KINETICS AND THERMODYNAMIC PROPERTIES OF PARBOILED BURGOS WHEAT (*TRITICUM DURUM*) IN TURKEY DURING DRYING

YILDIRIM, A.

Department of Food Engineering, Faculty of Engineering, University of Harran
Osmanbey Campus, 63000 Şanlıurfa, Turkey
e-mail: ayildirim10@gmail.com; phone:+90-414-318-3731; fax:+90-414-318-3682

(Received 24th Aug 2017; accepted 6th Dec 2017)

Abstract. The influence of temperature and dryer types on kinetics, thermodynamic properties of parboiled wheat (bulgur) in Turkey was studied during drying. Durum wheat (local name in Turkey, Burgos) was cooked under atmospheric conditions, and then it was dried at 50, 60 and 70 °C. Six semi-theoretical and Fick's diffusivity models with Arrhenius and Eyring–Polanyi approaches were employed to predict drying kinetics and thermodynamic properties. Among all the models, Midilli model was found to have the best fit as suggested average R^2 value of 0.9987, and corresponding RMSE value of 0.010. Effective diffusion coefficient (D_{eff}) increased significantly ($P \leq 0.05$) from 2.38×10^{-11} to 5.84×10^{-11} (59% increase), 4.65×10^{-11} to 8.51×10^{-11} (45% increase), and 8.70×10^{-11} to 14.10×10^{-11} (38% increase) for natural convective air, forced convective air and vacuum drying systems with temperature increase from 50 to 70 °C. The activation energy values of the samples of natural convective air drying (NCAD) (41.46 kJ mol^{-1}) compared with that of forced convective air drying (FCAD) (27.71 kJ mol^{-1}) and vacuum drying (VD) (22.28 kJ mol^{-1}) show a decrease trend which suggests more effective drying. The enthalpy and entropy decreased with increasing temperature for all dryers. The Gibbs free energy increased with increasing temperature. For each dryer, also, general equations to describe the moisture ratio of parboiled wheat as a function of time and temperature were developed. It was concluded that vacuum dryer has provided more effective drying than the other dryers.
Keywords: *model, vacuum, activation energy, bulgur, mass transfer*

Introduction

Wheat is one of the major staple foods in all over world because of ease of storage and ability of its flour to be made into many food materials. Many special food products can be prepared from wheat; one of such special food product is parboiled wheat (bulgur). It is very popular in western countries as frozen food materials and quick cooking foods. Bulgur is a cleaned, washed, parboiled, debranned, crushed and sifted wheat product (Bayram and Öner, 2006). It is an excellent ingredient in pilaf, salad, casseroles, stuffing's, soups, baked goods, and as a meat substitute in vegetarian dishes (Yu and Kies, 1993). It is widely consumed in Turkey, Greece, Cyprus, Middle East, North Africa, and East Europe. From a producer's point of view, the main factors of interest are production costs, processing time, product shelf life and product quality. The selection of one particular drying method above another is dependent on its ability to produce a shelf stable product, as optimizing quality and cost.

Drying of food material depends upon heat and mass transfer characteristics of the product being dried. Knowledge of temperature and moisture distribution in the product is vital for equipment and process design and quality control (Mohapatra and Rao, 2005). Many studies have reported the importance of the kinetics of the drying for various agricultural products such as bean and chickpea (Shafaei et al., 2016), yellow peas (Mercier et al., 2015), pumpkin (Hashim et al., 2014), spearmint (Ayadi et al., 2014) and rice (Correa et al., 2016). These studies identified the effect of temperature

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

on the rate and the amount of moisture that is moved between the product and the environment.

The most widely used theoretical model has been Fick's second law of diffusion. Drying of many food products such as rice (Ece and Cihan, 1993), soybean (White et al., 1981), rapeseed (Crisp and Woods, 1994) and sorghum (Suarez et al., 1980) has been successfully predicted using Fick's second law with Arrhenius-type temperature dependent diffusivity (plotting the natural logarithm of effective moisture diffusivity, D_{eff} versus the reciprocal of the absolute temperature).

Semi-theoretical models offer an ease of use that is valid within the temperature, relative humidity, moisture content range for which they were developed. Among the drying semi-theoretical models, the Henderson & Pabis, Lewis, Page's, Wang & Singh, Logaritmic, and Weibull models are used frequently (*Table 1;* Liu et al., 2016).

Table 1. *Mathematical models used for drying curves*

Model name	Number	Model equation	Reference
Lewis	1	$MR = \exp(-kt)$	Bruce (1985)
Page	2	$MR = \exp(-kt^n)$	Page (1949)
Midilli	3	$MR = a * \exp(-kt^n) + bt$	Midilli et al. (2002)
Henderson & Pabis	4	$MR = a * \exp(-kt)$	Henderson and Pabis (1961)
Logarithmic	5	$MR = a * \exp(-kt) + c$	Toğrul and Pehlivan (2002)
Weibull	6	$MR = \exp\left[-(\frac{t}{\alpha})^{\beta}\right]$	Blasco et al. (2006)

k: drying coefficient, t: drying time (min)

Henderson & Pabis model had been used to model drying of corn (Mishra and Brooker, 1980), wheat (Becker, 1959; Watson and Bhargava, 1974), parbolied wheat (Chakraverty and Kaushal, 1982), and rough rice (Wang and Singh, 1978). This drying model was based on the assumption that entire dying process occurred in the falling rate period. The two-term model had been used to describe thin layer drying of parboiled wheat (Mohapatra and Rao, 2005). The Lewis model was used to predict drying of barley (Bruce, 1985). The Page model was the modification of Lewis model and used extensively in determining the drying characteristics of short and medium grain rough rice (Wang and Singh, 1978), soybean (White et al., 1981), shelled corn (Mishra and Brooker, 1980), barley (Bruce, 1985). Empirical model was developed, which suitably predicted drying characteristics of rough rice (Watson and Bhargava, 1974).

Some researchers have reported on thermodynamic properties such as enthalpy, entropy, Gibbs free energy in different products such as rice (Correa et al., 2016), chia (Velasquez et al., 2015), potato flakes (Lago et al., 2013), pineapple (Bispo et al., 2015), and bulgur (Bayram et al., 2004b).

Although extensive work has been done on drying of wheat and parboiled wheat, limited literature is available on vacuum drying characteristics of parboiled wheat of Burgos variety comparison with natural convective air and forced convective air drying systems. Whereby drying is an important process to produce parboiled wheat, present study has given importance on drying behaviour of parboiled wheat.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

The aims of the present study were to demermine the influence of the time, temperature and dryer type on parbolied wheat (Local name, Burgos (*Triticum durum*)) during drying, to examine the capabilities of six semi-theoretical and Fick's Diffusion models, to find the best drying kinetics model, to calculate the thermodynamic parameters (Activation energy, Entalpy, Entropy and Gibbs free energy), and to derive the new equations related to moisture ratio, time and temperature of parboiled wheat for each dryer.

Material and methods

Material

Wheat sample (Burgos, *Triticum durum*), which is one of the main cultivars used for pasta and bulgur production, was obtained from Şanlıurfa Commodity Exchange, Turkey. The moisture content was determined by standard oven method (AOAC, 2002). The average dimensions (L: length, W: width and T: thickness in mm) of wheat kernels were measured with Mutitoyo No. 505-633, Japan, digital micrometer. The average equivalent diameter ($D_e = (LWT)^{1/3}$) and sphericity ($\phi = (LWT)^{1/3} L^{-1}$) of grains were also calculated (Mohsenin, 1980).

Wheat cooking

Wheat kernels, cleaned from extraneous matter, were combined with water at a ratio of 1:6 (weight basis) and cooked by a heater (IKA Model HP 30, Staufen, Germany) at 97 °C until the starch was entirely gelatinized (about 80 to 95 min). The average initial moisture content of parboiled wheat on a dry basis (d.b) was 126.98%.

Drying systems

The drying process was carried out at 50, 60 and 70 °C for 480 min. Parboiled wheat samples were laid on each pan of dryers (1600 g m^{-2}). Natural convective air dryer (NCAD) (Elektromag, M7040-R, Turkey), forced convective air dryer (FCAD) (Elektromag, M7040-R, Turkey) with air velocity of 1.2 m s^{-1} and vacuum dryer (VD) (WiseVen, WOV-70, Witeg, Germany) with a pressure of 33.33 kPa were used for dehydration of parboiled wheat.

Experimental procedure

Fifty grams of representative parboiled wheat samples was uniformly spread in single layer over the drying pans of dryers. The moisture loss from the parboiled wheat, during drying was determined every 1 h, by lifting the drying pan and quickly weighing the sample with an electronic balance. The drying experiments were carried out till 8 h. The experiments were conducted in triplicate. Average values of moisture loss were taken for final calculations. The moisture content of samples in dry basis at any drying time was calculated by *Equation 1:*

$$M_t = \left[\frac{(M_o + 1) * W_t}{W_o} - 1 \right] * 100 \qquad \text{(Eq. 1)}$$

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

where W_o is initial weight (g), W_t is weight of sample (g) at any drying time (t). M_o and M_t are the moisture contents of wheat samples in dry basis initially and at different drying time, respectively.

Theory

Modeling of drying curves

For studying the drying characteristics of parboiled wheat, it is very important to model the drying behavior effectively. The data obtained at different temperatures of drying were fitted into six commonly used drying models, listed in *Table 1*.

In the drying experiments, the moisture ratio (MR) of parboiled wheat was calculated using the following equation (*Eq. 2*):

$$MR = \frac{M_t - M_e}{M_o - M_e} \qquad \text{(Eq. 2)}$$

where M_t is the moisture content at any time (%, d.b.); M_e is the equilibrium moisture content (%, d.b.); and M_o is the initial moisture content (%, d.b.) of the samples. In the present study, this equation was simplified to *Equation 3*, considering that M_e is negligible compared to M_t or M_o (Rayaguru and Routray, 2012).

$$MR = \frac{M_t}{M_o} \qquad \text{(Eq. 3)}$$

The drying rate (DR) of parboiled wheat samples was calculated using *Equation 4* (Kavak Akpinar, 2002)

$$DR = \frac{MR_{t+dt} - MR_t}{dt} \qquad \text{(Eq. 4)}$$

where MR_{t+dt} and MR_t are moisture ratio at the time t + dt and t (dimensionless). t is the drying time in min.

Effective diffusivities calculation

Fick's diffusion model is generally used to describe the drying characteristics of the biological products. The solution of Fick's diffusion model in spherical coordinates, with the assumptions of moisture migration being by diffusion, negligible shrinkage, constant diffusion coefficients and temperature, is given by (*Eq. 5;* Crank, 1975):

$$MR = \sum_{n=1}^{\infty} \frac{6}{\pi^2 n^2} \exp\left(-\frac{D_{eff} * n^2 * \pi^2 * t}{R_e^2}\right) \qquad \text{(Eq. 5)}$$

where n is the positive integer, D_{eff} is the effective moisture diffusion coefficient ($m^2 s^{-1}$), t is drying time (s) and R_e is the average radius of wheat (m). Simplifying this by taking the first term of the series solution, gives (*Eq. 6*)

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

$$MR = \frac{6}{\pi^2}\exp\left(-\frac{D_{eff} * \pi^2 * t}{R_e^2}\right) \quad \text{(Eq. 6)}$$

Thermodynamic properties

Effect of temperature on effective diffusivity is generally expressed using an Arrhenius-type relationship, since temperature has the significant effect over the drying process rather initial moisture content of the product (*Eq. 7*).

$$\ln(D_{eff}) = \ln(D_{ref}) - (\frac{E_a}{R}) * (\frac{1}{T}) \quad \text{(Eq.7)}$$

where D_{eff}, T, E_a and R are effective diffusion coefficient of the Fick's model, soaking temperature (K), activation energy for the drying process in kJ mol^{-1} and ideal gas constant in 8.314×10^{-3} kJ mol^{-1} K^{-1}, respectively. D_{ref} is reference diffusion coefficient for the Fick's model.

The thermodynamic properties of mass transfer process in parboiled wheat were determined by Eyring–Polanyi model (*Eqs. 8*, *9* and *10*; Correa et al., 2012):

$$\Delta H = E_a - RT \quad \text{(Eq. 8)}$$

$$\Delta S = R[\ln(A_o) - \ln(\frac{k_B}{h_p}) - \ln(T)] \quad \text{(Eq. 9)}$$

$$\Delta G = \Delta H - T\Delta S \quad \text{(Eq. 10)}$$

where ΔH is the enthalpy, J mol^{-1}; ΔS is the entropy, J mol^{-1} K^{-1}; ΔG is the Gibbs free energy, J mol^{-1}; k_B is Boltzmann's constant, 1.38×10^{-23} J K^{-1}; and h_p is Planck's constant, 6.626×10^{-34} J s^{-1}.

Statistical analysis

The drying data were fitted to different models using Sigma plot 10 (Jandel Scientific, San Francisco, USA) software. Nonlinear regression analysis was performed on all runs to estimate the parameters associated with considered models from the experimental data. Data were compared using the Duncan's test at $p \leq 0.05$ (SPSS Inc., version 16, USA). Correlation coefficient squared (R^2) and root mean square error (RMSE) (*Eq. 11*) was used as the criteria for the accuracy of the fit.

$$RMSE = \sqrt{\frac{1}{n}\sum_{1}^{n}\left[(MR_{\exp} - MR_{pre})\right]^2} \quad \text{(Eq. 11)}$$

where n, MR_{exp} and MR_{pre} are the numbers of observations, the experimental moisture ratio and predicted moisture ratio, respectively.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

Results and discussion

Moisture ratio and drying rate change

Initial moisture content of the wheat grain was about 9.99 (%, d.b.). The average L, W, T, D_e and R_e (equivalent radius) values of raw wheat grains were found to be 7.81±0.12, 3.21±0.09, 3.10±0.07, 4.22±0.15 and 2.11±0.18 mm, respectively. The sphericity of it was calculated as to be 0.54±0.01.

By recording the weight change over time in the different dryers, moisture contents (%, d.b.), moisture ratios and drying rates of samples were calculated by *Equations 1*, *3* and *4*, respectively (*Figs. 1* and *2*). The initial moisture content of parboiled wheat was found to be 126.98 (%, d.b.). Moisture contents after 8 h drying of parboiled wheat at 50 °C were found to be decreasing as 16.39, 15.63 and 9.15 (%, d.b.) for the natural convective air, forced convective air and vacuum dryers, respectively. Similarly, increasing of temperature to 60 °C decreased the final moisture contents to 11.26, 10.96 and 6.83 (%, d.b.). Also, drying at 70 °C temperature showed that the final moisture contents were found to be 6.44, 6.11 and 5.63 (%, d.b.) that were in the decreasing trend.

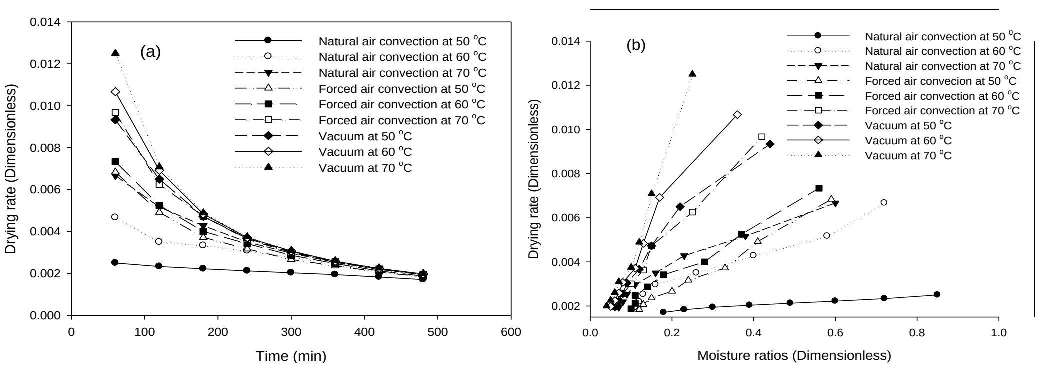

Figure 1. *Drying rate curves of parboiled wheat at different temperatures for different dryers (a: drying rate vs. time(min), b: drying rate vs. moisture ratio)*

Change of drying rate is shown in *Fig. 1*. It can be seen from *Fig. 1* that significant ($P \leq 0.05$) differences in drying rate were found between the three drying methods, i.e. natural convective air drying, forced convective air drying and vacuum drying. At the beginning when moisture ratio was high, the drying rate under all drying conditions increased with time. The constant drying period is rarely observed in food drying studies and several authors reported that no constant rate period occurred during drying of different agricultural products, such as potato (McMinn and Magee, 1996), carrot (Toğrul, 2006), parboiled wheat (Mohapatra and Rao, 2005), bell pepper, pumpkin, tomato and several others (Krokida et al., 2003). The entire drying process was found to be taken place in falling rate period only, which indicated that moisture diffusion was the governing factor (Singh and Sodhi, 2000) deciding drying behaviour of parboiled wheat (*Fig. 2*). It was observed that the drying of the parboiled wheat is accompanied by the falling drying rate stage (*Figs. 1* and *2*). Lack of a constant drying rate period was also observed in other studies of vacuum drying of porous materials (Sander, 2007).

As can be seen from these values, the temperature increase for the three dryers caused a decrease in the final moisture values. In other words, in order to reach the final

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

moisture content, the vacuum dryer required a shorter time. Likewise, the increase in temperature also shortened the drying time. As the drying temperature increased, the drying rate increased during drying of parboiled wheat (*Fig. 1*). In all dryers and temperatures during the first hour of drying, the initial drying rate is high due to easy separation of free water.

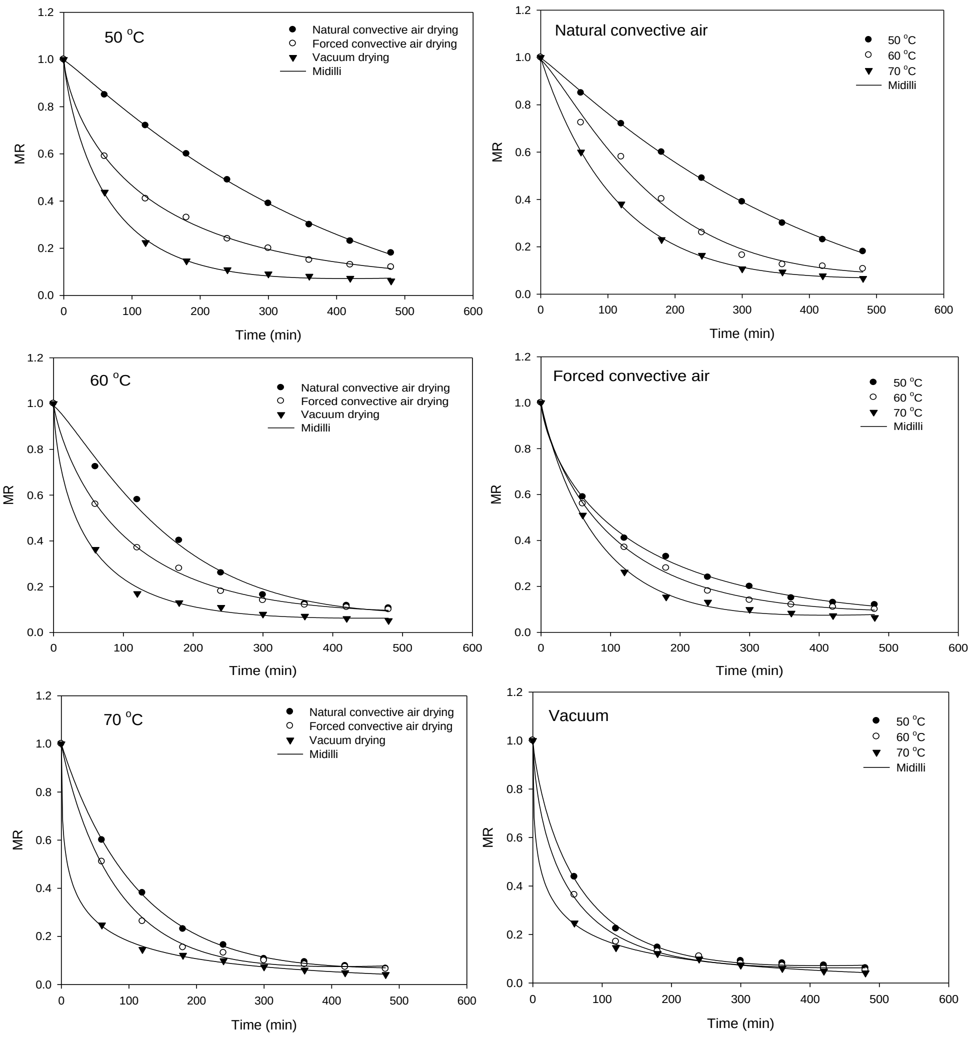

Figure 2. *Simulated moisture ratio during drying of parboiled wheat at different temperatures (a) for different dryers (b) from Midilli model*

For NCAD system, during 60 min drying period, increase in temperature from 50 to 60 °C resulted 46.43% increase in drying rate, and 62.50% increase from 50 to 70 °C. Similarly, FCAD increased the drying rate by 6.82% and 29.31% at the same temperature increments for the same drying period. We see similar temperature effect during vacuum drying system that the drying rate increased by 12.50% and 29.69%. During 60 min drying periods at 50, 60 and 70 °C temperatures, 63.41% and 73.21%, 36.36% and 56.25%, 31.03% and 46.67% increments were found respectively when we compared drying rates of NCAD with FCAD and vacuum dryers. Results are confirmed by previous studies that vacuum drying is more effective for similarly forced convective

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

air drying for mints (85-90% reduction) (Giri and Prasad, 2007) and mushrooms (70-90% reduction) (Therdthai and Zhou, 2009). Mohapatra, and Rao (2005), Ghaitaranpour et al. (2013) investigated that the drying temperature of parboiled wheat was affected the rate of drying. The results of this study are also confirmed by studies of Özdemir and Derves (1999) for hazelnut, Mohapatra and Rao (2005) for bulgur and Tulek (2011) for mushroom. Drying temperature, forced convective air and vacuum drying systems have greatly increased the drying rates.

Fitting of the drying curves of parboiled wheat

The drying kinetics is often used to describe the combined macroscopic and microscopic mechanisms of mass transfer during drying, and it is affected by drying conditions, types of dryer and characteristics of materials to be dried. The drying kinetics models are essential for equipment design, process optimization and product quality improvement.

Parboiled wheat samples were dried in different dryers, and at different temperatures to obtain experimental data for the change in moisture ratio (MR) over time (*Fig. 2*). Data obtained from drying experiment; basically the moisture content was converted to moisture ratio (MR) and was fitted to the six models listed in *Table 1*. As root mean square error (RMSE) values approach zero, the closer the prediction is to experimental data. Different drying models were compared on the basis of their R^2 and RMSE so as to evaluate their respective goodness of fit. The statistical results of different model including their model coefficients are listed in *Table 2*. In all models and all cases, R^2 values were higher than 0.9526, and RMSE values were lower than 0.063. The average R^2 value of Midilli model at all temperatures and dryers were 0.9987, and corresponding RMSE value was 0.010. Among the used models, Midilli model was exhibited the best fit for drying kinetics of parboiled wheat.

It can be seen from *Table 2* that the drying rate constant 'k' for Midilli model increases in absolute values with increasing temperatures. This fact is expected because higher temperatures lead to a higher drying rate, reaching equilibrium water content faster. Also, effect of dryer on k value can be seen from *Table 2*.

Table 2. *Statistical constants of the six drying models ($p \leq 0.05$)*

Dryer*	Model	T^a (°C)	k**	a	b	c	n	α	β	R^2	RMSE
NCAD	1	50	$5.27x10^{-5}$							0.9898	0.027
		60	$8.78x10^{-5}$							0.9923	0.026
		70	$12.9x10^{-5}$							0.9928	0.025
	2	50	$8.45x10^{-6}$				1.19			0.9989	0.009
		60	$4.86x10^{-5}$				1.06			0.9932	0.025
		70	$4.73x10^{-4}$				0.86			0.9974	0.015
	3	50	$1.50x10^{-5}$	1.00	$-2.90x10^{-6}$		1.09			0.9997	0.005
		60	$1.85x10^{-5}$	0.99	$1.75x10^{-6}$		1.20			0.9948	0.022
		70	$1.70x10^{-4}$	1.00	$1.91x10^{-6}$		0.98			0.9997	0.005
	4	50	$5.47x10^{-5}$	1.03						0.9921	0.024
		60	$8.87x10^{-5}$	1.01						0.9924	0.026
		70	$1.27x10^{-4}$	0.98						0.9932	0.025
	5	50	$3.33x10^{-5}$	1.35		$-3.48x10^{-1}$				0.9995	0.006
		60	$8.73x10^{-5}$	1.01		$-6.57x10^{-3}$				0.9924	0.026

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

		70	1.51x10^{-4}	0.95		5.39x10^{-2}				0.9997	0.005
	6	50						1.86x10^{4}	1.19	0.9989	0.009
		60						1.15x10^{4}	1.06	0.9932	0.025
		70						0.75x10^{4}	0.86	0.9974	0.015
FCAD	1	50	1.03x10^{-4}							0.9606	0.054
		60	1.22x10^{-4}							0.9696	0.049
		70	1.68x10^{-4}							0.9780	0.043
	2	50	1.98x10^{-3}				0.68			0.9991	0.008
		60	1.89x10^{-3}				0.70			0.9973	0.014
		70	2.02x10^{-3}				0.72			0.9928	0.025
	3	50	3.76x10^{-4}	1.00	8.04x10^{-7}		0.72			0.9992	0.007
		60	7.51x10^{-4}	1.00	1.91x10^{-6}		0.81			0.9991	0.009
		70	1.45x10^{-3}	1.00	2.41x10^{-6}		0.92			0.9984	0.012
	4	50	9.55x10^{-5}	0.94						0.9683	0.048
		60	11.60x10^{-5}	0.95						0.9734	0.046
		70	16.40x10^{-5}	0.98						0.9787	0.043
	5	50	1.49x10^{-4}	0.86		1.23x10^{-1}				0.9941	0.021
		60	1.67x10^{-4}	0.89		9.93x10^{-2}				0.9970	0.015
		70	2.13x10^{-4}	0.93		7.19x10^{-2}				0.9991	0.009
	6	50						8.89x10^{3}	0.69	0.9991	0.008
		60						7.44x10^{3}	0.70	0.9973	0.014
		70						5.43x10^{3}	0.72	0.9928	0.025
VD	1	50	1.94x10^{-4}							0.9698	0.050
		60	2.37x10^{-4}							0.9632	0.055
		70	3.17x10^{-4}							0.9526	0.063
	2	50	5.45x10^{-3}				0.62			0.9951	0.020
		60	14.20x10^{-3}				0.53			0.9962	0.018
		70	61.40x10^{-3}				0.38			0.9996	0.006
	3	50	1.18x10^{-3}	1.00	2.20x10^{-6}		0.81			0.9993	0.008
		60	4.37x10^{-3}	1.00	1.69x10^{-6}		0.67			0.9982	0.012
		70	65.00x10^{-3}	1.00	-9.69x10^{-8}		0.38			0.9996	0.006
	4	50	1.89x10^{-4}	0.97						0.9707	0.049
		60	2.32x10^{-4}	0.98						0.9638	0.055
		70	3.12x10^{-4}	0.99						0.9529	0.062
	5	50	2.54x10^{-4}	0.92		7.63x10^{-2}				0.9993	0.008
		60	3.14x10^{-4}	0.92		7.50x10^{-2}				0.9973	0.015
		70	4.37x10^{-4}	0.92		7.48x10^{-2}				0.9929	0.024
	6	50						4.32x10^{3}	0.62	0.9951	0.020
		60						3.09x10^{3}	0.53	0.9962	0.018
		70						1.46x10^{3}	0.38	0.9996	0.006

*NCAD: Natural convective air dryer, FCAD: forced convective air dryer, VD: vacuum dryer. T^{a}: Drying temperature. ** drying rate constant

Comparing k value of natural convective air drying with forced convective air drying and vacuum drying systems, k values increased from 1.50×10^{-5} to 3.76×10^{-4} and 1.18×10^{-3} at 50 °C, respectively. Similar effect was obtained at 60 and 70 °C drying temperatures. As a result, vacuum drying provides faster drying than the natural convective and forced convective air drying systems.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

Determination of effective diffusivities of parboiled wheat during drying

The statistical data of the Fick's model used to explain the drying phenomenon that occurred in the falling rate stage of parboiled wheat were investigated and the experimental data obtained at different temperatures and different dryers were applied to the Fick's model by nonlinear regression analysis. As shown in *Table 3*, the regression coefficients (R^2) and the root mean standard error (RMSE) values ranged from 0.9534 to 0.9923 and 0.06 to 0.03. The theoretical moisture ratios were calculated using the results of the model and compared with the experimental data in *Fig. 2*. As shown in the *Fig. 2*, it was observed that the experimental data were compatible with the theoretical data.

Table 3. *Thermodynamic properties (E_a: activation energy, ΔH: enthalpy; ΔS: entropy; ΔG: Gibbs free energy) and effective moisture diffusivity of dried parboiled wheat for different drying systems*

Dryer	T^a (° C)	D_{eff} x 10^{11} ($m^2 s^{-1}$)	R^2	RMSE	E_a kJ mol^{-1}	ΔH J mol^{-1}	ΔS J $mol^{-1} K^{-1}$	ΔG J mol^{-1}
NCAD*	50	2.38 ±0.10^{a,x}	0.9898	0.03	41.46 ±3.24^{z}	38774.75 ±9.21^{a,x}	-320.49 ±1.25^{a,x}	142291.46 ±22.45^{a,x}
	60	3.97 ±0.13^{b,x}	0.9918	0.03		38691.61 ±6.37^{b,x}	-320.74 ±1.69^{a,x}	145497.59 ±18.42^{b,x}
	70	5.84 ±2.72^{c,x}	0.9923	0.03		38608.47 ±7.12^{c,x}	-320.98 ±0.87^{a,x}	148706.21 ±15.67^{c,x}
FCAD*	50	4.65 ±1.45^{a,y}	0.9606	0.05	27.71 ±2.68^{y}	25028.13 ±5.25^{a,y}	-357.98 ±2.38^{a,x}	140656.10 ±9.28^{a,y}
	60	5.52 ±1.21^{b,y}	0.9696	0.05		24944.99 ±8.78^{b,y}	-358.23 ±1.45^{a,x}	144237.19 ±18.45^{b,y}
	70	8.51 ±1.46^{c,y}	0.9628	0.05		24861.85 ±5.44^{c,y}	-358.48 ±1.65^{a,x}	147820.77 ±12.27^{c,y}
VD*	50	8.70 ±1.28^{a,z}	0.9693	0.05	22.28 ±1.29^{x}	19591.03 ±2.36^{a,z}	-369.29 ±2.66^{a,x}	138871.17 ±23.56^{a,z}
	60	10.80 ±1.29^{b,z}	0.9634	0.06		19507.89 ±4.92^{b,z}	-369.54 ±0.98^{a,x}	142565.32 ±19.31^{b,z}
	70	14.10 ±0.35^{c,z}	0.9534	0.06		19424.75 ±8.98^{c,z}	-369.79 ±1.55^{a,x}	146261.98 ±32.21^{c,z}

*NCAD: natural convective air dryer, FCAD: forced convective air dryer, VD: vacuum dryer. T^a: Drying temperature. Means in the same column with different superscript letters are significantly different, a-c (temperature), x-z (dryer), and P ≤ 0.05. Second values are standard deviations

When we look at the calculated D_{eff} values for the parboiled wheat samples from the Fick's model in *Table 3*, we see that increase in temperature for three drying systems increased D_{eff} values. Increase of temperature from 50 to 70 °C increased in D_{eff} values from 2.38×10^{-11} to 5.84×10^{-11} (59% increase), 4.65×10^{-11} to 8.51×10^{-11} (45% increase), and 8.70 $x10^{-11}$ to 14.10×10^{-11} (38% increase) for natural air convection, forced air convection and vacuum drying systems, respectively. Mohapatra and Rao (2005) reported that the effective diffusion coefficient of parboiled wheat during drying at a temperature range of 40-60 °C varies between 1.20×10^{-10} and 2.90×10^{-10} m^2s^{-1}. The D_{eff} values lie within in general range of 10^{-11}–10^{-9} m^2 s^{-1} for food materials (Rizvi, 1986).

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

These results show that the Fick model can represent drying behavior of parboiled wheat in all dryers at all drying temperatures. When the drying kinetics of different foods such as sour yeast produced with Amaranth flour (Rozylo et al., 2014), popcorn (Doymaz and Pala, 2003), saffron (Acar et al., 2015) and Izmir Crispy snack are examined (Turkut et al., 2015), it has been seen that the Fick's diffusion model is a suitable model.

Compared to NCAD, FCAD and vacuum drying systems at the same temperatures, diffusion coefficients increased. This can be explained by easy evaporation of the moisture in the product at higher temperatures and an increase in drying rate in different dryers. The higher the diffusion coefficient, the higher the mass transfer. Salehi et al. (2017) and Walde et al. (2006) reported that D_{eff} was higher in vacuum drying compared to forced convection in the drying of the mushroom.

The temperature effect was the highest in natural air convection, and the least in vacuum drying. This shows that the effect of vacuum is greater than temperature effect due to more mass transfer of water in vacuum system. Similarly, compared to natural air convection, the movement of hot air by forced air convection drying reduced the temperature effect. In other words, mass transfer is affected by heat transfer. Mass transfer (moisture) in the vacuum dryer is less affected by temperature. Also, at the constant temperatures, D_{eff} values of the forced air convection dryer were higher than that of the natural air convection, while that of the vacuum drying was faster than both the forced air convection and the natural air convection dryers (*Table 3*). The increase in D_{eff} value indicates that drying is faster. The increase in drying speed means that it will dry up in a shorter time. As seen in *Fig. 2,* both the temperature and the type of dryer affected the drying rate. As a result, vacuum drying provides faster drying than the other two drying systems.

Thermodynamic properties

Thermodynamically, the activation energy is expressed as water molecules passing through the energy barrier when moisture transfers from the inside to the outside of the product. The lower values of the activation energy give higher values of moisture diffusion in the drying process. The reduction in the activation energy of a process is due to the increase in the average energy of the water molecules (Devahastin, 2000). Activation energy can be interpreted as the energy barrier that must be overcome in order to activate moisture diffusion (Babalis and Belessiotis, 2004).

The temperature dependence of D_{eff} can be described by an equation of the Arrhenius type as given in *Equation 7*. The moisture diffusivity was plotted against reciprocal of absolute temperature in *Fig. 3*. The slope of the curve gives the E_a/R, while the intercept gives the D_{ref} value. The R^2 values, which indicate regression compliance, were found between 0.9329 and 0.9961. The linear regressed equations from the Arrhenius approach for NCAD, FCAD and vacuum dryer were found as to be $\ln(D_{eff}) = -9.01 - \frac{4986.76}{T}$, $\ln(D_{eff}) = -13.52 - \frac{3333.36}{T}$ and $\ln(D_{eff}) = -14.88 - \frac{2679.39}{T}$, respectively.

The activation energy values for natural convective air, forced convective air and vacuum drying were found to be 41.46, 27.71 and 22.28 kJ mol^{-1}, respectively. These values are close to the value of the dried boiled wheat (37.013 kJ mol^{-1}) found by Mohapatra and Rao (2005). In addition, the activation energy values we found were found to be less than the value found in the drying of raw wheat (51.00 kJ mol^{-1})

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

(Becker, 1959). Turkut et al. (2015) also found the activation energy of Izmir Crispy snack to be 32.78 kJ mol^{-1}. In another study (Ah-Hen et al., 2013), the activation energy values of blueberry was found to be 59.27 and 34.30 kJ mol^{-1} for natural air convection and vacuum drying, respectively. The smaller the activation energy is, the more easily a particular process occurs, in other words, the lower the energy that is required for the physical processing. Thus, vacuum drying of parboiled wheat showed the lower activation energy that indicates less temperature effect. However, it can be concluded that the drying rate is faster than other dryers.

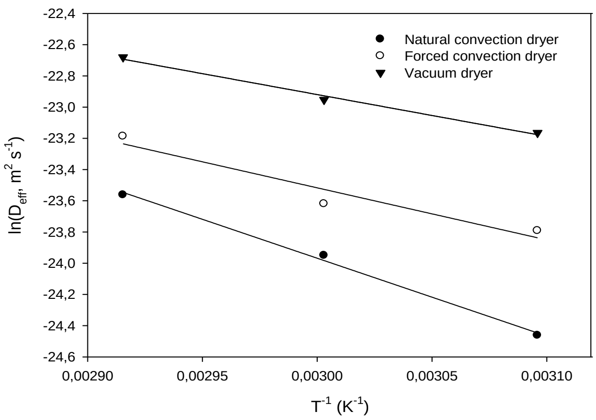

Figure 3. *Arrhenius plot of Fick's law model of D_{eff}, of parboiled wheat over the drying temperature range of 50-70 °C*

Table 3 shows the values that were obtained from the thermodynamic properties relating to the drying process of parboiled wheat. The differential enthalpy decreased significantly ($P \leq 0.05$) with increasing temperature for natural convective air dryer, forced convective air dryer and vacuum dryer. The differential enthalpy values were positive as this is a process with heat absorption, that is, endothermic (Shafaei et al., 2016). Similar results are reported in previous studies (Jideani and Mpotokwana, 2009; Correa et al., 2016; Shafaei et al., 2016). Lower values of enthalpy difference indicate that a lower energy is required for the process to occur. Differential entropy is a thermodynamic quantity that is associated with the degree of disorder, as it is a state function where the values increase during a natural process in an isolated system. Analyzing the behavior of the entropy, it is concluded that this thermodynamic property showed similar behavior to the enthalpy in which the values decreased with increasing temperature (*Table 3*). This trend indicates that there is an increase in the system order, as it is entropically unfavorable (Jideani and Mpotokwana, 2009). This fact can be explained by the theory of activated complex in which a substance in an activation condition may acquire negative entropy if the degrees of freedom of translation or rotation are lost during the formation of the activated complex (Dannenberg and Kessler, 1988).

The Gibbs free energy increased with increasing temperature, and their values were positive, indicating that the drying in this research conditions were not spontaneous. The positive value of the Gibbs free energy is characteristic of an endergonic reaction that requires the addition of energy from the environment in which the product is involved for the reaction to occur (Reusch, 2007). The similar results were reported previously by Jideani and Mpotokwana (2009), Correa et al. (2016) and Shafaei et al. (2016).

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

General model as a function of drying time and temperature

When the equations found from the regression of Arrhenius relationship (*Eq. 7*) in *Table 3* were combined with *Equation 6* for three dryers, time and temperature dependence of moisture ratio, the following general models were derived to describe the drying kinetics of parboiled wheat:

Natural convective air dryer (*Eq. 12*),

$$MR = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2}{R_e^2} 1.22x10^{-4} \exp(\frac{-4986.76}{T})t \right) \quad \text{(Eq.12)}$$

Forced convective air dryer (*Eq. 13*),

$$MR = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2}{R_e^2} 1.34x10^{-6} \exp(\frac{-3333.36}{T})t \right) \quad \text{(Eq.13)}$$

Vacuum dryer (*Eq. 14*),

$$MR = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2}{R_e^2} 3.45x10^{-7} \exp(\frac{-2679.39}{T})t \right) \quad \text{(Eq.14)}$$

Equations 12-14 can be used to find the moisture ratio of parboiled wheat during drying at any time (seconds) and temperature (K) providing that R_e is known. Also, when the moisture ratio and drying temperature of parboiled wheat are known, the drying time can be found for the dryers. Using these equations can be beneficial to each dryer during drying processing of bulgur.

Conclusions

The changes of moisture ratio have been described by six semi-theoretical and Fick's second diffusion models. The model yielded the best description. The effective moisture diffusivity was significantly ($P \leq 0.05$) increased when forced air convection and vacuum drying was applied, compared with natural air convection drying. When the temperature of drying changed from 50 to 70 °C, 59, 45 and 38% changes in D_{eff} values were found for natural convective air, forced convective air and vacuum drying systems, respectively. The effective moisture diffusivity during drying of parboiled wheat by natural air convection, forced air convection and vacuum dryers varied from 2.38×10^{-11} to 14.10×10^{-11} $m^2 s^{-1}$, in the range from 10^{-11} to 10^{-9} $m^2 s^{-1}$ reported for other food stuffs. Drying temperature, forced convective air and vacuum drying systems have greatly increased the drying rates. Results confirmed that the dehydration rates of the vacuum dried parboiled wheat were higher than those of the forced convective and natural convective air dried ones. The activation energy values for natural convective air, forced convective air and vacuum drying systems were found to be 41.46, 27.71 and 22.28 kJ mol^{-1}, respectively. In the processes of parboiled wheat drying, both differential enthalpy and entropy decreased with increasing temperature. The

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

differential enthalpy values are positive, indicating endothermic drying process. The Gibbs free energy increased with increasing temperature and with positive values, indicating that drying does not occur spontaneously in the working conditions; thus, this process requires the addition of energy from an external source. In this study, vacuum drying of parboiled wheat showed the lower activation energy, higher effective diffusivity and rate constant (k) that indicates less temperature effect while the drying rate is faster than other dryers. New equations related to the moisture ratio at any time and temperatures for different dryers were derived. Using these equations can be beneficial to each dryer during drying processing of bulgur. Further investigation about the effect of natural convective air dryer, forced convective air dryer and vacuum dryer on quality characteristics of parboiled wheat is needed during bulgur production.

REFERENCES

[1] Acar, B., Sadikoğlu, H., Doymaz, İ. (2015): Freeze-drying kinetics and diffusion modeling of saffron (Crocus sativus L.). – Journal of Food Processing and Preservation 39: 142-149.

[2] Ah-Hen, K., Zambra, C. E., Aguero, J. E., Vega-Gálvez, A., Lemus-Mondaca, R. (2013): moisture diffusivity coefficient and convective drying modelling of murta (Ugni molinae Turcz): Influence of temperature and vacuum on drying kinetics. – Food and Bioprocess Technology 6: 919-930.

[3] AOAC. (2002): Official Methods of Analysis of AOAC International, 17th Ed. – AOAC, Gaithersburg, MD, USA.

[4] Babalis, S. J., Belessiotis, V. G. (2004): Influence of the drying conditions on the drying constants and moisture diffusivity during the thin-layer drying of figs. – Journal of Food Engineering 65: 449-458.

[5] Bayram, M., Öner, M. D. (2006): Determination of applicability and effects of colour sorting system in bulgur production line. – Journal of Food Engineering 74: 232-239.

[6] Bayram, M., Öner, M. D., Eren, S. (2004b): Thermodynamics of the dimensional changes of the wheat kernel during the cooking operation for the bulgur production. – Food Science and Technology International 10: 243-253.

[7] Becker, H. A. (1959): A study of diffusion in solids of arbitrary shape, with application to the drying of wheat kernel. – Journal of Applied Polymer Science 1: 212-226.

[8] Blasco, M., Garcia-Perez J. V., Bon J., Carreres J. E., Mulet, A. (2006): Effect of blanching and air flow rate on turmeric drying. – Food Science and Technology International 12: 315-323.

[9] Bruce, D. M. (1985): Exposed-layer barley drying, three models fitted to new data up to 150 °C. – Journal of Agricultural Engineering Research 32: 337-348.

[10] Chakraverty, A., Kaushal, R. T. (1982): Determination of optimum drying conditions and development of drying equations for thinlayer drying of parboiled wheat. – American Marketing Association 1982(winter): 33-36.

[11] Correa, P. C., Oliveira, G. H. H., Oliveira, A. P. L. R., Botelho, F. M., Gonelid, A. L. D. (2016): Thermodynamic properties of drying process and water absorption of rice grains. – CYTA-Journal of Food 15: 204-210.

[12] Crank, J. (1975): The Mathematics of Diffusion. – Oxford University Press, Oxford, New York, USA.

[13] Crisp, J., Woods, J. L. (1994): The drying properties of rapeseed. – Journal of Agricultural Engineering Research 57: 89-97.

[14] Devahastin, S. (2000): Mujumdars Practical Guide to Industrial Drying. Principles, Equipment and New Developments. – Exergex Corporation, Montreal.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

[15] Doymaz, İ., Pala, M. (2003): the thin-layer drying characteristics of corn. – Journal of Food Engineering 60: 125-130.

[16] Ece, M. C., Cihan, A. (1993): A liquid diffusion for drying rough rice. – Transactions of the ASAE 36: 837-840.

[17] Ghaitaranpour, A., Tabatabaie Yazdi, F., Alizadeh Behbahani, B., Mortazavi, A., Mohebbi, M. (2013): The effect of wheat boiling time, bulgur particle size, drying time and temperature on some physical properties of hot air dried Tarkhineh. – Scientific Journal of Pure and Applied Sciences 2: 175-182.

[18] Giri, S. K., Prasad, S. (2007): Drying kinetics and rehydration characteristics of microwave-vacuum and convective hot-air dried mushrooms. – Journal of Food Engineering 78: 512-521.

[19] Henderson, S. M., Pabis, S. (1961): Grain drying theory. II: temperature effects on drying coefficients. – Journal of Agricultural Engineering Research 6: 169-174.

[20] Kavak Akpinar, E. (2002): The development of a cyclone type dryer for agricultural products. – PhD Thesis, Firat University, Elazığ.

[21] Krokida, M., Karathanos, V., Maroulis, Z., Marinos-Kouris, D. (2003): Drying kinetics of some vegetables. – Journal of Food Engineering 59: 391-403.

[22] Liu, Y., Li, X., Zhu, W., Luo, L., Duan, X., Yin, Y. (2016): Drying characteristics, kinetics model and effective moisture diffusivity of vacuum far-infrared dried Rehmanniae. – International Journal of Agricultural and Biological Engineering 9: 208-2017.

[23] McMinn, W. A. M., Magee, T. R. A. (1996): Air drying kinetics of potato cylinders. – Dry Technology 14: 2025-2040.

[24] Midilli, A., Kucuk, H., Yapar, Z. A. (2002): New model for single-layer drying. – Dry Technology 20: 1503-1513.

[25] Mishra, M. K., Brooker, D. B. (1980): Thin-layer drying and rewetting equations for shelled yellow corn. – Transactions of The ASAE 23: 1254-1260.

[26] Mohapatra, D., Rao, P. S. (2005): A thin layer drying model of parboiled wheat. – Journal of Food Engineering 66: 513-518.

[27] Mohsenin, N. N. (1980) Physical properties of plants and animal materials. – Gordon and Breach Science Publishers, New York.

[28] Özdemir, M., Devres, Y. O. (1999): The thin layer drying characteristics of hazelnuts during roasting. – Journal of Food Engineering 42: 225-233.

[29] Page, G. E. (1949): Factors influencing the maximum rates of air drying shelled corn in thin layers. – MSc Thesis, Purdue University, West Lafayette, IN, USA.

[30] Rayaguru, K., Routray, W. (2012): Mathematical modeling of thin layer drying kinetics of stone apple slices. – International Food Research Journal 19: 1503-1510.

[31] Rizvi, S. S. (1986): Thermodynamic properties of foods in dehydration. – Engineering Properties of Foods. 2: 239-251.

[32] Rozylo, R., Rudy, S., Krzykowski, A. S., Dziki, D. (2014): Novel application of freeze-dried amaranth sourdough in gluten-free bread production. – Journal of Food Process Engineering 38: 135-143.

[33] Salehi, F. Kashaninejad, M., Jafarianlari, A. (2017): Drying kinetics and characteristics of combined infrared‑vacuum drying of button mushroom slices. – Heat and Mass Transfer 53: 1751-1759.

[34] Sander, A. (2007): Thin-layer drying of porous materials: selection of the appropriate mathematical model and relationships between thin-layer models parameters. – Chemical Engineering and Processing 46: 1324-1331.

[35] Singh, H., Sodhi, N. (2000): Dehydration kinetics of onions. Journal of Food Science and Technology (Mysore) 37: 520-522.

[36] Suarez, C., Viollaz, P., Chirife, J. (1980): Kinetic of Soybean Drying. – In: Mujumdar, A. S. (ed.) Drying. Hemisphere Publishing Company, Washington, USA.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510

[37] Therdthai, N., Zhou, W. (2009): Characterization of microwave vacuum drying and hot air drying of mint leaves (Mentha cordifolia Opiz ex Fresen). – Journal of Food Engineering 91: 482-489.
[38] Toğrul, H. (2006): Suitable drying model for infrared drying of carrot. – Journal of Food Engineering 77: 610-619.
[39] Toğrul, I. T., Pehlivan, D. (2002): Mathematical modeling of solar drying of apricots in thin layers. – Journal of Food Engineering 55: 209-216.
[40] Tulek, Y. (2011): Drying kinetics of oyster mushroom (Pleurotus ostreatus) in a convective hot air dryer. – Journal of Agricultural Science and Technology 13: 655-664.
[41] Turkut, G. M., Çakmak, H., Tavman, Ş. (2015): Proteince Zenginleştirilmiş İzmir Gevreğinin Kuruma Davranışının İncelenmesi. – Pamukkale Univiversites Mühendislik Bilimleri Dergisi 21: 421-427.
[42] Walde, S. G., Velu, V., Jyothirmayi, T., Math, R. G. (2006): Effects of pre-treatments and drying methods on dehydration of mushroom. – Journal of Food Engineering 74: 108-115.
[43] Wang, C. Y., Singh, R. P. (1978): Use of variable equilibrium moisture content in modeling rice drying. ASAE paper 78-6505. – ASAE, St. Joseph, MI.
[44] Watson, E. L., Bhargava, V. K. (1974): Thin layer studies on wheat. – Canadian Journal of Agricultural Engineering 16: 18-22.
[45] White, G. M., Brigges, T. C., Loewer, O. J., Ross, I. J. (1981): Thin layer drying models for soybeans. – Transactions of The ASAE 24: 1643-1646.
[46] Yu, B. H., Kies, C. (1993): Wheat products as acceptable substitutes for rice. – Plant Foods for Human Nutrition 44: 79-85.

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1601_495510