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Thin-layer convective air drying of lemon verbena (*lippia citriodora*) leaves

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Abstract

Lemon verbena leave is a flavoring food additive as well as a good source of valuable compounds such as essential oils, flavonoids and phenolic acids. However, similar to many other aromatic plants, lemon verbena leave is perishable due to its high moisture content. The aim of this work was to study the effect of air temperature (45, 55, and 65°C) on the quality attributes of lemon verbena leaves during hot-air drying (HAD). The drying kinetics were also modeled. The results showed that higher drying temperature led to a significant decrease ($p<0.05$) in the rehydration ratio due to a change in the structural features of the dried leaves. The essential oil content of dried samples was also significantly different ($p<0.05$) from that of the fresh leaves due to high loss of volatile components and ranged from 0.42 to 0.85. Moreover, a significant increase in the value of effective moisture diffusivity (D_{eff}) and color change was observed when the samples were dried at 65°C compared to 45°C. The value of D_{eff} varied from 1.140×10^{-10} to 2.280×10^{-9} m^2/s and the activation energy was found to be 31.04 kJ/mol. The greatest R^2 (≥0.999) and the lowest RMSE and SSE were obtained for the Naghavi *et al.* model (proposed in this research)

Keywords: Color change, convective drying, effective moisture diffusivity, essential oil, modeling, lemon verbena leaves, rehydration ratio

Introduction

Lemon verbena (*Lippia citriodora*) is a type of herb which is widely raised in western South America. It is also cultivated in Iran and mainly consumed as a spice and a medicinal plant (Funes *et al.*, 2009). There is an increasing interest in using lemon verbena leave in the food industry, because it is generally considered as a flavoring food additive. The leaves of lemon verbena have compounds such as essential oils, flavonoids and phenolic acids, which possess antioxidant activity (Pereira *et al.*, 2007). They are mainly used to make herbal teas and refreshing sorbets as well as creating a lemon flavor in a number of food products such as fish and poultry dishes, jams, salad dressings, puddings, and beverages (Funes *et al.*, 2009). Moreover, the leaves have digestive, sedative, antispasmodic, stomachic, and antipyretic properties (Pereira *et al.*, 2007; Funes *et al.*, 2009). However, similar to many other aromatic plants and herbs, lemon verbena leaves are perishable to microbial growth, mainly due to their high moisture content (around 84-85% wet basis).

Drying is used to extend the shelf life of fruits, vegetables and aromatic plants as well as to reduce or suppress their enzymatic and microbial activities (Doymaz 2009; Doymaz 2012). Aromatic plants are dried in order to extract their valuable compounds by solvents. Among the drying methods, hot-air drying (HAD) is still the most popular method, which is being employed to decrease the moisture content of foods and plants. Although HAD is time and energy consuming (Erbay and Icier 2010), it has gained considerable attention by researchers due to its low capital cost compared to other drying techniques such as freeze-drying and infrared-drying. For this reason, it is still extensively employed by many researchers for long-term preservation of foods and herbs (Erbay and Icier 2010; Doymaz 2012; Lemus-Mondaca *et al.*, 2015;

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Oberoi and Sogi 2015; Aral and Beşe 2016; Nozad *et al.*, 2016; Roshanak *et al.*, 2016; Salarikia *et al.*, 2016).

Effective moisture diffusivity (D_{eff}) and activation energy (E_a) are two important physical properties of dehydrated foods which represent the rate of moisture loss during HAD and the level of energy needed to initiate a chemical reaction and to activate moisture diffusion, respectively (Lemus-Mondaca *et al.*, 2015). D_{eff} can highly affect the drying kinetics and consequently the quality of dehydrated foodstuffs. Also, mathematical modeling of mass transfer during HAD requires the values of D_{eff}. On the other hand, rehydration ratio (RR) is a key physical characteristic of dried foods which can reflect the degree of textural damage (such as shrinkage and tissue collapse) to foodstuffs during HAD (Doymaz *et al.*, 2015).

Numerous research papers can be found on the determination of D_{eff}, E_a, and RR during HAD of various aromatic plants and herbs (Doymaz 2012; Tasirin *et al.*, 2014; Lemus-Mondaca *et al.*, 2015; Nozad *et al.*, 2016; Salarikia *et al.*, 2016). However, to the best of our knowledge, no study has been conducted on the determination of D_{eff}, E_a, RR, and color change for lemon verbena leaves under HAD conditions. The purpose of this research was to investigate the influence of hot-air temperature on the drying kinetics, color change, RR, and essential oil content of lemon verbena leaves under HAD and to calculate D_{eff} and E_a, as well as empirical modeling of the dimensionless moisture ratio as a function of drying time.

Materials and methods

Materials

Fresh lemon verbena leaves were collected every morning from a farm located in Tabriz (Iran), and immediately transferred to the laboratory. The leaves were sorted visually based on size, shape, color, and freshness and stored under refrigerated conditions (at 5°C) (Lemus-Mondaca *et al.*, 2015) until use. The initial moisture content of the leaves was measured using the AOAC method (AOAC 1984) and found to be equal to 84.72% (wet basis).

Hot-air drying

First, the leaves were removed from the refrigerator and arranged uniformly as a thin layer in a stainless steel basket. Then, they were dried using the HAD technique. The experiments were carried out in a pilot plant hot-air drier (UOP 8 Tray dryer, Armfield, UK, equipped with automatic data recording system and temperature and airflow velocity controller units) at 45, 55, and 65±1°C and the airflow rate of 1 m/s (Doymaz 2012; Lemus-Mondaca *et al.*, 2015). Moisture loss was calculated by measuring the mass loss of the samples at 15 min intervals (based on preliminary experiments) by a precision balance with an accuracy of ±0.01 g. Moisture content data were recorded throughout the drying experiments using a data logger connected to a PC. The experiments were continued until reaching a final moisture content of 10% (wet basis).

Modeling of drying curves

Eighteen different empirical and semi-empirical models were used to evaluate the kinetics of moisture loss during HAD of lemon verbena leaves (Table 1) (Ertekin and Heybeli 2014). The model parameters or drying constants (a, b, c, g, h, k, and n) were estimated by applying non-linear regression analysis using MATLAB software (Version 8.1.0.604 R2013a, The Math works, Inc., USA). The coefficient of determination (R^2), adjusted R^2, root mean squared error (RMSE), and sum of squared error (SSE) were used to evaluate the goodness of fit in order to select the suitable model(s) to predict the drying kinetics. These statistical criteria are as follows (Lemus-Mondaca *et al.*, 2015):

$$R^2 = 1 - \frac{\sum_{i=1}^{N}(MR_{exp,i} - MR_{pre,i})^2}{\sum_{i=1}^{N}(\overline{MR}_{exp} - MR_{pre,i})^2} \tag{1}$$

$$\mathrm{RMSE} = \left(\frac{1}{N}\sum_{i=1}^{N}(\mathrm{MR}_{\exp,\,i} - \mathrm{MR}_{\mathrm{pre},\,i})^2\right)^{\frac{1}{2}} \qquad (2)$$

$$\mathrm{SSE} = \frac{1}{N}\sum_{i=1}^{N}(\mathrm{MR}_{\exp,\,i} - \mathrm{MR}_{\mathrm{pre},\,i})^2 \qquad (3)$$

Where $\mathrm{MR}_{\exp,i}$ is the i^{th} experimental moisture ratio, $\mathrm{MR}_{\mathrm{pre},i}$ shows the ith predicted moisture ratio, $\overline{\mathrm{MR}}_{\exp}$ stands for the average experimental moisture ratio, and N denotes the number of observations or the number of data values.

Table 1. Kinetic models used to describe the drying of lemon verbena leaves*

Model number	Model equation	Model name
1	$\mathrm{MR} = \exp(-kt)$	Lewis (Newton)
2	$\mathrm{MR} = \exp(-kt^{n})$	Page
3	$\mathrm{MR} = \exp(-(kt)^{n})$	Modified Page-I
4	$\mathrm{MR} = a\exp(-kt)$	Henderson & Pabis
5	$\mathrm{MR} = a\exp(-kt^{n})$	Modified Page-II
6	$\mathrm{MR} = a\exp(-kt^{n}) + bt$	Midilli et al.
7	$\mathrm{MR} = a\exp(-kt)^{n} + b$	Demir et al.
8	$\mathrm{MR} = (a-b)\exp(-kt^{n})$	Weibull distribution-I
9	$\mathrm{MR} = (a-b)\exp(-(kt)^{n})$	Weibull distribution-II
10	$\mathrm{MR} = \exp(\frac{-at}{1+bt})$	Aghlasho
11	$\mathrm{MR} = \frac{a}{1+b\exp(kt)}$	Logistic
12	$\mathrm{MR} = a\exp(-kt) + b\exp(-gt)$	Two-term
13	$\mathrm{MR} = a\exp(-kt^{n}) + b\exp(-gt^{n})$	Hii et al.
14	$\mathrm{MR} = a\exp(-kt) + (1-a)\exp(-kat)$	Two-term exponential
15	$\mathrm{MR} = a\exp(-kt) + (1-a)\exp(-bt)$	Modified two-term exponential
16	$\mathrm{MR} = a\exp(-kt) + (1-a)\exp(-kbt)$	Diffusion approximation
17	$\mathrm{MR} = (1-a)\exp(-kt) + (1-b)\exp(-gt^{n}) + c$	Naghavi et al. (present study)
18	$\mathrm{MR} = a\exp(-kt) + b\exp(-gt) + c\exp(-ht)$	Modified Henderson & Pabis

*All models (except model-17) are available in the paper published by Ertekin and Heybeli (2014).
a, b, c, g, h, k, and n are model parameters (empirical constants).

Determination of the effective moisture diffusivity

The Fick's law-based model (Eq. 4) is often used to determine the effective moisture diffusivity (D_{eff}) of different food materials.

$$\frac{\partial M}{\partial t} = D_{eff}\,\frac{\partial^2 M}{\partial x} \qquad (4)$$

The following initial and boundary conditions can be considered (Doymaz 2012):

$t = 0, \quad 0 < x < L, \quad M = M_0$
$t > 0, \quad x = L, \quad M = M_e$
$t > 0, \quad x = 0, \quad \frac{dM}{dx} = 0$

In the present study, the analytical solution of Fick's second law for an infinite slab (Eq. 5) was applied to calculate D_{eff} (Erbay and Icier 2010; Doymaz 2012):

$$\mathrm{MR} = \frac{M_t - M_e}{M_0 - M_e} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\pi^2 D_{eff}t}{4L^2}\right) \qquad (5)$$

where M is the moisture content (dry basis), D_{eff} represents the effective moisture diffusivity (m^2/s), L is the half thickness of the slab (m), t stands for the time (s), MR is the moisture ratio (dimensionless), M_t shows the moisture content at any time (kg water/kg dry solid), M_0 is the initial moisture content (kg water/kg dry solid), M_e denotes the equilibrium moisture content (kg water/kg dry solid), and n is the number of the terms taken into consideration.

This method has also been used previously by several researchers (Doymaz 2012; Aral and Beşe 2016) and is based on the assumptions that shrinkage is negligible, D_{eff} remains constant and moisture loss occurs through the diffusion phenomenon (Crank 1975). For long drying times (M_e=0), the use of one-term approximation (n=1) to the series summation is reasonable and Eq. 5 reduces to (Doymaz 2012):

$$MR = \frac{M_t}{M_0} = \frac{8}{\pi^2}\exp\left(-\frac{\pi^2 D_{eff} t}{4L^2}\right) \quad (6)$$

By taking the natural logarithm, Eq. 6 can be further simplified to (Doymaz 2012; Oberoi and Sogi 2015):

$$\ln(MR) = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff} t}{4L^2}\right) \quad (7)$$

A plot of the experimental data in terms of ln (MR) versus time gives a straight line with a slope of k_0 (Oberoi and Sogi 2015):

$$k_0 = \frac{-\pi^2 D_{eff}}{4L^2} \quad (8)$$

Determination of the activation energy

The Arrhenius model describes the relationship between D_{eff}, drying temperature (T), and the activation energy (E_a). Therefore, for quantifying E_a and investigating the effect of temperature on D_{eff}, the Arrhenius type equation (Eq. 9) was employed (Doymaz 2012):

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (9)$$

Where E_a denotes the activation energy (kJ/mol), R is the universal gas constant [8.314 J/(mol K)], T is the absolute air temperature (K), and D_0 is the pre-exponential factor (constant) (m^2/s). This approach has been used by a number of researchers (Doymaz 2012; Aral and Beşe 2016).

Determination of the rehydration ratio

Measurement of the rehydration ratio (RR) of dried leaves was carried out according to the method described by Doymaz *et al.* (2015) and Nozad *et al.* (2016). Based on this method, 5 g of the dehydrated samples were poured into a glass beaker (750 mL) containing 500 mL of distilled water (25°C) and kept for 24 h. Next, the leaves were removed from the beaker and their surface water was blotted up using a tissue paper. Finally, the weight of the resulted sample was measured precisely using a digital balance. In all cases, the tests were triplicated for each sample and the mean values of the three replications ± standard deviation were reported. The RR calculation was carried out using Eq. 10 as employed by Doymaz *et al.* (2015), Nozad *et al.* (2016), and Salarikia *et al.* (2016):

$$RR = \frac{W_2 - W_1}{W_1} \quad (10)$$

Where RR denotes the rehydration ratio [kg water/kg dry matter (DM)], W_1 is the weight of the dried leaves (kg), and W_2 represents the weight of the rehydrated leaves (kg).

Color measurement

The color changes of leaves (fresh and hot-air dried) were quantified using image processing in MATLAB (Version 8.1.0.604 R2013a, The Math works, Inc., USA) (Nozad *et al.* 2016). The color test instrument was designed and constructed in the Department of Agricultural Machinery Engineering, University of Tabriz, Tabriz, Iran. It consists of a chamber with a trapezoidal cross section that was equipped by two D_{65} (daylight) lamps as the light source for illumination of sample. At first, a sample was put in the chamber. After zooming the lens and focusing, the images were taken by camera. A digital camera (Nikon, D3200, Japan) was used to capture images from leaf surfaces. The camera calibration was performed prior to each drying experiment.

In each experimental run, the color of the leaves (10 fresh and 10 dried samples) was measured as L^*, a^* and b^* values, which known as Hunter parameters. It is well known that the L^* value represents the degree of lightness/darkness, a^* stands for the degree of redness/greenness, and b^* shows the degree of yellowness/blueness. Changes in the color of the leaves were calculated as follows (Nozad *et al.*, 2016; Salarikia et al., 2016):

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \qquad (11)$$

Where ΔE denotes the total color change of leaves and ΔL^*, Δa^*, and Δb^* represents the difference between the color parameters of initial samples (L_0^*, a_0^*, and b_0^*) and final dried leaves (L^*, a^*, and b^*).

Determination of the essential oil content

The essential oil was extracted from the leaves using a flask connected to Clevenger hydro-distillation apparatus (Nozad *et al.*, 2016). Based on this method, a given amount of the samples (30 g) were put into a round-bottomed distillation flask filled with a given amount of distilled water (250 mL). Then, the heating was performed for 3 h and the distilled essential oil collected in the side arm was separated. The data of essential oil (%) were expressed on the basis of dry matter weight.

Statistical analysis

The experimental data were analyzed statistically by the analysis of variance (ANOVA) using Minitab statistical software (Minitab Release 14, Minitab Inc., USA). The significant difference between the means was determined using Tukey's honestly significant difference (HSD) test at the significance level of 5% ($p<0.05$). The data were expressed as the mean ± standard deviation and all experiments were carried out in triplicate.

Results and discussion

Drying kinetics

The effects of the drying temperature (45, 55, and 65°C) on the dimensionless moisture ratios of lemon verbena leaves are illustrated in Fig. 1.

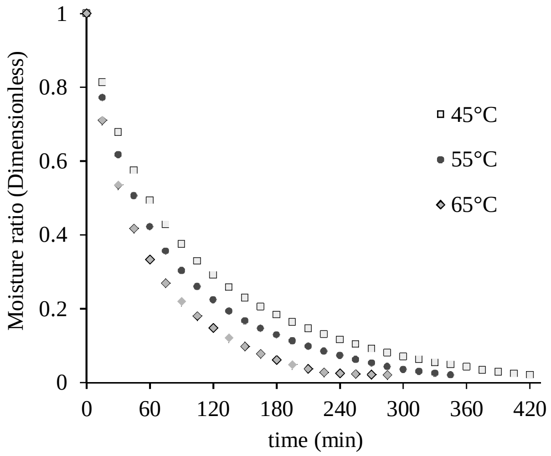

Fig. 1. Moisture ratios (dimensionless) as a function of the drying time at different temperatures during hot-air drying of lemon verbena leaves

It can be seen that the moisture ratio declined quickly in the initial period of HAD (almost up to 75-90 min) and was subsequently followed by a gradual non-linear decrease (almost exponential) with an increase in the process time. This result was similar to the findings of other researchers (Doymaz 2012; Lemus-Mondaca *et al.*, 2015; Said *et al.*, 2015; Aral and Beşe 2016).

Fig. 1 also shows that all drying temperatures exhibited a relatively similar behavior for the dried samples. Moreover, by increasing the drying temperature, the moisture ratios and consequently the drying kinetics were altered. Based on ANOVA results, the drying time was significantly ($p<0.05$) lower in the case of the samples dried at 65°C than those dehydrated at lower temperatures (45 or 55°C). The total drying time was 420, 345, and 285 min for the leaves dried at 45, 55, and 65°C, respectively. This result indicates that a temperature increase of 20°C (i.e. from 45 to 65°C) caused a reduction of approximately 135 min in the total drying time ($p<0.05$). This might be due to the increased vapor pressure in lemon verbena leaves at higher drying temperatures, which in turn results in a faster moisture loss from the samples and thus, a shorter drying time (Aral and Beşe 2016). Other studies have reported similar findings (Ertekin and Heybeli 2014; Lemus-Mondaca *et al.*, 2015; Said *et al.*, 2015; Aral and Beşe 2016).

Modeling of the drying curves

In the literature, several empirical and semi-empirical models have been applied to describe the drying kinetics of food materials and plants under different drying conditions, which are based on the dimensionless moisture ratio as a function of drying time. In the present work, the experimental data of moisture loss in lemon verbena leaves during HAD at different drying temperatures (45, 55, and 65°C) were fitted to eighteen models summarized in Table 1 (Ertekin and Heybeli 2014), which allows of using and comparing different model correlations based on the fitting criteria (R^2, RMSE, and SSE) on a defined set of experimental data

Table 2. Statistical analysis of different kinetic models for different drying temperatures

Model number	T (°C)	R^2	Adjusted R^2	RMSE	SSE	Model number	T (°C)	R^2	Adjusted R^2	RMSE	SSE
1	45	0.9875	0.9875	0.0283	0.0225	10	45	0.9977	0.9976	0.0124	0.0041
	55	0.9870	0.9870	0.0294	0.0199		55	0.9981	0.9980	0.0116	0.0029
	65	0.9907	0.9907	0.0256	0.0125		65	0.9981	0.9980	0.0120	0.0026
2	45	0.9995	0.9995	0.0056	0.0008	11	45	0.9744	0.9735	0.0413	0.04611
	55	0.9996	0.9996	0.0050	0.0005		55	0.9723	0.9710	0.0439	0.04233
	65	0.9997	0.9997	0.0049	0.0004		65	0.9766	0.9753	0.0417	0.03132
3	45	0.9995	0.9995	0.0056	0.0008	12	45	0.9998	0.9998	0.0034	0.00028
	55	0.9996	0.9996	0.0050	0.0005		55	0.9998	0.9999	0.0032	0.00019
	65	0.9997	0.9997	0.0049	0.0004		65	0.9999	0.9998	0.0033	0.00017
4	45	0.9927	0.9924	0.0221	0.0131	13	45	0.9999	0.9999	0.0030	0.00021
	55	0.9916	0.9912	0.0241	0.0128		55	0.9997	0.9996	0.0051	0.00049
	65	0.9934	0.9931	0.0221	0.0088		65	0.9997	0.9996	0.0053	0.00042
5	45	0.9995	0.9995	0.0057	0.0008	14	45	0.9996	0.9996	0.0048	0.00063
	55	0.9996	0.9996	0.0051	0.0005		55	0.9995	0.9994	0.0061	0.00083
	65	0.9997	0.9996	0.0050	0.0004		65	0.9998	0.9998	0.0041	0.00030
6	45	0.9997	0.9997	0.0044	0.0005	15	45	0.9998	0.9998	0.0033	0.00029
	55	0.9997	0.9997	0.0046	0.0004		55	0.9999	0.9998	0.0032	0.00027
	65	0.9998	0.9997	0.0044	0.0003		65	0.9999	0.9998	0.0031	0.00026
7	45	0.9997	0.9997	0.0047	0.0005	16	45	0.9998	0.9998	0.0033	0.00030
	55	0.9997	0.9996	0.0048	0.0005		55	0.9999	0.9998	0.0030	0.00025
	65	0.9998	0.9997	0.0044	0.0003		65	0.9999	0.9999	0.0032	0.00017
8	45	0.9995	0.9995	0.0058	0.0008	**17**	**45**	**1**	**1**	**0.0007**	**0.000011**
	55	0.9996	0.9996	0.0052	0.0005		**55**	**1**	**0.9999**	**0.0013**	**0.000031**
	65	0.9997	0.9996	0.0052	0.0004		**65**	**0.9999**	**0.9999**	**0.0020**	**0.000056**
9	45	0.9995	0.9995	0.0058	0.0008	18	45	0.9998	0.9998	0.0035	0.00028
	55	0.9996	0.9996	0.0052	0.0005		55	0.9999	0.9998	0.0035	0.00022
	65	0.9997	0.9996	0.0052	0.0004		65	0.9997	0.9997	0.0049	0.00034

Table 3. Estimated coefficients of different kinetics models at different drying temperatures*

Model number	T (°C)	Coefficients		Model number	T (°C)	Coefficients	
1	45	a = 0.0102		10	45	a = 0.0124	b = 0.0014
	55	a = 0.0130			55	a = 0.0159	b = 0.0019
	65	a = 0.0177			65	a = 0.0212	b = 0.0022
2	45	a = 0.0230	n = 0.8315	11	45	a = 1.7520	k = 0.0128
	55	a = 0.0294	n = 0.8213		55	a = 1.7650	k = 0.0164
	65	a = 0.0360	n = 0.8346		65	a = 1.8030	k = 0.0229
3	45	a = 0.0107 n = 0.8315		12	45	a = 0.7404 b = 0.2604	g = 0.0350 k = 0.0078
	55	a = 0.0137 n = 0.8213			55	a = 0.7025 b = 0.2977	g = 0.0402 k = 0.0096
	65	a = 0.0186 n = 0.8346			65	a = 0.7515 b = 0.2490	g = 0.0625 k = 0.0138
4	45	a = 0.9339 k = 0.0095		13	45	a = 0.6834 b = 0.3152 g = 0.0268	k = 0.0051 n = 1.0690
	55	a = 0.9370 k = 0.0121			55	a = 1.0290 b = -0.0292 g = 3.1770	k = 0.0338 n = 0.7970
	65	a = 0.9500 k = 0.0168			65	a = 0.9833 b = 0.0168 g = 7.8360	k = 0.0334 n = 0.8485
5	45	a = 1.0020 k = 0.0233	n = 0.8298	14	45	a = 0.2325 k = 0.0349	
	55	a = 1.0020 k = 0.0298	n = 0.8195		55	a = 0.2449 k = 0.0417	
	65	a = 0.9993 k = 0.0359	n = 0.8352		65	a = 0.2307 k = 0.0612	
6	45	a = 1.0060 b = -3.089×10^{-5}	k = 0.0259 n = 0.8041	15	45	a = 0.2599 b = 0.0078	k = 0.0349
	55	a = 1.0040 b = -2.328×10^{-5}	k = 0.0317 n = 0.8036		55	a = 0.2977 b = 0.0096	k = 0.0401
	65	a = 1.0010 b = -2.562×10^{-5}	k = 0.0380 n = 0.8199		65	a = 0.2487 b = 0.0138	k = 0.0624
7	45	a = 1.0210 b = -0.0150	k = 0.0104 n = 0.8015	16	45	a = 0.2598 b = 0.2246	k = 0.0349
	55	a = 1.012 b = -0.0084	k = 0.0135 n = 0.8030		55	a = 0.2977 b = 0.2390	k = 0.0401
	65	a = 1.0100 b = -0.0087	k = 0.0183 n = 0.8154		65	a = 0.2490 b = 0.2214	k = 0.0623
8	45	a = 0.7216 b = -0.2803	k = 0.0232 n = 0.8298	17	45	a = 0.6936 b = 0.2731 c = -0.0333	g = 0.0114 k = 0.0256 n = 0.9001
	55	a = 1.1360 b = 0.1335	k = 0.0298 n = 0.8194		55	a = 0.6157 b = 1.9780 c = 0.6156	g = 6.0080 k = 0.0153 n = -0.4296
	65	a = 0.5534 b = -0.446	k = 0.0359 n = 0.8351		65	a = 0.3155 b = 0.6998 c = 0.0144	g = 0.0001 k = 0.0352 n = 1.8710
9	45	a = -6.0690 b = -7.0710	k = 0.0108 n = 0.8298	18	45	a = 0.7466 b = 0.2643 c = -0.0109	g = 0.0373 h = 10.300 k = 0.0079
	55	a = 1.3370 b = 0.3346	k = 0.0137 n = 0.8195		55	a = -0.1141 b = 0.4036 c = 0.7106	g = 0.0495 h = 0.0096 k = 0.0802
	65	a = 0.5256 b = -0.4736	k = 0.0186 n = 0.8352		65	a = 0.8052 b = -1.424 c = 1.6190	g = 1.4230 h = 0.2176 k = 0.0144

* a, b, c, g, h, k, and n are model parameters (empirical constants).

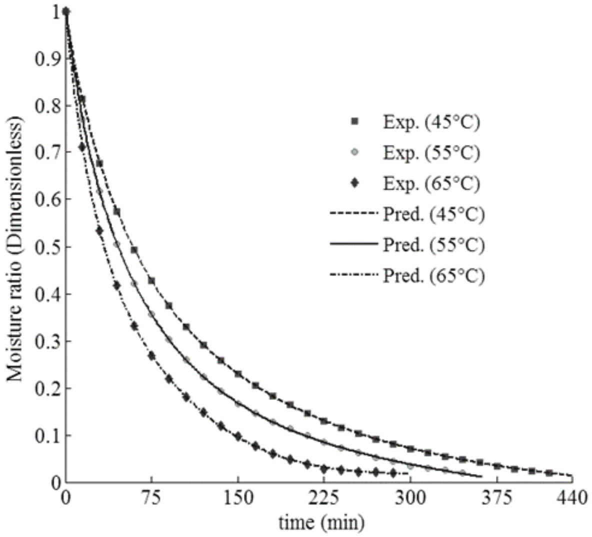

Fig. 2. Comparison of the experimental (exp.) and predicted (pred.) moisture ratios for lemon verbena leaves dehydrated at different drying temperatures

Table 2 indicates that for the most of tested models, R^2 and adjusted R^2 values were higher than 0.999, and RMSE and SSE values were between 0.0007-0.0413 and 0.000011-0.04611, respectively.

Genrally, the closer the experimental and predicted moisture ratios, the better they explain the adequacy of the regression model. As expected, the models with a larger number of coefficients (models 12, 13, 15-18 in Table 2) had higher R^2 and lower RMSE and SSE values. The data in Table 2 suggested that the employed models were suitable to describe the drying behavior of lemon verbena leaves. However, for plotting the predicted moisture ratios against the drying time, only the model presented in this research (model-17 in Table 1) was fitted to the experimental data (Fig. 2) which had greater R^2 (0.9999-1) and adjusted R^2 (0.9999-1) values and lower RMSE (0.0007-0.0020) and SSE (0.000011-0.000056) values than the other 17 models (Table 2). The models coefficients (constants) obtained at different drying temperatures are represented in Table 3. By increasing drying temperature, different coefficients did not follow a similar trend. As can be obtained from Table 3, drying rate constant (k) in the studied drying models increased with increasing drying temperatures. Thus, it may be assumed that this kinetic parameter would be directly proportional to drying temperature (Lemus-Mondaca *et al.*, 2015). Similar results were reported by other investigators (Vega-Gálvez *et al.*, 2012; Lemus-Mondaca *et al.*, 2015). Furthermore, there was no clear trend on the effect of drying temperature on the other constants (a, b, c, g, h, and n).

Rehydration ratio (RR)

Comparison of the RR results for the samples dried at different drying temperatures are presented in Fig. 3.

It can be seen that there was no significant change ($p>0.05$) in the RR of the dried leaves when the drying temperature changed from 45 to 55°C. However, RR reduced significantly ($p<0.05$) with an increase in the air temperature from 45 to 65°C. This was attributed to the fact that HAD at higher temperatures resulted in a change in the structural features of the leaves (such as tissue collapse, development of a surface hard layer and volumetric shrinkage), which in turn can cause significant damages to the textural quality of the dried samples and therefore a decrease in RR (Doymaz 2012; Nozad *et al.*, 2016; Salarikia *et al.*, 2016). The highest RR value of the dried samples (78.24%) was observed for the leaves dried at 45°C, followed by those dehydrated at 55 (76.12%) and 65°C (73.36%). These results are in agreement with the results reported by f Doymaz (2012), who stated that the higher the drying temperature (40, 50, and 60 °C) resulted in a lower RR of the grape leaves, concluding that higher drying temperatures led to greater changes in the structural attributes and thus, lower RR values. Nozad *et al.*, (2016) also observed that in HAD of spearmint (*Mentha spicata* L.) leaves, an increase in the air temperature from 30 to 50°C had a considerable decreasing effect on RR. Similar findings were reported by other researchers (Jangam *et al.*, 2008; Vega-Gálvez *et al.*, 2012; Salarikia *et al.*, 2016).

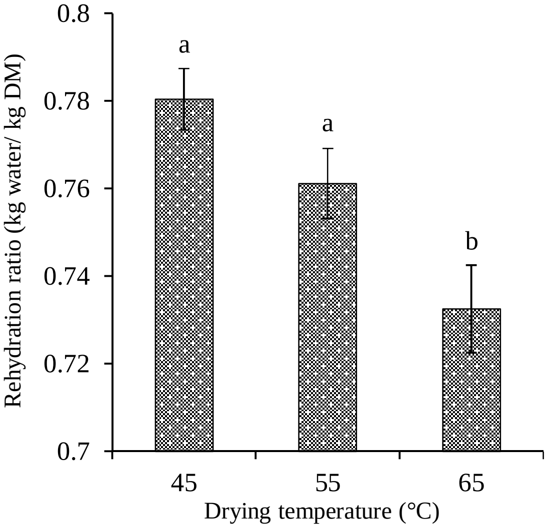

Fig. 3. Rehydration ratio of lemon verbena leaves at different drying temperatures. Error bars show one standard deviation from the mean and means with different letters are significantly different (p<0.05).

Effective moisture diffusivity (D_{eff})

In the present study, the value of D_{eff} at 45, 55, and 65°C was estimated by plotting ln(MR) versus the drying time (Eq. 4) (Oberoi and Sogi 2015). The slope of the corresponding line represents the value of D_{eff}. The D_{eff} values varied from 1.140 × 10^{-10} to 2.280 × 10^{-9} m^2/s (Table 4). Other researchers found similar values for the D_{eff} of dried foods (in particular leaf materials), which were in general in the range of 10^{-12} to 10^{-8} m^2/s (Zogzas *et al.*, 1996). D_{eff} values have been determined for other herbs as follows: mint leaves 3.067 × 10^{-9} to 1.941 × 10^{-8} m^2/s (Doymaz 2006), spinach leaves 6.590 × 10^{-10} to 1.927 × 10^{-9} m^2/s (Doymaz 2009), nettle leaves 1.744 × 10^{-9} to 4.992 × 10^{-9} m^2/s (Kaya and Aydın 2009), mint leaves 0.965 × 10^{-11} to 1.190 × 10^{-11} m^2/s (Therdthai and Zhou 2009), olive leaves 1.054 × 10^{-9} to 4.973 × 10^{-9} m^2/s (Erbay and Icier 2010), grape leaves 4.13 × 10^{-10} to 1.83 × 10^{-9} m^2/s (Doymaz 2012), kaffir lime leaves 2.61 × 10^{-11} to 9.24 × 10^{-11} m^2/s (Tasirin *et al.*, 2014), stevia leaves 4.67 × 10^{-10} to 14.90 × 10^{-10} m^2/s (Lemus-Mondaca *et al.*, 2015), and wild edible plant (*Allium roseum*) leaves 2.55 × 10^{-12} to 8.83 × 10^{-12} m^2/s (Said *et al.*, 2015).

Table 4. The values of effective moisture diffusivity (D_{eff}) for lemon verbena leaves at different drying temperatures

Drying temperature (°C)	D_{eff} (m^2/s)
45	1.140 × 10^{-10} ^{c}
55	1.710 × 10^{-10} ^{b}
65	2.280 × 10^{-9} ^{a}

Different letters in the same column indicate significant differences (p<0.05)

As can be realized from Table 4, significant differences (p<0.05) of the D_{eff} values were observed between the leaves dried at different drying temperatures. This indicates that hot-air temperature has a considerable effect on D_{eff} during HAD of plants and foods, as reported by numerous authors (Erbay and Icier 2010; Doymaz 2012; Lemus-Mondaca *et al.*, 2015; Said *et al.*, 2015; Aral and Beşe 2016). This may be related to the higher thermal energy transferring to the leaves at higher drying temperatures, which subsequently results in an increase in the kinetic energy of the water molecules (Aral and Beşe 2016). A higher D_{eff} value indicates the increasing rate of moisture loss with the rise of drying temperature (Fig. 1).

Activation energy (E_a)

The value of E_a in the drying of lemon verbena leaves was estimated from the slope of the linearized Arrhenius equation (Eq. 9) (Doymaz 2012) and was found to be 31.04 kJ/mol. The E_a value obtained in this research was in the range that reported for other aromatic plants and fruits. Experimentally-determined E_a values have been reported by several researchers, for example Ahmed *et al.* (2001) for coriander leaves (26.50 kJ/mol in the temperature range of 45-65°C), Doymaz (2006) for mint leaves (62.96 kJ/mol in the temperature range of 35-60°C), Doymaz (2009) for spinach leaves (34.35 kJ/mol in the temperature range of 50-80°C), Kaya and Aydın (2009) for nettle leaves (79.873-109.003 kJ/mol in the temperature range of 35-55°C and at airflow rates of 0.2-0.6 m/s), Erbay and Icier (2010) for olive leaves (60.97 kJ/mol in the temperature range of 50-70°C), Doymaz (2012) for grape leaves (64.56 kJ/mol in the temperature range of 40-60°C), Lemus-Mondaca *et al.* (2015) for stevia leaves (38.78 kJ/mol in the temperature range of 30-80°C), and Said *et al.* (2015) for wild edible plant (*Allium roseum*) leaves (46.80-52.68 kJ/mol in the temperature range of 30-80°C and 1 and l.5 m/s airflow velocity).

It has been reported that the value of E_a is influenced by several factors, including the drying air temperature, the moisture content of food or herb, and variations in the D_{eff} value with the drying temperature (Aghbashlo *et al.*, 2008), which makes it difficult to compare the E_a values for different foods and herbs dehydrated at different process conditions. However, from numerous conducted studies on the calculation of the E_a value, it can be concluded that long dehydration time, high initial moisture content, remarkable variation in the D_{eff} value with the drying temperature (at constant airflow rate) (Aghbashlo *et al.*, 2008) or with both temperature and airflow rate (Erbay and Icier 2010), low hot-air flow rate, low drying temperature, and textural changes in the sample due to the percentage of shrinkage and tissue collapse, are all the reasons for a considerable increase in the E_a value.

Color measurement

The value of color change (ΔE) represents the degree of total color change in dehydrated leaves compared to the color of fresh samples. The lower ΔE the better the quality of dried leaves (Salarikia *et al.*, 2016). The color of aromatic plants and herbs are very sensitive to heat damage during HAD. Fig. 4 shows the value of ΔE for dried samples. It can be seen that the value of ΔE increase significantly ($p<0.05$) with increasing of hot-air temperature from 45 to 65°C. Chlorophyll a and chlorophyll b are responsible for natural green color of leaves. The increase in ΔE is due to the increase in substitution of magnesium with hydrogen in chlorophyll with drying temperature. Under this condition, chlorophylls are converted to pheophytins (Therdthai and Zhou 2009). This finding confirmed the previous observations obtained by Therdthai and Zhou (2009) for mint leaves (*Mentha cordifolia* Opiz ex Fresen), Chenarbon *et al.* (2012) for St. John's wort (*Hypericum perforatum* L.) leaves, Akbudak and Akbudak (2013) for parsley, and Salarikia *et al.* (2016) for peppermint leaves.

Determination of the essential oil content

Essential oil content of lemon verbena leaves before (fresh sample) and after drying is shown in Fig. 5. The fresh samples had the highest value of essential oil (1.10%) between the treatments. Furthermore, no significant difference ($p>0.05$) of essential oil content was observed between the leaves dried at different temperatures, while significant difference ($p<0.05$) of essential oil content was observed between fresh leaves and samples dehydrated at 55 and 65°C. The reduction in essential oil content with increasing drying temperature ($p>0.05$) might be explained by the fact that the relatively high temperature of hot-air result in an increase in rupture of oil glands and as a consequence, rapid evaporation or higher loss of volatile components (Argyropoulos and Müller 2014). This result is consistent with those obtained in previous studies, for example *Laurus nobilis* L. leaves (Sellami *et al.*, 2011), *Thymys daenensis* subsp. *daenensis*. Celak leaves (Rahimmalek and Goli, 2013), Lemon verbena (Shahhoseini *et al.*, 2013), and peppermint leaves (Salarikia *et al.*, 2016).

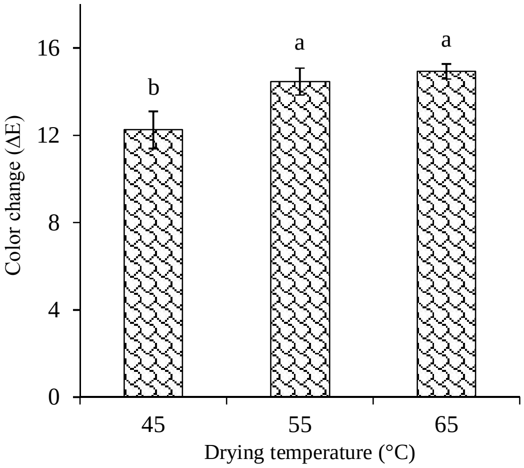

Fig. 4. Color change in lemon verbena leaves at different drying temperatures. Error bars show one standard deviation from the mean and means with different letters are significantly different ($p<0.05$).

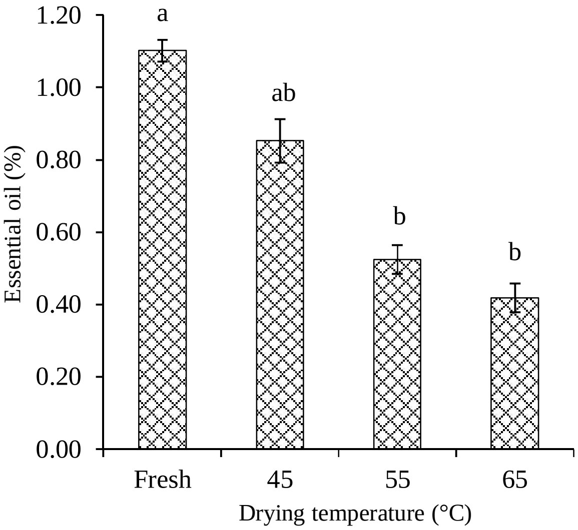

Fig. 5. Essential oil content of lemon verbena leaves at different drying temperatures .Error bars show one standard deviation from the mean and means with different letters are significantly different ($p<0.05$).

Conclusions

This study was focused on investigation of some selected properties of lemon verbena leaves (moisture loss, D_{eff}, color change, essential oil content, and RR) during HAD at different drying temperatures as well as the empirical modeling of the drying kinetics. A shorter drying time and a higher D_{eff} value were observed ($p<0.05$) with an increase in the drying temperature from 45 to 65°C. The values of D_{eff} ranged from 1.140×10^{-10} to 2.280×10^{-9} m^2/s and the E_a value was found to be 31.04 kJ/mol, all of which were in agreement with the results reported by other investigators in the literature. Our results also showed that the percentage of RR was significantly ($p<0.05$) affected by the air temperature and its maximum (78.24%) and minimum (73.36%) values were attained at 45°C and 65°C, respectively. Essential oil content of the samples dried at different drying temperatures was not significant ($p>0.05$) with respect to each other but was significantly ($p<0.05$) different from the fresh samples. Furthermore, the value of ΔE increased significantly ($p<0.05$) with increasing of hot-air temperature from 45 to 65°C and ranged from 12.24 to 14.92, respectively. The results of modeling ($R^2>0.99$ and low RMSE and SSE values for most of the tested models) indicated a good fit to the experimental data of moisture ratio. Among these, the model proposed in the present study had a better goodness of fit (with an adjusted $R^2 \geq 0.999$ and the lowest RMSE and SSE) and was considered as the best model.

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خشک‌کردن همرفتی لایه نازک برگ‌های به لیمو

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تاریخ دریافت: 1395/09/25
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چکیده

برگ به‌لیمو یک افزودنی غذایی طعم‌زا و همچنین منبع خوبی از ترکیبات با ارزش مانند روغن‌های فرّار، فلاوونوئیدها و اسیدهای فنلی است. با این‌حال، همانند بسیاری از گیاهان معطر دیگر، برگ به‌لیمو به دلیل داشتن محتوای رطوبت بالا فسادپذیر است. هدف از این کار پژوهشی مطالعه اثر دمای هوا (45، 55 و 65 درجه سانتی‌گراد) روی ویژگی‌های کیفی برگ به لیمو طی خشک‌کردن هوای داغ (HAD) بود. همچنین، کینتیک خشک‌کردن مدل‌سازی شد. نتایج نشان داد که دمای خشک‌کردن بالاتر منجر به کاهش معنی‌دار ($p<0/05$) نسبت جذب آب مجدد به علت تغییر ویژگی‌های ساختاری برگ‌های خشک شده گردید. محتوای روغن فرار برگ‌های خشک شده نیز به دلیل از دست رفتن مقادیر بالای اجزای فرار به طور معنی‌داری ($p<0/05$) در مقایسه با برگ‌های تازه متفاوت بود و در محدوده 0/42 تا 0/85 قرار داشت. علاوه بر این، با خشک‌کردن نمونه‌ها در 65 درجه سانتی‌گراد در مقایسه با 45 درجه سانتی‌گراد ، افزایش معنی‌دار مقدار ضریب انتشار مؤثر رطوبت (D_{eff}) و تغییر رنگ مشاهده شد. مقدار D_{eff} از $1/140\times10^{-10}$ تا $2/280\times10^{-9}$ m/s متغیر بود و مقدار انرژی فعال‌سازی 31/04 kJ/mol تعیین شد. بیشترین مقدار R^2 ($\geq0/999$) و کمترین مقدار RMSE و SSE برای مدل نقوی و همکاران (پیشنهاد شده در این پژوهش) به دست آمد.

واژه‌های کلیدی: تغییر رنگ، خشک‌کردن همرفتی، ضریب انتشار مؤثر رطوبت، روغن فرّار، مدل‌سازی، برگ به‌لیمو، نسبت جذب آب مجدد

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