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Mathematical modeling of drying kinetics of milky mushroom in a fluidized bed dryer

T. Arumuganathan¹, M.R. Manikantan²*, R.D. Rai¹, S. Anandakumar², and V. Khare¹

¹National Research Centre for Mushroom, Indian Council of Agricultural Research, Chambaghat, Solan - 173 213 Himachal Pradesh, India

²Agricultural Engineering College and Research Institute, Tamil Nadu Agricultural University, Coimbatore - 641 003 Tamil Nadu, India

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A b s t r a c t. Drying kinetics of milky mushroom slices (10 mm) in a fluidized bed dryer was studied at air temperatures of 50, 55 and 60°C. Drying of milky mushroom slices occurred in falling rate period. In order to select a suitable drying curve, eight thin layer-drying models were fitted to the experimental moisture ratio data. Among the mathematical models investigated, Wang and Singh model best described the drying behaviour of mushroom slices with high correlation coefficient (R^2) values. The effective moisture diffusivity (D_{eff}) of mushroom increased as the drying air temperature increased. The moisture diffusivity in milky mushroom was found to increase from 1.55 to 4.02 x 10⁻⁹ m² s⁻¹ during the initial stage of drying, and from 8.76 to 16.5 x 10⁻⁹ m² s⁻¹ during the later stage of drying. Drying at temperature of 60°C required minimum activation energy to detach and move the water during the drying process.

K e y w o r d s: milky mushroom, drying models, moisture ratio, diffusivity, activation energy

INTRODUCTION

Mushrooms are highly perishable in nature, with extremely short shelf-life as they contain moisture in the range of 87 to 95% wet basis (w.b.). Milky mushroom (*Calocybe indica*), a robust, fleshy and milky white colour mushroom is of Indian origin. It has become the third commercially grown mushroom in India, after button and oyster mushrooms. The protein content of this tropical mushroom is 32.3% and the crude fibre is about 41% (Krishnamoorthy, 2003). Quality deterioration takes place if fresh mushrooms are not immediately processed. Therefore, their processing to the forms of more stable products is important. Long term preservation methods such as canning, pickling and drying are most commonly used methods of preservation of mushrooms to make the product available throughout the year. Drying reduces bulk quantity, thus facilitating transportation, handling and storage. Although sun-drying is economical, mechanical drying speeds up the process, prevents losses, ensures use of safer drying temperatures and produces superior product compared to sun drying (Mudahar and Bains, 1982). Dehydrated mushrooms are used as an important ingredient in several food formulations including instant soups, pasta salads, snack seasonings, stuffing, casseroles, and meat and rice dishes (Tuley, 1996).

The drying kinetics of food is a complex phenomenon and requires simple representations to predict the drying behaviour and to optimise the drying parameters. Thus, layer drying equations were used for drying time prediction and for generalisation of drying curves (Karathanos and Belessiotis, 1999). Limited research in drying characteristics of mushrooms was carried out and data was reported on moisture loss and drying rates (Pruthi et al., 1978; Deshpande and Tamhane, 1981; Nehru et al., 1995; Suguna et al., 1995). However, systematic studies on the drying kinetics of milky mushrooms are lacking. The objectives of the present study were: i) to study the drying kinetics of milky mushroom in a fluidized bed dryer, ii) to evaluate a suitable thin layer drying model, and iii) to determine the moisture diffusivity and activation energy during drying of milky mushroom.

MATERIALS AND METHODS

Freshly harvested milky mushrooms (*Calocybe indica*) of uniform maturity were obtained from the Environment Controlled Research Facility (ECRF) of National Research

^{*}Corresponding author's e-mail: maniciphet@yahoo.co.in

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Centre for Mushroom, Solan, India. The mushrooms were cleaned, sliced uniformly (average thickness: 10 ± 0.5 mm) and were dried on the same day. The initial moisture content of the mushrooms was 91.40% w.b. and was determined by the AOAC method No. 934.06 (AOAC, 2000). Mushroom slices were then dried at three different temperatures *viz.*, 50, 55 and 60°C to safe final moisture content.

Moisture ratio of samples during drying was calculated by the following equation:

$$MR = \frac{(M - M_e)}{(M_o - M_e)},\tag{1}$$

where: MR is the dimensionless moisture ratio, M is the moisture content at time t, and M_o and M_e are the initial and equilibrium moisture contents, respectively, on dry basis. During thin-layer drying of milky mushroom in fluidized bed dryer, the samples were not exposed to uniform relative humidity and temperature continuously. So the moisture ratio was simplified according to Pala *et al.* (1996) and Doymaz (2004), to:

$$MR = \frac{M}{M_{o}}.$$
 (2)

To select a suitable model for describing the drying process of milky mushroom, drying curves were fitted with eight thin-layer drying equations. The moisture ratio models that are evaluated are presented in Table 1.

To determine the drying kinetics, mushrooms were dried in a fluidized bed dryer (Retsch-TG 100, Germany) at 50, 55 and $60\pm1^{\circ}$ C. About 500 g sliced mushroom sample was uniformly spread in a thin layer on perforated stainless steel tray for drying. Moisture loss was recorded at 30 min intervals by a digital balance of 0.01 g accuracy (D'Arts-DG 25, India). The drying was continued till there was no large variation in the moisture loss. The relative humidity of the drying air was not regulated and it varied from 18 to 45%. The hot air velocity passing through the mushroom sample was kept at a constant value of 1.5 m s⁻¹ for all drying experiments. Experiments were conducted in triplicate.

T a b l e 1. Thin layer drying models given by various authors

The non-linear regression analysis was done using MATLAB (version 6.5) software package. Coefficient of correlation, R^2 was one of the main criteria for selecting the best model. In addition to coefficient of correlation, the goodness of fit was determined by various statistical parameters such as reduced chi-square (χ^2), mean bias error (MBE) and root mean square error (*RMSE*) values. For quality fit, R^2 value should be higher and χ^2 , *MBE* and *RMSE* values should be lower (Demir *et al.*, 2004; Erenturk *et al.*, 2004; Pangavhane *et al.*, 1999; Sarsavadia *et al.*, 1999; Togrul and Pehlivan, 2002). The parameters were calculated by using the following expressions:

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

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

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N} \left(MR_{exp} - MR_{pre}\right)^2\right]^{\frac{1}{2}}, \qquad (5)$$

where: MR_{exp} – experimental moisture ratio, MR_{pre} – predicted moisture ratio, N – number of observations, z – number of drying constants.

Fick's diffusion equation for particles with slab geometry was used for calculation of effective moisture diffusivity. Since the mushrooms were dried after slicing, the samples were considered to be of slab geometry. The equation is expressed as (Maskan *et al.*, 2002):

$$MR = \frac{8}{\pi^2} \exp\left(\frac{-\pi^2 D_{eef} t}{L^2}\right),\tag{6}$$

where: D_{eff} is the effective diffusivity in m² s⁻¹, t is the time of drying in seconds, and L is the slab thickness in metres.

Model name	Equation	References
Newton	$MR = \exp(-kt)$	O'Callaghan et al. (1971), Liu and Bakker-Arkema (1997)
Page	$MR = \exp\left(-kt^n\right)$	Zhang and Litchfield (1991)
Modified Page	$MR = \exp\left(-(kt)^{n}\right)$	Overhults et al. (1973)
Henderson and Pabis	$MR = a \exp(-kt)$	Henderson and Pabis (1961), Chhinnman (1984)
Logarithmic	$MR = a \exp\left(-kt\right) + c$	Yagcioglu et al. (1999), Yaldiz et al. (2001)
Two term	$MR = a \exp(-k_0 t) + b \exp(-k_1 t)$	Henderson (1974)
Two term exponential	$MR = a \exp(-kt) + (1-a) \exp(-kat)$	Sharaf-Eldeen et al. (1980)
Wang and Singh	$MR = 1 + at + bt^2$	Wang and Singh (1978)

 a, b, c, k, k_0, k_1 – drying constants.

As the moisture diffusivity value changes with moisture content of the drying material, it is not possible to get a linear relationship for the entire moisture content range, that is, a single moisture diffusivity value to represent the entire drying range. Hence, as explained by Demirel and Truhan (2003), the entire plot of $\ln (MR) vs$ drying time was divided into two portions such that it could be well represented by two linear relationships with higher R^2 value. Hence, for each drying experiment there are two moisture diffusivity values for initial and later stages of drying.

The activation energy can be interpreted as the minimum energy that must be supplied to break water-solid and/or water-water interactions, and to move the water molecules from one point to another in the solid. The smaller E_a value of the sample indicates that water molecule can more readily move in the sample. The activation energy required for drying was calculated by using the Arrehenius equation (Gaston *et al.*, 2004):

$$D_{eff} = D_o \exp\left(\frac{E_a}{RT}\right),\tag{7}$$

where: D_{eff} – effective moisture diffusivity (m² s⁻¹), D_o – constant (measured as intercept at y axis), E_a – activation energy (kJ mol⁻¹), R – universal gas constant (8.314 kJ mol⁻¹ K⁻¹), T – absolute temperature (K).

The equation can be linearized by taking natural logarithm on both sides:.

$$\ln(D_{eff}) = \ln(D_o) - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right).$$
(8)

The activation energy E_a was determined from the slope of the plot ln (D_{eff}) vs 1/T using the above Eq. (8).

RESULTS AND DISCUSSION

The time taken for drying of mushroom slices at different temperatures is given in Table 2. The final moisture content of mushroom slices ranged from 11.34 to 13.13% (w.b.). It is evident that drying air temperature has an important effect on drying. When the temperature was increased, the drying time reduced. The results are similar with the earlier observations on drying of garlic slices (Madamba *et al.*, 1996), onion slices (Sarsavadia *et al.*, 1999), egg plants (Akpinar and Bicer, 2005), peach slices (Kingsly *et al.*, 2007) and plum slices (Goyal *et al.*, 2007).

T a b l e 2. Drying time of milky mushroom

Drying temperature (°C)	Drying time (min)		
50	450		
55	360		
60	300		

The drying rates were computed and the typical drying rate curves are shown in Figs 1-3. The drying curves show that moisture ratio decreases continuously with drying time. The drying rate decreased continuously throughout the drying period. An increase of drying rate was observed with the increase in drying temperature. It is obvious from the drying curves that the constant rate period was absent, and drying of mushrooms took place in the falling rate period for the entire duration. Similar observations have been reported for the drying of onion (Mazza and Maguer, 1980; Rapusas and Driscoll, 1995), red chillies (Chandy et al., 1992), lettuce and cauliflower leaves (Lopez et al., 2000), apricots (Doymaz, 2004), figs (Piga et al., 2004), peach (Kingsly et al., 2007) and plums (Goyal et al., 2007). The drying in falling rate period shows that internal mass transfer has occurred by diffusion.



Fig. 1. Variation of moisture content of milky mushroom with drying time during fluidized-bed drying.



Fig. 2. Moisture ratio of fluidized-bed dried milky mushroom. Legend as in Fig. 1.



Fig. 3. Drying rate (g water g⁻¹ dry matter min⁻¹) of milky mushrooms dried by fluidized-bed drying method. Legend as in Fig. 1.

T a b l e 3. Values of model constants and statistical parameters

The average moisture ratio of milky mushroom dried at different temperatures was test verified with eight different drying models to find out their suitability to describe the drying process. The correlation coefficient and results of statistical analyses obtained from non linear regression analysis using MATLAB are summarized in Table 3. The best model to describe the drying behaviour of milky mushroom was selected on the basis of high R^2 and low χ^2 , *MBE* and *RMSE* values. It is observed from Table 3 that the value of R^2 for the Page, logarithmic, two term, two term exponential and Wang and Singh were greater than 0.90, indicating good fit. From the results, the Wang and Singh model gave comparatively the higher R^2 values of in all the drying temperatures, where asthe χ^2 , *MBE* and *RMSE* values were also found to be the lowest. Thus, the Wang and Singh model may be assumed to represent the thin layer drying of milky mushroom slices in a fluidized bed dryer.

Name of model	Temperature (°C)	SSE	R^2	Adj. R^2	χ^2	RMSE	MBE
Newton	50	0.2064	0.8297	0.8297	0.0059	0.1214	0.0192
	55	0.1666	0.8229	0.8229	0.0051	0.1243	0.0198
	60	0.1387	0.8542	0.8542	0.0031	0.1241	0.0166
Page	50	0.0295	0.9759	0.9740	0.0027	0.0477	0.0125
	55	0.0281	0.9707	0.9678	0.0017	0.0530	0.0108
	60	0.0078	0.9918	0.9907	0.0008	0.0313	0.0082
	50	0.2115	0.8270	0.8137	0.0064	0.1276	0.0192
Modified Page	55	0.1699	0.8229	0.8052	0.0057	0.1304	0.0198
	60	0.1387	0.8542	0.8359	0.0034	0.1317	0.0166
	50	0.1658	0.8644	0.8539	0.0005	0.1129	0.0053
Henderson	55	0.1338	0.8606	0.8467	0.0004	0.1157	0.0053
and Pabis	60	0.1052	0.8893	0.8755	0.0012	0.1147	0.0097
	50	0.5117	0.9582	0.9512	0.0006	0.0653	0.0055
Logarithmic	55	0.0460	0.9521	0.9415	0.0003	0.0715	0.0040
	60	0.0195	0.9795	0.9737	0.0001	0.0527	0.0027
Two term	50	0.1066	0.9128	0.8891	0.0038	0.0984	0.0136
	55	0.0612	0.9362	0.9299	0.0002	0.0782	0.0032
	60	0.0362	0.9662	0.9587	0.0009	0.0634	0.0073
Two term exponential	50	0.0763	0.9376	0.9328	0.0013	0.0766	0.0086
	55	0.0541	0.9436	0.9225	0.0009	0.0823	0.0078
	60	0.0321	0.9662	0.9620	0.0013	0.0634	0.0103
	50	0.0026	0.9979	0.9977	0.0000	0.0141	0.0007
Wang	55	0.0047	0.9951	0.9946	0.0000	0.0218	0.0008
and Singn	60	0.0034	0.9964	0.9960	0.0000	0.0206	0.0019

5,0

4,0

3,0

2,0

1,0

0,0

-1,0

-2,0

-3.0

3,0

30 60 90 120 1

-0,0017x + 0,0204 $R^2 = 0,9862$

In (RM)

The effective moisture diffusivity, D_{eff} was calculated using the method of slopes (Doymaz, 2004; Maskan et al., 2002). Figures 4, 5 and 6 depict the relationship between ln (MR) and drying time for milky mushroom dried at different temperature. From these figures, using the slope of the best fit linear equations, the moisture diffusivity values were calculated using Eq. (6). The best-fit regression equations for different temperatures during initial and later stages of drying are given in Table 4. Values of D_{eff} with coefficient of correlation are given in Table 5. Effective moisture diffusivity of milky mushroom ranged from 1.55 to 4.02 x $10^{-9} \text{ m}^2 \text{ s}^{-1}$ and 8.76 to 16.5 x $10^{-9} \text{ m}^2 \text{ s}^{-1}$ during the first falling rate period and second falling rate period, respectively (Table 5). These values are within the general range of $10^{-9} - 10^{-11}$ m² s⁻¹ for drying of food materials (Maskan et al., 2002). The drying temperature greatly affected the $D_{\rm eff}$ values of milky mushroom. It is observed from the table that the moisture diffusivity increased as drying air temperature was increased. A similar result of the influence of drying temperature on moisture diffusivity during air drying has been found in apricots (Pala et al., 1996; Doymaz, 2004), peach (Kingsly et al., 2007) and plums (Goyal et al., 2007).

The activation energy used to detach and move water molecules during drying was calculated for milky mushroom using the Arrhenius expression between effective moisture diffusivity and absolute temperature. Among the different drying temperatures, during the initial stage of drying, 50°C registered the highest activation energy (79.43 kJ mol⁻¹), followed by 55°C (79.26 kJ mol⁻¹) and 60°C (79.08 kJ mol⁻¹). During the later stage of drying, 50°C temperature recorded the highest activation energy (73.54 kJ mol⁻¹), followed by 55°C (73.35 kJ mol⁻¹) and 60°C (73.23 kJ mol⁻¹). It is clear that 60°C required minimum activation energy to detach and move the water during the drying process. Demirel and Turhan (2003) observed similar lesser activation energy requirement for banana slices during high air temperature drying.

CONCLUSIONS

1. Increase in drying air temperature decreased the drying time.

2. The drying process occurred in both falling rate and constant rate periods.

3. Wang and Singh drying model showed better fit with highest correlation coefficient and low χ^2 , *MBE* and *RMSE* values during the drying behaviour of milky mushroom.

4. The effective moisture diffusivity ranged from 1.55 to $16.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, with higher values for high temperature dried samples.

5. Drying at temperature of 60°C required minimum activation energy to detach and move the water during the drying process.

Fig. 4. Relationship between $\ln (MR)$ and drying time for milky mushroom dried at 50°C.

Drying time (min)

300

-0.0096x + 1.955

 $R^2 = 0.9209$



Fig. 5. Relationship between $\ln (MR)$ and drying time for milky mushroom dried at 55°C. Legend as in Fig. 4.



Fig. 6. Relationship between $\ln (MR)$ and drying time for milky mushroom dried at 60°C. Legend as in Fig. 4.

First falling rate period

Second falling rate period

Second falling rate period

First falling rate period

330 360 390 420 450 480

Drying temperature(°C)	1st falling rate of drying		2nd falling rate of drying		
	Equation	R^2	Equation	R^2	
50	y = -0.0017 x + 0.0204	0.9862	y = -0.0096 x + 1.9551	0.9209	
55	y = -0.0025 x + 0.0518	0.9580	y = -0.0156 x + 3.0217	0.8897	
60	y = -0.0044 x + 0.1020	0.9113	y = -0.0181 x + 2.5688	0.9130	

T a b l e 4. Moisture diffusivity equations at different temperatures

T a b l e 5. Effective moisture diffusivity, D_{eff} (m² s⁻¹), for drying of milky mushroom

Drying temperature (°C)	$D_{ef^{ar}}(m^2 s^{-1})$				
	1st falling rate period (x 10 ⁻⁹)	R^2	2nd falling rate period (x 10 ⁻⁹)	R^2	
50	1.55	0.9862	8.76	0.9209	
55	2.28	0.9580	14.2	0.8897	
60	4.02	0.9113	16.5	0.9130	

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