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Dehydration Characteristics and Mathematical Modeling of Thyme Leaves using the Microwave Process

Issa Loghmanieh [α] & Hossein Bakhoda [σ]

Abstract- Thyme leaves (Thymus vulgaris) with 50 g weight and 83.7% humidity on wet basis were dried in a laboratory scale microwave dryer using six different microwave power levels ranging between 200 to 700 W. The effect of drying power microwave on the coefficients of the best moisture ratio model was determined by non-linear regression method. Results from the mathematical modeling showed that the Midilli et al. model gave the best fit to describe the drying curve of thyme. In addition, the effective diffusivities of thyme under microwave drying were obtained from 2.94×10-7 to 7.38×10-7 m2/s. Also, the activation energy for the moisture diffusion was found to be 16.471 W/g.

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I. Introduction

Thyme with scientific name (Thymus vulgaris) has a long and varied history of both medicinal and culinary use. It is best cultivated in a hot, sunny location with well-drained soil. It is generally planted in the spring, and thereafter grows as a perennial. It can be propagated by seed, cuttings, or by dividing rooted sections of the plant. This herb is used in a number of herbal remedies, including as a treatment for coughing, asthma and more. The use of fresh thyme herb in food is rather limited owing to a very short shelf- life. Most thyme crops are dried before further use or processing. Drying is the most critical process owing to volatility and susceptibility to chemical change of the voltaic oil. Whole dried thyme as such can find numerous culinary; however, its direct use in food processing is rather limited (Peter, 2004).

Drying is perhaps the oldest and most common processes used to improve the food stability, since it decreases the water activity of the material, reduces microbiological activity, and minimizes physical and chemical changes during its storage (Koc et al., 2088). It also one of the advantages of dried foods is that they take much less storage space than canned or frozen foods (Brooker et al., 1992). Drying can be defined as a unit operation in which a liquid–solid separation is accomplished by the supply of heat, with separation resulting from the evaporation of liquid. Drying occurs by effecting vaporization of the liquid by supplying heat to the wet feedstock. Heat may be supplied by convection (direct dryers), by conduction (contact or indirect dryers), radiation or volumetrically by placing the wet material in a microwave or radio frequency electromagnetic field (Barbosa-Canovas and Vega-Mercado, 1996, van't Land, 2012). Over 85% of industrial dryers are of convective type with hot air. One of the disadvantages of these dryers is high energy consumption. Due to these difficulties, more rapid, safe and controllable drying methods are required (Kavak Akpinar et al., 2005, Motevali et al., 2011). In microwave drying can improve final product quality in from of better aroma, faster and better dehydration, considerable savings in energy and much shorter drying times, compared with hot air drying (Motevali et al., 2011, Darvishi et al., 2012a, Balbay et al., 2012).

Several studies have been carried out to investigate Microwave drying characteristics of various agriculture products and food materials such as onion slices (Abbasi and Azari, 2009), sardine fish (Darvishi et al., 2012b), sliced mushroom (Lombraña et al., 2010) carrot (Wang and Xi, 2005), apple (Li et al., 2010), garlic cloves (Sharma and Prasadb, 2006b, Sharma and Prasadb, 2006a), pharmaceutical granules (Loha et al., 2008), tomato (Al-Harahsheha et al., 2009), spinach (Ozkan et al., 2007), coriander (Sarimeseli, 2011), and etc., no investigation of thyme leaves has not been reported with microwave drying yet.

The objective of this study is (a) to investigate the drying behavior of the thyme leaves (b) to determine the best mathematical model to describe the drying kinetics (c) to compute effective moisture diffusivity and activation energy in microwave drying method.

II. Material and Methods

a) Sample preparation

The samples were prepared from a Faculty of Agriculture Herb Farm in Tehran University. Thyme herbs were cleaned and were stored in a refrigerator at about 4°C for the experiments. AOAC standard (1980) was used to determine sample initial moisture content. According to this standard, for determining thyme leaves moisture content, the samples were placed in a 105 ±1 °C oven for 24 hours (AOAC, 1990). Initial

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moisture content of the thyme leaves 83.7% on a wet basis was achieved.

b) Equipment and Methodology

A domestic digital microwave oven (M945, Samsung Electronics Ins) with maximum output of 1000 W at 2450 MHz was used for the drying experiments. The oven had the dimensions of 51× 44× 31 cm with a rotating glass plate having 300 mm in diameter. The microwave dryer was operated by a control terminal which could control microwave power level. Experiments were performed at seven microwave powers which have adjustable output microwave power of 200, 300, 400, 500, 600 and 700 W, respectively. About 15 gr samples were placed drier's chamber and were dried. Samples were weighted by a digital balance (GF-600, A & D, Japan) with ±0.01 accuracy per 30s. Each drying process was done until the moisture content about 5% on a wet basis was achieved. All measurements were carried out in triplicate.

c) Determining the best mathematical model

Effectively modeling the drying behavior is important for investigation of drying characteristics of samples. In this study, the microwave experimental drying data of thyme at different power levels were fitted into 6 commonly used thin-layer drying models, listed in Table 1.

Table 1 : Thin layer drying curve models considered

Model name	Model	References
Lewis	MR=exp (-kt)	(Roberts et al., 2008)
Page	MR=exp (-kt^n)	(Motevali et al., 2010)
Henderson and Pabis	MR=a.exp (-kt)	(Chhinnan, 1984)
Wang and Singh	MR=1+a.t+bt^2	(Wang and Singh, 1978)
Logarithmic	MR=a.exp (-kt)+c	(Dandamrongrak et al., 2002)
Midili et al.	MR=a.exp(-kt^n)+b.t	(Midilli et al., 2002)

The moisture ratio (MR) of the samples is defined according to Eq. (1):

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

where, MR is the moisture ratio (dimensionless), Mt, M0 and Me are moisture content at any time, initial moisture content, and equilibrium moisture content (kg water/kg dry mater), respectively, and t is drying time (min). The values of Me are relatively small compared to Mt or M0 for long drying time, hence the error involved in the simplification be assuming that Me is equal to zero is negligible (Senadeera et al., 2003).The goodness of fit of the tested mathematical models to the experimental data was evaluated with the coefficient of determination (R2), root mean square error (RMSE) and the reduced chi-square (χ2). These parameters were calculated using Eq. (2, 3 and 4): (Ertekin and Yaldiz, 2004).

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

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

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

Where, MRexp is the experimental dimensionless moisture ratio, MRpre is the predicted dimensionless moisture ratio, N is the number of experimental data points, and z is the number of parameters in model. The higher the R2 values and the lower the χ2 and RMSE values, the better is the goodness of fit.

The drying rate (DR) of thyme leave was calculated using Eq. (5):

$$DR = \frac{M_{t+\Delta t} - M_t}{\Delta t} \quad (5)$$

where, Mt+Δt is moisture content at time t+Δt (kg water/kg dry mater), t is the time (min) and DR is the drying rate (kg water/kg dry mater.min).

d) Moisture Diffusivity

The mechanism of moisture movement within a food and agricultural product can be represented with effective moisture diffusion. The effective diffusivity can be defined from Fick's second law that was calculated using Eq. (6) (Aghbashlo et al., 2008):

$$\frac{\partial M}{\partial t} = D_{eff}\frac{\partial^2 M}{\partial x^2} \quad (6)$$

The solution to the Fick's equation with the assumptions of moisture migration by diffusion only, negligible volume shrinkage, diffusion coefficients and constant temperature is solved Eq. (7) (Crank, 1975):

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$$MR = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-(2n+1)^2\frac{D_{eff}t}{4L^2}\right) \quad (7)$$

Where, Deff is the effective diffusivity (m2/s), and L is the half-thickness of samples (m)), n is a positive integer. For long drying times Eq. (8) can be simplified by using only the first term in the series without much affecting the accuracy of the prediction (Tütüncü and Labuza, 1996):

$$MR = \frac{8}{\pi^2}\exp\left[-\frac{\pi^2 D_{eff}t}{4a^2}\right] \quad (8)$$

The slope (K) is calculated by plotting Ln(MR) versus time according to Eq. (9).

$$K = \frac{\pi^2 \ D_{eff}}{4L^2} \quad (9)$$

e) Activation energy

Effective moisture diffusivity is related to mass transfer, while air boundary heat and mass transfer coefficients are related to external heat and mass transfer, respectively. Knowledge of effective moisture diffusivity is necessary for designing and modeling mass transfer processes such as dehydration, adsorption and desorption of moisture during storage (Pathare and Sharma, 2006). Dependence of the effective moisture diffusivity and the microwave output power versus the amount (weight) of based on Rynvs the activation energy of microwave was obtained. Equation (10) can be effectively used for microwave drying as follows (Özbek and Dadali, 2007):

$$D_{eff} = D_0 \ \exp\left(-\frac{E_a m}{P}\right) \quad (10)$$

where, Ea is the activation energy (W/g), m is the mass of raw sample (g), D0 is the pre-exponential factor (m2/s) and P is the microwave power (W).

III. Results and Discussion

a) Drying Curves

The moisture ratio versus drying time curves for microwave drying of thyme samples in difference microwave powers are shown in Fig. 1. According to curves in this figure, the total time required to reach the final moisture content for the thyme sample was 5.25, 3, 2.7, 2.3, 2 and 1.9 min at 200, 300, 400, 500, 600 and 700 W, respectively. The results showed that increasing the level of microwave power the drying time was decreased. The mass transfer within the samples is rapid during the larger microwave power heating because of microwave heating effect more heat was generated within the sample creating a large vapor pressure difference between the center and the surface of the product (Wang et al., 2007).

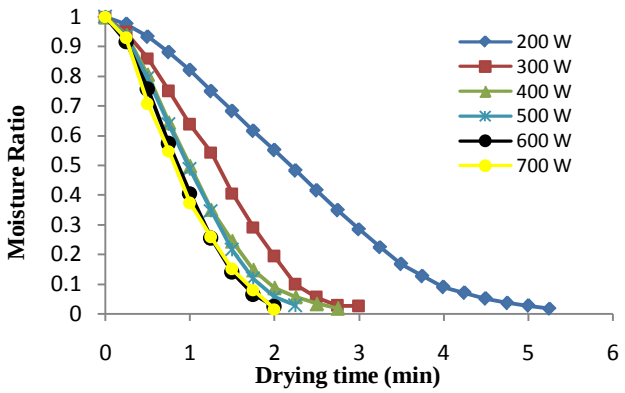

Fig. 1 : Variation of moisture content with drying time at different of microwave power

Figure 2 is plotted the curves of drying rate against drying time under various drying conditions. It is clearly seen from Figure 2 that a constant rate period was not observed in microwave drying of the thyme samples. During initial phase of the drying the drying rate increased rapidly because more energy of the microwave was absorbed and the moisture content of the material was very high. As the drying process continues, drying rate drops rapidly due to the solids surface moisture content decreases. Also drying rate increased when level of microwave power increased because more energy was absorbed and used to raise the temperature of samples. The maximum drying rates were approximately 1.27, 2.5, 2.8, 2.9, 3.34 and 4 kg water/kg dry mater .min in the microwave powers of 200, 300, 400, 500, 600 and 700 W, respectively.

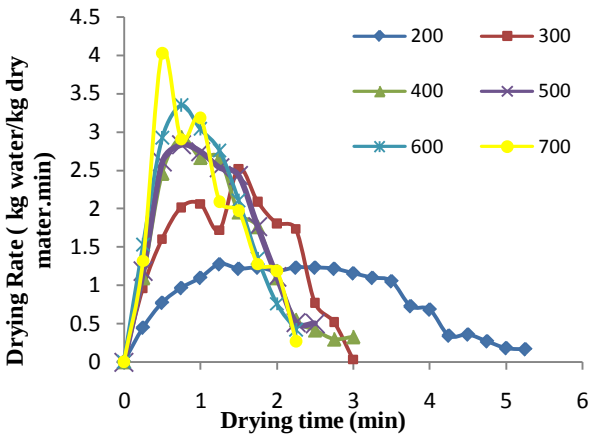

Fig. 2 : The relations of drying rate and time at different of microwave power

b) Modeling of Drying Curves

Knowledge of moisture profiles with time during is also of importance for proposing drying mechanisms. The changes in the moisture ratio with drying time of the thyme at a different power of microwave were fitted into

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five thin-layer drying models. Non-linear regression was used to obtain each parameter value of every model. The statistical results from models are summarized in Table 2. The best model describing the thin-layer drying Characteristics of thyme were chosen as the one with the highest R2 values and the lowest χ2, and RMSE values. According to Table 2, the statistical parameter estimations indicated that R2, χ2 and RMSE values were ranged from 0.9062 to 0.9999, 2.00×10-5 to 0.0123, and 0.004938 to 0.1113, respectively. The result showed that the Midili et al model gives the highest values of R2 and the lowest values of χ2 and RMSE. Thus, this model selected to represent the thin layer drying characteristics of thyme. Figure 3 compares experimental data with those fitted data for thyme samples at different power of microwave. This figure showed that there was a very good agreement between the experimental and predicted moisture ratio values, which is closely band around at a 45° straight line.

Table 2 : Statistical results obtained from different thin-layer drying models

Models	Power(W)	Constance				R^2	χ^2	RMSE
Lewis	200	k =0.3942				0.9127	0.0106	0.1031
	300	k = 0.666				0.9062	0.0123	0.1113
	400	k =0.8522				0.9343	0.00879	0.09373
	500	k =0.8622				0.9196	0.0107	0.1036
	600	k =0.9816				0.9224	0.0106	0.1031
	700	k =1.01				0.9368	0.008147	0.09174
Page	200	k =0.175	n = 1.83			0.9981	2.34×10^{-4}	0.01568
	300	k =0.4422	n =1.908			0.9964	4.71×10^{-4}	0.02267
	400	k =0.7111	n = 1.733			0.9998	2.08×10^{-5}	0.004703
	500	k =0.7457	n =1.813			0.9988	1.59×10^{-4}	0.01339
	600	k =0.9378	n =1.807			0.9993	0.0001	0.01073
	700	k =0.9854	n =1.664			0.9978	0.000296	0.01842
Henderson and Pabis	200	a =1.16	k =0.4568			0.942	0.0070	0.08611
	300	a = 1.139	k = 0.7572			0.9307	9.15×10^{-4}	0.09995
	400	a =1.127	k =0.9526			0.9534	0.00623	0.08278
	500	a = 1.121	k = 0.966			0.9401	0.00798	0.09476
	600	a =1.113	k =1.09			0.9406	0.00814	0.09645
	700	a =1.106	k =1.115			0.953	0.0062	0.08456
Wang and Singh	200	a = -0.2605	b =0.01136			0.9826	0.00212	0.04721
	300	a = -0.4273	b =0.02534			0.9809	0.00252	0.05252
	400	a =-0.6081	b =0.08592			0.982	0.00240	0.05143
	500	a = -0.5621	b =0.04706			0.9851	0.00198	0.04722
	600	a =-0.6447	b =0.06638			0.9855	0.00199	0.0477
	700	a =-0.6876	b =0.09134			0.9882	0.00156	0.04232
Logarithmic	200	a =1.902	c =-0.8256	k =0.171		0.9877	0.00149	0.04067
	300	a =2.248	c =-1.185	k =0.2278		0.9849	0.00198	0.04886
	400	a =1.461	c =-0.3864	k =0.520		0.9836	0.00219	0.05181
	500	a = 2.179	c =-1.124	k =0.3042		0.9886	0.0015	0.04425
	600	a = 2.113	c =-1.061	k =0.3557		0.9883	0.00159	0.04616
	700	a =1.786	c =-0.7352	k =0.4515		0.9905	0.00126	0.041
Midili et al.	200	a =0.9861	b =-0.006395	k =0.1654	n =1.802	**0.9991**	1.09×10^{-4}	**0.01129**
	300	a =0.9828	b =-0.01309	k =0.4044	n =1.881	**0.9979**	1.94×10^{-4}	**0.01914**
	400	a =0.9996	b =-0.003264	k =0.7115	n =1.736	**0.9999**	2.00×10^{-5}	**0.005247**
	500	a =0.9982	b = -0.01843	k =0.6956	n =1.729	**0.9996**	5.97×10^{-5}	**0.00947**
	600	a =0.9982	b =-0.01847	k =0.8731	n = 1.731	**0.9999**	1.59×10^{-4}	**0.004938**
	700	a =1.011	b =-0.02427	k =0.9142	n =1.538	**0.9986**	**0.000184**	**0.01718**

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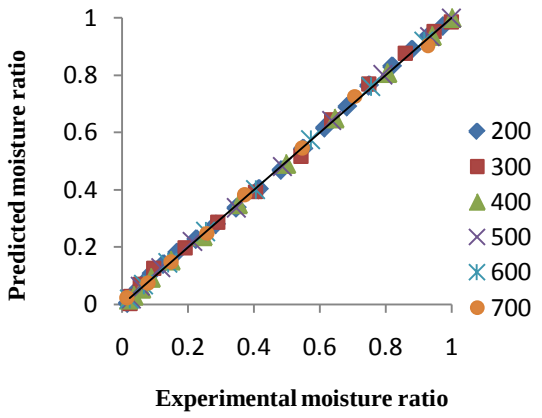

Fig. 3 : Comparison of experimental and predicted moisture ratio values using Midilli et al

c) Moisture Diffusivity and Activation Energy

Figs. 4 show the Ln (MR) versus time (s) in different levels of power of microwave. According to curves in this figure, the increasing in levels of power values increases the slop of straight line in other words the effective moisture diffusivity increases. The values of effective moisture diffusivity (Deff) for different microwave powers are given in Table 3. The effective diffusivities of thyme under microwave drying at 200 to 700 W was ranged from 2.94×10-7 to 7.38×10-7 m2/s. in the higher microwave power moisture diffusivity due to temperature rise and increased heating energy was enhanced. This result is similar to the results of drying garlic cloves (Sharma and Prasad, 2004), leek (Dadali and Ozbek, 2008), purslane (Demirhan and Ozbek 2010), Gundelia tournefortii L. (Evin, 2012) and etc.

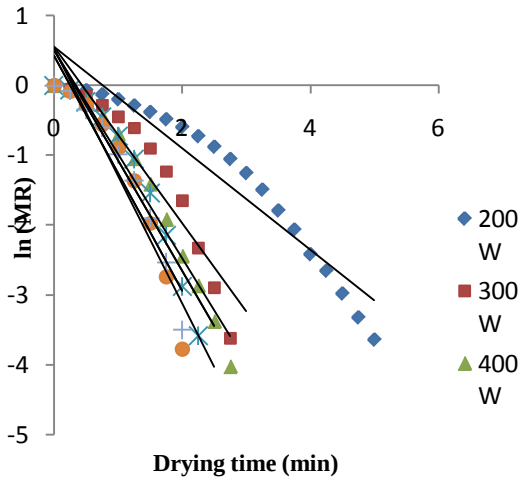

Fig. 4 : Ln (MR) versus time (s) in different microwave powers

Table 3 : Effective diffusivity values for microwave drying of thyme

Microwave Power(W)	Effective Moisture Diffusivity×10^7 (m^2/s)
200	2.94
300	5.11
400	6.04
500	6.36
600	6.81
700	7.38

The activation energy was calculated by plotting the natural logarithm of Deff versus sample amount/power (m/P) as presented in Fig. 5. The activation energy a value was calculated from the slopes of straight lines of Figure 5 was found to be 16.471 W/g with a value for R2 of 0.974. Eq. (11) showed the effect of microwave power on effective diffusivity with following coefficients:

$$D_{eff} = 1.06\times10^{-6}\ \exp\left(-16.471\frac{m}{P}\right) \qquad R^2 = 0.974 \quad (11)$$

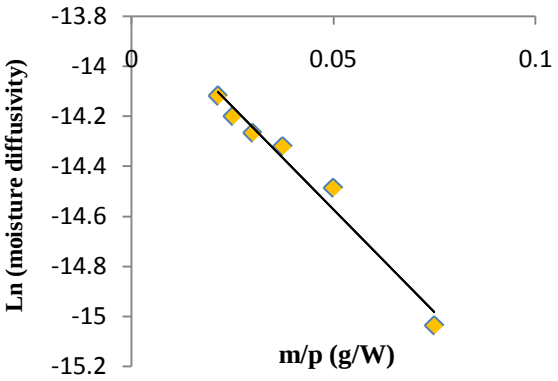

Fig. 5 : Logarithm of thermal diffusivity versus sample amount/power

IV. Conclusion

In this research work, the drying behavior of thyme was studied under four different microwave powers (200, 300, 400, 500, 600 and 700 W) in microwave drying. According to the result, drying time decreased significantly with increasing microwave power. From the study, it is also observed on multiple linear regression analysis the Midilli et al. model with R2, χ2 and RMSE values were ranged from 0.9062 to 0.9999, 2.00×10-5 to 0.0123, and 0.004938 to 0.1113, respectively, gave excellent fitting to the drying experimental data of thyme. Also, the effective diffusivity increases as the microwave output power increases. The values of effective diffusivity for microwave drying of thyme varied from a minimum of 2.94×10-7 to a maximum of 7.38 ×10-7 m2/s and activation energy was obtained 16.471 W/g.

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