1: 15–18.

Sharma, G.P. & Prasad, S. (2004). Effective moisture diffusivity of garlic cloves undergoing microwave-convective drying. *Journal of Food Engineering*, 65: 609-617.

Thompson, T. L., Peart, R. M. & FosteR, G. H. (1968). Mathematical simulation of corn drying-A new model. *Transactions of ASAE,* 11(4): 582- 586.

Togrul, I. T. & Pehlivan, D. (2002). Mathematical modelling of solar drying of apricots in thin layers. *Journal of Food Engineering,* 55: 209-216.

Wang, C. Y. & Singh, R. P. (1978). Use of variable equilibrium moisture content in modelling rice drying. *Transactions of the ASAE,* 11:668-672.

White, G. M., Ross, T. J. & Ponelert, R. (1981). Fully exposed drying of popcorn. *Transactions of the ASAE,* 24(2*)*: 466-468.

Zang, M., Jiang, H. & Lim, R. (2010). Recent developments in microwave-assisted drying of vegetables, fruits and aquatic products, Drying kinetics and quality considerations. *Drying Technology,* 28:1307-1316.