Kinetics and Mathematical Modeling of Microwave Drying of Sri Lankan Black Pepper (Piper nigrum)

B.M.W.P.K. Amarasinghe[1*], A.J.M.L.M. Aberathna[2], K.K.P.P. Aberathna[3]

Department of Chemical and Process Engineering, University of Moratuwa, Sri Lanka

***Abstract*—** *Drying characteristics of black pepper (Piper nigrum) was investigated in a microwave drying system. Drying experiments were carried out at three different microwave power levels, 180, 360 and 540 W and the moisture content was measured at different time intervals. Experimental results were fitted to seven thin layer drying models; Newton, Page, Henderson and Pabis, Logarithmic, Midilli et. al., Weibull and Kaleta et. al.. Statistical indicators; Coefficient of determination (R^2), Root mean square error (RMSE) and reduced chi square values (χ^2) showed Midilli et. al., Weibull and Kaleta et. al. models give better fit to the experimental values. Drying rate constants and the equation constants were compared and analyzed. Similarities of the drying models were observed and discussed with respect to the equation parameters. The absence of the constant drying rate period in drying curves show the drying of black pepper lies totally in the falling rate period where the drying rate is controlled by the moisture diffusion. Maximum drying rates observed were 0.02, 0.05 and 0.08 kg moisture/kg of dry material/ min at 180, 360 and 540 W power levels. Results revealed drying rate constant and the effective moisture diffusivity values increases with the microwave power level. Drying rate constants were 0.03, 0.09 and 0.16 min^{-1} and the effective moisture diffusivity values were 2.43×10^{-10}, 4.87×10^{-10}, 1.42×10^{-9} m^2/s for power levels of 180, 360 and 540 W respectively. The Activation energy of black pepper calculated based on the Arrhenius equation is 86.7 W/g.*

***Keywords*— Black pepper, Microwave drying, thin layer drying models, diffusivity.**

I. INTRODUCTION

Black pepper (BP) (*Piper nigrum*) is the most widely used spice in the world. BP is also used in perfume and pharmaceutical industries. The crop is grown in many tropical countries including Sri Lanka. The world production of pepper in 2017 is approximately 472,500 MT and is gradually growing. Sri Lanka produces around 3% of the world pepper production [1].

The mature peppercorns are green in colour and become red when ripe (Fig 1). This mixture of green and red peppercorns is dried after harvesting to reduce the moisture content to avoid fungal growth and wastage. The moisture content of the pepper is around 77% when harvested and reduced up to 11% (wet basis) before storage. Solar drying is the widely used method in Sri Lanka for drying of black pepper. However, improper drying specially during rainy season causes postharvest losses. National Committee on Postharvest Technology & Value Addition in Sri Lanka has identified BP as a high priority crop and further development of postharvest drying technologies is recommended as a main thrust research area [2].

Food and grain drying have been paid much attention by researchers. Solar drying, hot air drying, fluidized bed or spouted bed drying are the widely used techniques for food drying [3-8]. Application of Microwave technology has been investigated over the last few years for food and grain drying [9-13]. However, despite the wide use of BP as a spice in the world, the previous studies on drying of black pepper is limited. Solar tunnel dryers and fluidized bed or spouted bed dryers have been tested for black pepper drying [14-16].

Chacko *et. al.* [16] and Magda *et. al*. [13] have found that microwave drying is suitable for BP drying and have observed improvement in aroma despite minor losses of some volatiles. Drying kinetics is important in determining the drying time required and hence the dryer size.

Therefore, the objective of this work is to study drying kinetics of black pepper in microwave drying and determine moisture diffusivity and activation energy of the material.

FIG. 1: BLACK PEPPER PLANT (LEFT) AND DRY SEEDS (RIGHT)
(http://world-crops.com/black-pepper/ and http://www.fruitsvegetablecinnamonsuppliersrilanka.com)

II. THEORY

Drying is an important unit operation which involves simultaneous heat and mass transfer. The knowledge on drying kinetics, which determines the drying time and hence dryer size, is essential in dryer design. Numerous investigations have been reported on thin layer drying models. Newton or Lewis, Page, Henderson and Pabis, Logarithmic, Midilli *et.al* are among the widely used thin layer drying models to express drying kinetics. Some researchers have used less common models such as Weibull model. Kaleta *et.al.* have introduced several new models in their studies [3,5,17,18].

The moisture content (MC) of a material is expressed either on dry basis or wet basis. The dry basis moisture content is given by the equation (1).

$$MC = \frac{W - W_d}{W_d} \quad [1]$$

Where W and W_d are the weight of the material and weight of the dry material respectively

Equilibrium moisture content is negligible compared to the moisture content and the moisture ratio (MR) can be determined by equation (2).

$$MR = \frac{MC_t}{MC_i} \quad [2]$$

Where MC_i, MC_t are the Initial Moisture content and Moisture content at time t respectively.

The rate of drying largely depends on the rate of moisture diffusion within the solid material. Applying Fick's second law of diffusion for spherical particles leads to equation (3) which relates moisture ratio to the time of drying [8,19].

$$MR = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left[\frac{-n^2\pi^2}{R}\left(\frac{D_{eff}\, t}{R}\right)\right] \quad [3]$$

The equation (3) can be simplified in the following form;

$$ln(MR) = ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{R^2}\right) t \quad [4]$$

Where

n – number of terms
R- Particle radius (m)
D_{eff} - effective moisture diffusivity (m^2/s)
t – time (s)

The effective moisture diffusivity (D_{eff}) in solids is a function of the temperature and the moisture content. The temperature dependence of the diffusivity is adequately described by the Arrhenius equation as given by equation (5)[8].

$$D_{eff} = D_0 \, exp\left(\frac{-E_a}{RT}\right) \quad [5]$$

Where D_0 is the pre exponential factor (m^2/s) and T is the absolute temperature (K), R is the universal gas constant (J mol^{-1} K^{-1}), E_a is the Activation energy (J/mol).

For microwave drying, temperature measurement inside the dryer is not very precise and hence the modified versions of the Arrhenius equation, given by equations (6) and (7) are used to determine the activation energy [8,20].

$$k = k_o \; exp\left(-\frac{E_a m}{P}\right) \quad [6]$$

$$D_{eff} = D_0 \, exp\left(\frac{-E_a m}{P}\right) \quad [7]$$

k- drying rate constant (min^{-1})
k_0- pre exponential factor (min^{-1})
D_0- pre exponential factor (m^2/s)
E_a - Activation energy (W/g)
m –mass of raw sample (g)
P – microwave power (W)

III. METHODOLOGY

Matured fresh black peppercorns just harvested were provided by the local farmers. Microwave oven (singer, Model no.SMW23GA9, 23 L capacity) of variable power output setting and rated capacity of 900W was used for drying. The moisture content of pepper was determined by the oven drying method using the electric oven (model: LDO-060 E-DaihanLabTech Co Ltd).

20 g of black pepper was placed in the container as a thin layer and the microwave oven was set to the required power level. The weight of the sample was determined at selected time intervals using the analytical balance. The samples were weighed fast to avoid any interference with the drying process. The drying experiments were repeated for 3 power levels (180W, 360 W and 540 W). The pepper particle size was determined by the gravity settling method. Average size of the pepper particles were 4 mm diameter. All the experiments were duplicated to confirm the repeatability.

The moisture content (MC) of the pepper was calculated as a function of the time (equation (1)) and converted to moisture ratio (MR) values (equation (2)) for three different microwave power levels.

The MR as a function of time results were fitted to the seven different thin layer drying models given in Table 1 using Excel Solver. Among the large number of thin layer drying models the seven models were carefully selected. Kucuk *et. al*. have summarized and analyzed 67 thin layer drying models developed and used by various researchers. Simple and most widely used models such as Newton, Page and less common models namely Weibull, Kaleta *et. al*.were selected for data fitting so that the models can be compared [3].

TABLE 1
THIN LAYER DRYING MODELS[3,5,8]

Model Name	Model Equation	Comments
Newton or Lewis	$MR = exp(-kt)$	Simplest model, one model constant
Page	$MR = exp(-kt^n)$	Modification of the Newton's model with exponent 'n'. Commonly used model. Reported as the second best model for most products.
Henderson and Pabis	$MR = a\,exp(-kt)$	Modification of the Newton's model with constant 'a'. Ninth-best model
Logarithmic	$MR = a\,exp(-kt) + b$	Third best model. Second term 'b' included.
Midilli *et al*	$MR = a\,exp(-kt^n) + bt$	Reported as the best. However, 4 model constants.
Weibull	$MR = a\,exp(-kt^n) + b$	One form of the common Weibull equation. Twelfth best model.
Kaleta *et al*	$MR = a\,exp(-kt^n)$	Modification to the Page model with the parameter 'a'.

k in the equations in the Table 1 are drying rate constants and *a, b,* and *n* are the equation constants.

Three statistical parameters; Coefficient of determination (R^2), Root mean squar eerror (RMSE) and reduced chi square values (χ^2) given by equations 8,9 and 10 respectively, were used to determine the best fitted model [3,17,10].

$$R^2 = \frac{\sum_1^n (MR_{pre\,,i} - MR_{avg})^2}{\sum_1^n (MR_{exp\,,i} - MR_{avg})^2} \quad [8]$$

$$\chi^2 = \frac{\sum_1^n (MR_{exp\,,i} - MR_{pre\,,i})^2}{N - z} \quad [9]$$

$$RMSE = \left[\frac{1}{N}\sum_1^n (MR_{pre\,,i} - MR_{exp\,,i})^2\right]^{1/2} \quad [10]$$

Where

MR_{exp}, MR_{pre} and MR_{avg} are the experimental, predicted and average moisture ratios.

N – Number of observations z – Number of constants

Rate of drying (N), kg of moisture evaporated/kg of dry material/ min, was calculated using the equation 11, where *d(MC)/dt* is the gradient of moisture content (MC) as a function the time plot.

$$N = \frac{d(MC)}{dt} \quad [11]$$

IV. RESULTS AND DISCUSSION

The experimentally determined moisture content values were converted to the moisture ratio values and the data were fitted to the seven different thin layer drying models given in Table 1. The model parameters were determined using Excel Solver and the results are summarized in theTable2. Results show that all the seven models under investigation give a good fit to an acceptable level. However, statistical parameters shows that the Midilli *et. al*, Weibull and Kaleta *et. al* models give better fit to the experimental values. Experimental results and model predicted results using the Midilli *et.al*. equation are shown in Fig. 2.

Drying rate constant, k, values for all the models are in the range 0.02-0.03 $min^{-1}$for 180 W power levels, 0.07-0.09 $min^{-1}$for 360 W power level and 0.14-0.19 $min^{-1}$for 540 W power level. Values of the constant, *a*, in the Weibull, Kaleta *et. al*., Henderson and Pabis, Logarithmic and Midilli *et.al*. equations are approximately equal to one (1). This can be compared with the Lewis model and the Page model equations where *'a'* term is not appearing, which implies that the constant *'a'* is equal to one. Constant *'n'* in the Weibull, Kaleta *et. al*, Page and Midilli *et. al* equations are also approximately equal to one which are comparable with the Lewis, Hendarson & Pabis and Logarithmic models where the exponent of *'t'* is equal to one. Further, the very low parameter *'b'* values show that the effect of the second term in the Weibull, Logarithmic and Midilli *et. al.* equations are less significant. The above comparison of the parameters shows the similarity of the seven model equations valid for drying of black pepper in microwave drying.

The rate of drying can be determined using the gradient of moisture content (MC) vs time plot and the Fig. 3 shows drying rate (N) as a function of moisture content at three different microwave power levels. Constant drying rate period is negligible or not in existence showing that drying of BP in microwave is completely under the falling rate period. This shows diffusion of moisture within the solid is the rate controlling step in BP drying. This result is in agreement with the previous workers results on drying of food materials where the constant drying period is negligible [17].

Chacko *et. al.*[16] and Magda *et. al.* [13] showed that microwave oven is suitable for pepper drying; however low power range in suitable to avoid loss of volatiles. Therefore, 180 W powers are recommended for drying of BP in a microwave.

TABLE 2
THIN LAYER DRYING MODELS AND PARAMETERS FOR BLACK PEPPER DRYING IN A MICROWAVE OVEN (k in min^{-1})

Model	P (W)	Model Parameters	RMSE	R^2	χ^2
Newton or Lewis $MR = exp(-kt)$	180	k =0.0356	0.0185	0.9960	0.000347
	360	k =0.0726	0.0175	0.9957	0.000313
	540	k =0.1882	0.0242	0.9935	0.000620
Page $MR = exp(-kt^n)$	180	k =0.0268, n =1.0827	0.0132	0.9980	0.000179
	360	k = 0.0792, n =0.9687	0.0167	0.9961	0.000293
	540	k =0.1459, n =1.1369	0.0125	0.9983	0.000175
Henderson and Pabis $MR = a\ exp(-kt)$	180	*a* = 1.0459, k =0.0374	0.0105	0.9987	0.000112
	360	*a*=1.0018, k=0.0727	0.0174	0.9957	0.000313
	540	*a*=1.0432, k=0.1960	0.0197	0.9956	0.000442
Logarithmic $MR = a\ exp(-kt) + b$	180	*a*=1.0449, k=0.0376,b=0.0017	0.0105	0.9987	0.000113
	360	*a*=0.9960, k =0.0758,b=0.0133	0.0169	0.9959	0.000307
	540	*a* =1.0757, k =0.1713,b=0.0514	0.0119	0.9984	0.000171
Midilli *et al* $MR = a\ exp(-kt^n) + bt$	180	*a*=1.0317, k =0.0312 n =1.0536,b =0.000143	0.0094	0.9989	9.3012E-05
	360	*a* = 1.0368, k = 0.0955, n=0.9096, b=-0.0002	0.0153	0.9967	0.000256
	540	*a* = 1.0129,k =0.1603 n=1.0716, b=0.0014	0.0105	0.9987	0.000141
Weibull $MR = a\ exp(-kt^n) + b$,	180	*a*=1.0095, k =0.0302 n=1.0709b=0.0198	0.0090	0.9991	8.6998E-05
	360	*a*=1.049,k =0.0950 n=0.9061,b =0.0128	0.0153	0.9967	0.000262
	540	*a*=1.0409, k =0.1576 n=1.0664,b = 0.0279	0.0107	0.9987	0.000147
Kaleta *et al* $MR = a\ exp(-kt^n)$	180	*a* =1.0363,k=0.0338 n=1.0270	0.0100	0.9988	0.000104
	360	*a* = 1.0328,k=0.0912 n= 0.9298	0.0155	0.9966	0.000257
	540	*a*=1.0074,k=0.1500 n=1.1262	0.0123	0.9983	0.000182

4.1 Moisture diffusivity

Rate of drying hence the time required for drying depends on the moisture diffusivity within the solid. Equation (4) can be used to determine the moisture diffusivity within the solid. Plots of Ln(MR) as a function of time are shown in Fig.4. Average Effective moisture diffusivity values were calculated using the gradient of the plot and the results are shown in the Table 3. The diffusivity values obtained are in the same order of magnitude as the values obtained by other researchers for similar materials such as orange seeds and dika (Irvingiagabonensis) nuts and kernels [4,21]. Activation energy of pepper can be calculated using the Arrhenius type equation (5). Temperature measurements are only approximate in microwave ovens and therefore equations (6) and (7) which relates the drying rate constant (k) to the ratio of dry solid weight to the microwave power (*m/P*) is recommended for microwave drying. Fig. 5 shows a plot the drying rate constant values calculated using Midilli *et. al.* equation as a function of the ratio of dry solid weight to the microwave power (m/P). The activation energy of the pepper thus calculated is 89.4 W/g and the k_o value is 0.3484 min^{-1}. Similarly, effective diffusivity values calculated can be used to determine the activation energy of the BP using equation (7) and the activation energy calculated is 86.7 W/g and the pre-exponential term, D_0, was 2.0 x 10^{-9} m^2/s.

Therefore, based on the above results equations (11) and (12) are proposed to determine the drying rate constant and the effective moisture diffusivity for BP drying in a microwave oven.

$$k = 0.3484\, exp\left(-\frac{89.4\, m}{P}\right) \qquad [11]$$

$$D_{eff} = 2.0 \times 10^{-9}\, exp\left(\frac{-86.7\, m}{P}\right) \qquad [12]$$

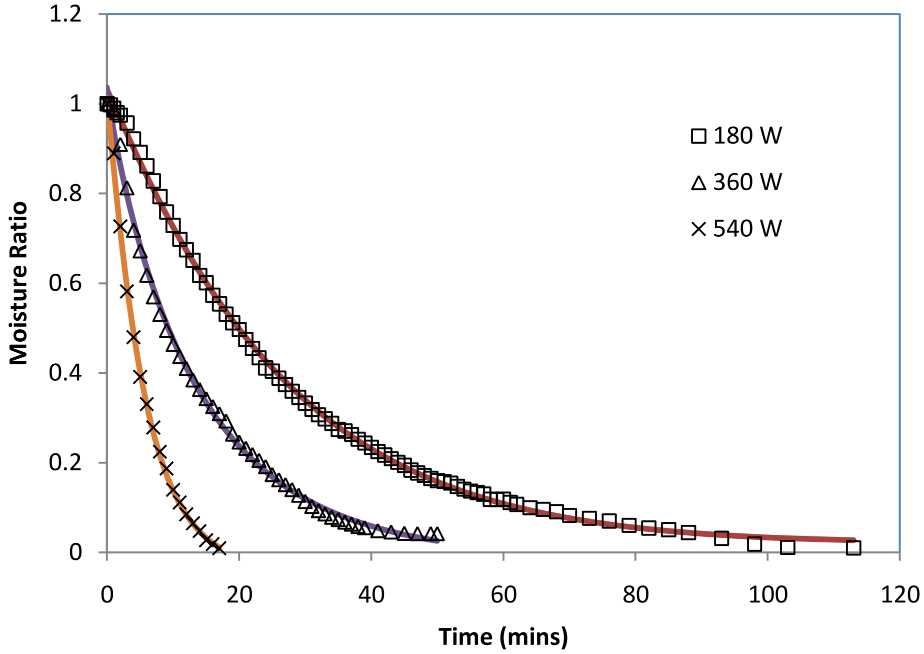

FIG 2: VARIATION OF MOISTURE RATIO (MR) OF BLACK PEPPER AS A FUNCTION OF TIME FOR THREE MICROWAVE POWER LEVELS (□, Δ, ×-EXP VALUES, SOLID LINES - PREDICTED CURVES MIDILLI ET. AL. MODEL)

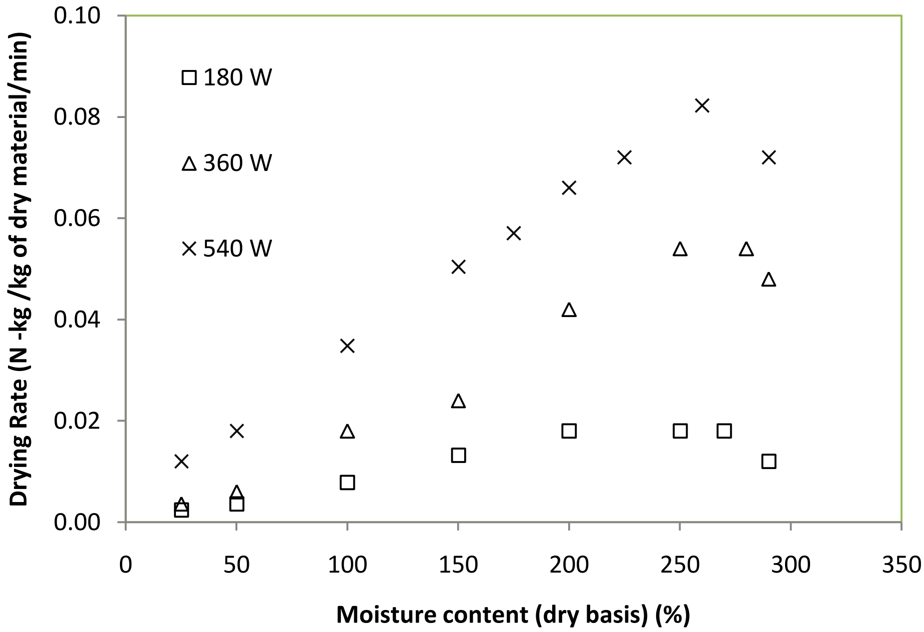

FIG 3: DRYING RATE AS A FUNCTION OF MOISTURE CONTENT FOR BLACK PEPPER DRYING AT THREE MICROWAVE POWER LEVELS

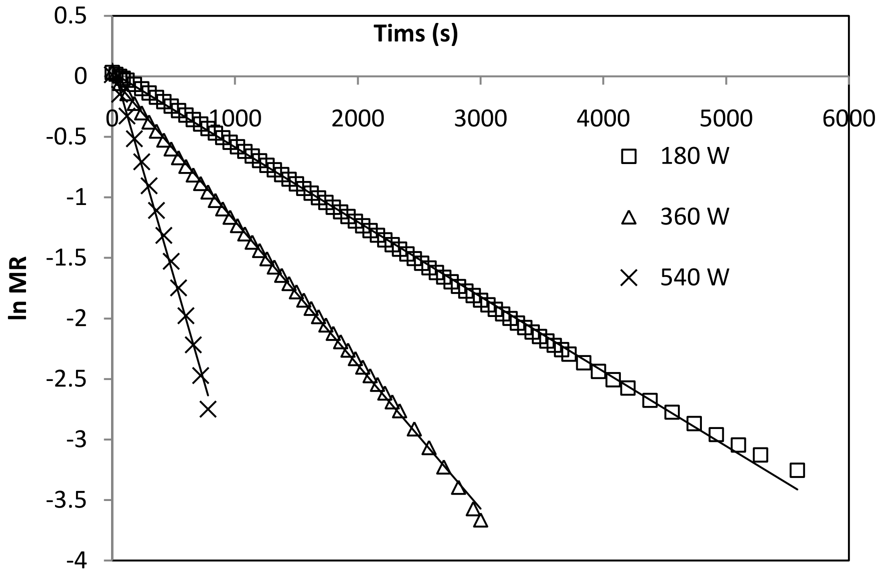

FIG 4: LN (MR) VALUES AS A FUNCTION TIME FOR THREE DIFFERENT MICROWAVE POWER LEVELS FOR BLACK PEPPER DRYING IN A MICROWAVE OVEN

TABLE 3
TIME REQUIRED FOR DRYING FROM 75 % – 11% MC WET BASIS, DRYING RATE CONSTANTS AND EFFECTIVE DIFFUSIVITY VALUES FOR BP DRYING IN A MICROWAVE OVEN

Power Level (W)	m/P (g/W)	Time required for drying (mins)	Drying rate constant, k, (Midilli *et. al* model) (min^{-1})	Effective Diffusivity (m^2/s)
180	0.0272	88	0.0312	2.43418E-10
360	0.0130	43	0.0955	4.86835E-10
540	0.0106	14	0.1603	1.41994E-09

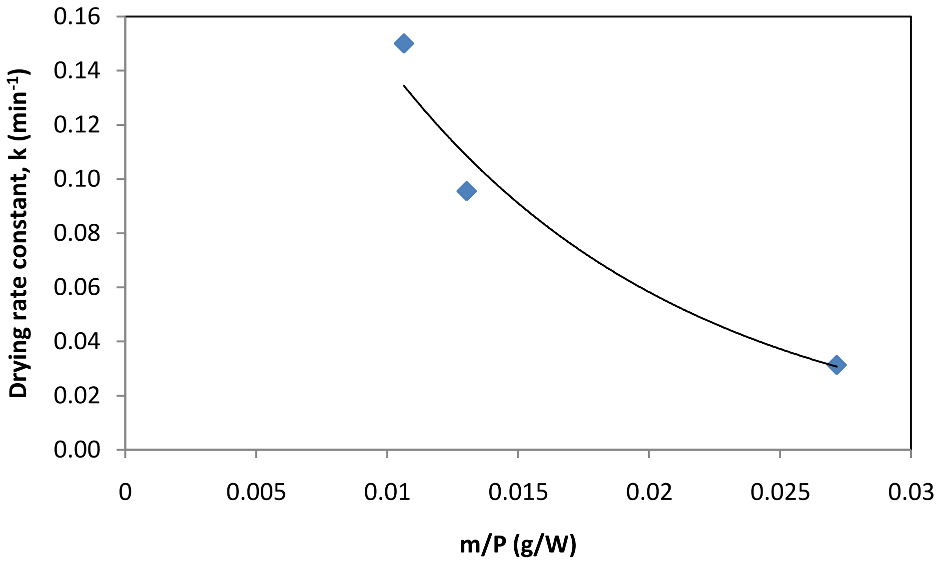

FIG 5: DRYING RATE CONSTANT, K, PREDICTED BY MIDILLI ET AL MODEL AS A FUNCTION OF THE RATIO OF WEIGHT OF BLACK PEPPER TO MICROWAVE POWER

V. CONCLUSION

Microwave drying kinetics of black pepper was studied and the experimental data was fitted to seven thin layer drying models. The Midilli *et. al.*, Weibull and Kaleta *et. al.* models showed statistically better fit compared to other models. Similarities of the model parameters were observed and the significance of the parameters was analyzed. The drying rate constants obtained by Midilli *et. al.*model were 0.03, 0.09 and 0.16 min^{-1} for power levels of 180, 360 and 540 W respectively and the other models also showed values in the similar range. The Effective moisture diffusivity increased with the microwave power level and values were in the range $2.43x\ 10^{-10}$- $1.42\ x\ 10^{-9}\ m^2/s$. The drying rate constants and the effective diffusivity values were in the same order of magnitude as the values obtained by other workers for similar products. The Activation energy of black pepper calculated based on the Arrhenius equation is 86.7 W/g. Drying of BP under low microwave power level is recommended to preserve volatile matter in the product. The time required to dry peppercorns from 75% MC to 11% MC wet basis under 180 W power level is 88 minutes compared to several days under sun drying.

ACKNOWLEDGEMENTS

Authors wish to thank University of Moratuwa, Sri Lanka, for providing funds for the project.

REFERENCES

[1] NEDSPICE, Pepper Crop Report, Alfons van Gulick ESA Conference, Bordeaux, France,1st June 2017.
[2] National Priorities in Post harvest & Value Addition Research in Agriculture, 2011-2015National Committee on Postharvest Technology and Value Addition (NCPHT & VA),Sri Lanka Council for Agricultural Research Policy (SLCARP), Sri Lanka,(2011).
[3] H.Kucuk, A.Midilli, A. Kilic and I.Dincer, Review Article: A Review on Thin-Layer Drying-Curve Equations, , Drying Technology, 32, (2014), 757–773.
[4] O.A.Aregbesola, B.S.Ogunsina, A.E.Sofolahan and N.N. Chime, Mathematical modeling of thin layer drying characteristics of dika (Irvingiagabonensis) nuts and kernels, Nigerian food journal, 33 (2015) 83-89.
[5] A. Kaleta, K.Górnicki, R.Winiczenko and A. Chojnacka, Evaluation of drying models of apple (var. Ligol) dried in a fluidized bed dryer, Energy Conversion and Management, 67 (2013) 179–185.
[6] R. Sivakuar, R. Saravanan, A. ElayaPerumal and S. Iniyan, Fluidized bed drying of some agroproducts-A review, Renewable and sustainable Energy Reviews, 61, 2016 , 280-301.
[7] K.J. Chua and S.K. Chou, Low-cost drying methods for developing countries, Trends in Food Science and Technology, 14 (12), (2003) 519-528.
[8] D.I.Onwude, N. Hasim,R B Janius, N.M. Nawi and K Abdan, Modeling the Thin-layer Drying of Fruits and Vegetables:A Review, Comprehensive Reviews in Food Science and Food Safety, 15, 2016.
[9] M. Hemis, Y. Gariépy, R. Choudhary and V. Raghavan,New coupling model of microwave assisted hot-air drying of a capillaryporous agricultural product: Application on soybeans and canola seeds, Applied Thermal Engineering 114 (2017) 931–937.
[10] A. Balbay,Y.Kaya, O.Sahin, Drying of black cumin (Nigella sativa) in a microwave assisted drying systemand modeling using extreme learning machine, , Energy, 44 (2012) 352-357.
[11] A.C.da Silva, H. J. Sarturi, E. L. Dall'Oglio, M. A.Soares, P. T. de Sousa, L. G. de Vasconcelos and C. A.Kuhnen, Microwave drying and disinfestation of Brazil nut seeds, , Food Control 70 (2016) 119-129.
[12] A.S., Kassem, A.Z. Shokr, A.R. El-Mahdy, A.M.Aboukarima and E.Y.Hamed, Comparison of drying characteristics of Thompson seedless grapes using combined microwave oven and hot air drying, J.of the Saudi society of Agricultural Sciences, 10, (2001) 33-40.
[13] A. Magda, A.E.Mageed , A. F. Mansour , K, F. E.Massry , M. M. Ramadan and M. S.Shaheen, The Effect of Microwaves on Essential oils of White and Black Pepper (Piper nigrum L.) and their Antioxidant Activities, Journal of Essential Oil Bearing Plants, 14 (2), (2011) 214-223.
[14] C.M.I. Joy, G.P.Pittappilli and K.P. Jose, Drying of Black Pepper *(Piper nigrum*L.) Using Solar Tunnel Dryer, PertanikaJ. Trap. Agric. Sci. 25(1),(2002) 39 – 45.
[15] G.K. Jayatunga and B.M.W. P.K. Amarasinghe, Drying Kinetics of Black Pepper Dried in A Spouted Bed Dryer with or without Draft Tubes, International Journal of Manufacturing and Industrial Engineering (IJMIE), Vol. 1(2) June (2014), 6-10.
[16] S. Chacko, A. Jayalekshmy, M.Gopalakrishnan and C.S. Narayanan, Roasting studies on Black Pepper (Piper nigrum L.), Flavour and Fragrance journal, 11, (1996)305-310.
[17] I.Doymaz, Evaluation of some thin-layer drying models of persimmon slices (Diospyros kaki L.), Energy Conversion and Management, 56 (2012) 199–205.
[18] S. K. Pandey, S. Diwan and R Soni, Review of mathematical modeling of thin layer drying process, , online 2394-0697, 2 (11), 2015.
[19] Arun S.Mujumdar and S. Devahastin, Fundamental principles of Drying, Exergex, Brossard,Canada, (2000).
[20] H. Darvishia, A. R. Asl, A.Asghari, M.Azadbakht, ,G. Najafi and J.Khodaei,Study of the drying kinetics of pepper, Journal of the Saudi Society of Agricultural Sciences,13 (2014) 130–138.
[21] D. P. Rosa, D.Cantú-Lozano, G. Luna-Solano,T. C.Polachini and J.T.elis-Romero Mathematical modeling of orange seed drying kinetics,Ciênc. Agrotec.,Lavras, 39 (3), (2015) 291-300.