Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 9 (17): 3116-3120, 2009
ISSN 1812-5654

Determination of Effective Diffusivity of Cocoa Beans using Variable Diffusivity Model

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Abstract: Effective diffusivity is an overall mass transport property of water which includes liquid diffusion, vapour diffusion, hydrodynamic flow and other possible mass transfer mechanisms. These mechanisms control the moisture migration process in material during drying. The objective of this study is to determine the effective diffusivities of cocoa beans using a variable diffusivity model based on Fick's second law of diffusion. Experiments were conducted using forced air at temperatures of 39.3 and 53.3°C. Three empirical models were used namely the linear, quadratic and exponential types. Modeling was carried out using the explicit finite difference method based on drying kinetics. The goodness of fit was compared using the mean relative error (E%) between the experimental and predicted data. Mean relative error was the lowest using the quadratic empirical model (E (%) = 3.01-4.93) as compared to the linear (E (%) = 8.16-11.11) and exponential (E (%) = 3.91-7.47) models. The effective diffusivity values are in the order of 10^{-10} to 10^{-11} which is within the range as those reported in literatures.

Key words: Cocoa, drying, diffusivity, modelling, mass transfer

INTRODUCTION

Various methods have been used in the determination of diffusivities by solving Fick's second law of diffusion (Eq. 1).

$$\frac{\partial X}{\partial t} = \nabla.(D_{eff}\nabla X) \qquad (1)$$

where, X is moisture content (kg water/kg dry matter) and D_{eff} is effective diffusivity ($m^2\ sec^{-1}$).

The effective diffusivity is an overall mass transport property of water in the drying material which includes liquid diffusion, vapour diffusion, hydrodynamic flow and other possible mass transfer mechanisms (Karathanos *et al*., 1990). By using appropriate initial and boundary conditions, together with some reasonable assumptions, the analytical solution can be derived for some standard geometry such as slab, cylinder and sphere (Crank, 1975). Equation 2 shows an example solution derived for spherical object.

$$MR = \frac{6}{\pi^2}\sum_{n=1}^{\infty} .\frac{1}{n^2}.\exp^{-\frac{n^2\pi^2 D_{eff} t}{R^2}} \qquad (2)$$

where, MR is moisture ratio (dimensionless) and R is radius in (m).

Many researchers predicted the effective diffusivity values by taking only the first term of Eq. 2 through regression analysis. However, this method predicts a single value of diffusivity for the entire process, which could result in not representing the kinetics of the entire drying process, because diffusivity should vary with time and moisture content throughout the drying cycle.

Karathanos *et al*. (1990) reported the use of the slopes method to predict the variation of diffusivity with moisture content. This was done by calculating the slope of the drying curve $(dMR/dt)_{exp}$ and the theoretical curve $(dMR/dF_0)_{theo}$ at a given moisture ratio and the effective diffusivity is hence estimated from Eq. 3 and 4.

$$D_{eff} = \left[\frac{(dMR/dt)_{exp}}{(dMR/dF_0)_{theo}}\right]R^2 \qquad (3)$$

$$F_0 = \frac{D_{eff}t}{R^2} \qquad (4)$$

where, F_o is fourier number.

However, the theoretical equation used in this model is similar to Eq. 2, which assumed constant diffusivity in the first place. Nevertheless, the use of this method is reported in some published literatures (Luangmalawat *et al*., 2008; Tuwapanichayanan *et al*., 2008; Chemkhi and Zagrouba, 2005).

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The objective of this study was to determine a variable diffusivity model by using the one-dimensional Fick's second law of diffusion in the drying of cocoa beans.

MATERIALS AND METHODS

Cocoa beans: Fresh cocoa beans were obtained from Jengka, Pahang and fermented using wooden boxes for 5 days. The fermenting mass weighed about 25 kg based on the fresh beans weight using box dimension measuring 30.5×30.5×30.5 cm. The beans were turned every 48 h to ensure uniformity during fermentation. The conditions of the beans were carefully monitored such that the temperature developed in the proper manner (range within 30 to 50°C from the start to the end) and that no mould growth was observed.

Drying: A hybrid heat pump dryer (Fig. 1) was used in all the drying trials. Two product chambers measuring 101×32×33 cm each were connected to the hot and cold air supplied from the heat pump. The cold temperature setting was adjusted by using a temperature controller and the corresponding hot temperature would depend on the amount of heat evolved from the condenser. Drying was conducted at cold temperature setting of 5°C with heater at 60°C (HHPD1) and 10°C without heater (HHPD2). These combinations were able to generate hot air at 53.3 and 39.3°C for HHPD1 and HHPD2, respectively. About 700 g of fermented beans were placed thinly on meshed surface and air flow parallel to the bean layer during drying in each chamber.

Moisture content: The beans used in each experiment were weighed prior to mixing during drying by using an analytical balance. The moisture content of the beans was determined with reference to the bone-dry weight of the beans using Eq. 5.

$$\text{Moisture content} = \frac{(W_i - W_{bd})\times 100}{W_{bd}} \quad (\%\text{ dry basis}) \tag{5}$$

where, the subscripts W_i and W_{bd} refer to the intial and bone-dry weight, respectively. The Equilibrium Moisture Contents (EMC) were determined by prolonging the drying process until no further change in weight was observed for the beans in each treatment.

Method of slopes: The method of slopes was carried out by calculating the slope of the drying curve $(dMR/dt)_{exp}$ and the theoretical curve $(dMR/dF_0)_{theo}$ at a given moisture ratio (Karathanos *et al*., 1990). The slopes of the experimental drying curves were determined using experimental data while the slopes of the theoretical curves were calculated by differentiating the general solution with respect to the Fourier number (F_o). Calculation was carried out using Microsoft Excel (MS Office, version 2003, USA). Equation 3 and 4 are referred.

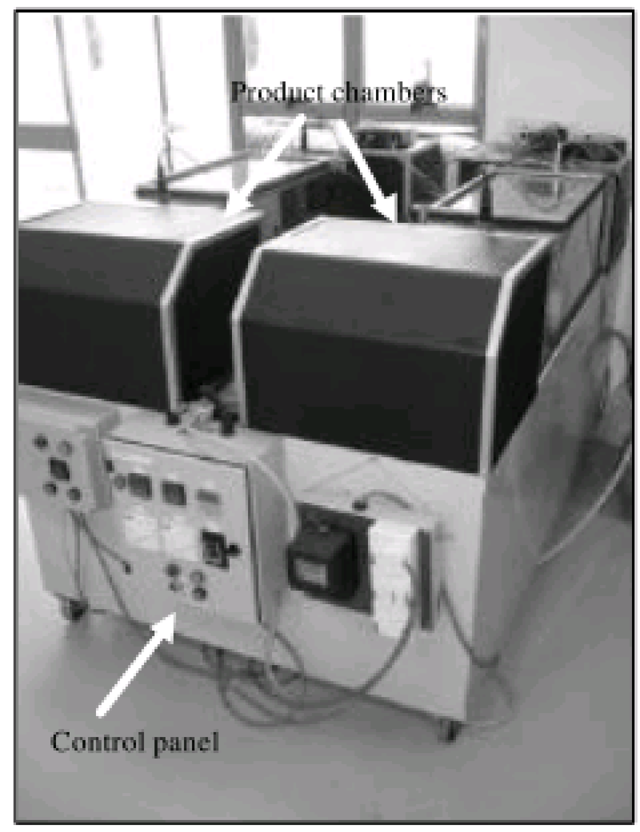

Fig. 1: The hybrid heat pump dryer

Constant diffusivity model: The one dimensional Fick's second law diffusional model for spherical geometry was discretized according to the radius (i) and time (t) intervals. The model was solved using explicit finite difference method with 0.01 h time step and grid with 20 constant subdivisions on the radius.

$$\frac{\partial X}{\partial t} = D_{eff}\left[\frac{\partial^2 X}{\partial r^2} + \frac{2}{r}\frac{\partial X}{\partial r}\right] \tag{6}$$

Boundary conditions:

At t = 0, $X(r,t) = X_o$ (7)

At t>0, r = R $X(R,t) = X_e$ (8)

At t>0, r = 0 $\frac{\partial X(0,t)}{\partial r} = 0$ (9)

The effective diffusivity was determined through a curve optimization process to the experimental data by minimizing the Sum Squared of the Residuals (SSR) using the SOLVER tool in Microsoft Excel spreadsheet (MS Office, version 2003, USA).

Variable diffusivity model: The one dimensional Fick's second law diffusional model taking into account the variation of moisture diffusivity with local moisture content (X) was used. The model was discretized and solved using explicit finite difference method with 0.01 h time step and grid with 20 constant subdivisions on the radius. Similar boundary conditions were used Eq. 7-9.

$$\frac{\partial X}{\partial t} = D_{eff}\frac{\partial^2 X}{\partial r^2} + \frac{\partial D_{eff}}{\partial r}.\frac{\partial X}{\partial r} + \frac{2D_{eff}}{r}.\frac{\partial X}{\partial r} \quad (10)$$

The following empirical equations were defined for the variable diffusivity model.

Linear $D_{eff} = a+bX$ (11)

Quadratic $D_{eff} = a+bX+CX^2$ (12)

Exponential $D_{eff} = a\ \exp^{bX}$ (13)

Coefficients a and b were generated through a curve optimization process to the experimental data by minimizing the Sum Squared of the Residuals (SSR) using the SOLVER tool in Microsoft Excel spreadsheet (MS Office, version 2003, USA).

Fitting criteria: The mean relative error (E) between the experimental and predicted data was obtained to select the best-fit solution. Percentage of E-value of less than 5 indicates an excellent fit.

$$E(\%) = \frac{100}{n}\sum_{i=1}^{n}\frac{|\text{Experimental value} - \text{Predicted value}|}{\text{Experimental value}} \quad (14)$$

The coefficient of determination (R^2) was also determined to compare the goodness of fit.

RESULTS AND DISCUSSION

Comparison between the predicted and experimental data can be shown from Fig. 2a and b. Table 1 shows the results of the coefficient of determination and E (%) values obtained from the modeling. Results showed that the constant diffusivity model obtained the lowest R^2 and the highest E (%) values which indicate poor fitting. This shows that the model with constant diffusivity assumption is not adequate in describing the mass transfer process inside the cocoa beans. Good fitting was observed in the entire variable diffusivity model with E (%) values ranging from 3.0 to 11.1 and 4.9 to 8.2 in HHPD1 and HHPD2, respectively. The corresponding coefficient of determination was found ranging from 0.9947 to 0.9995 and 0.9935 to 0.9987, respectively. Excellent fitting was observed when using the quadratic model with E (%) values of less than 5.

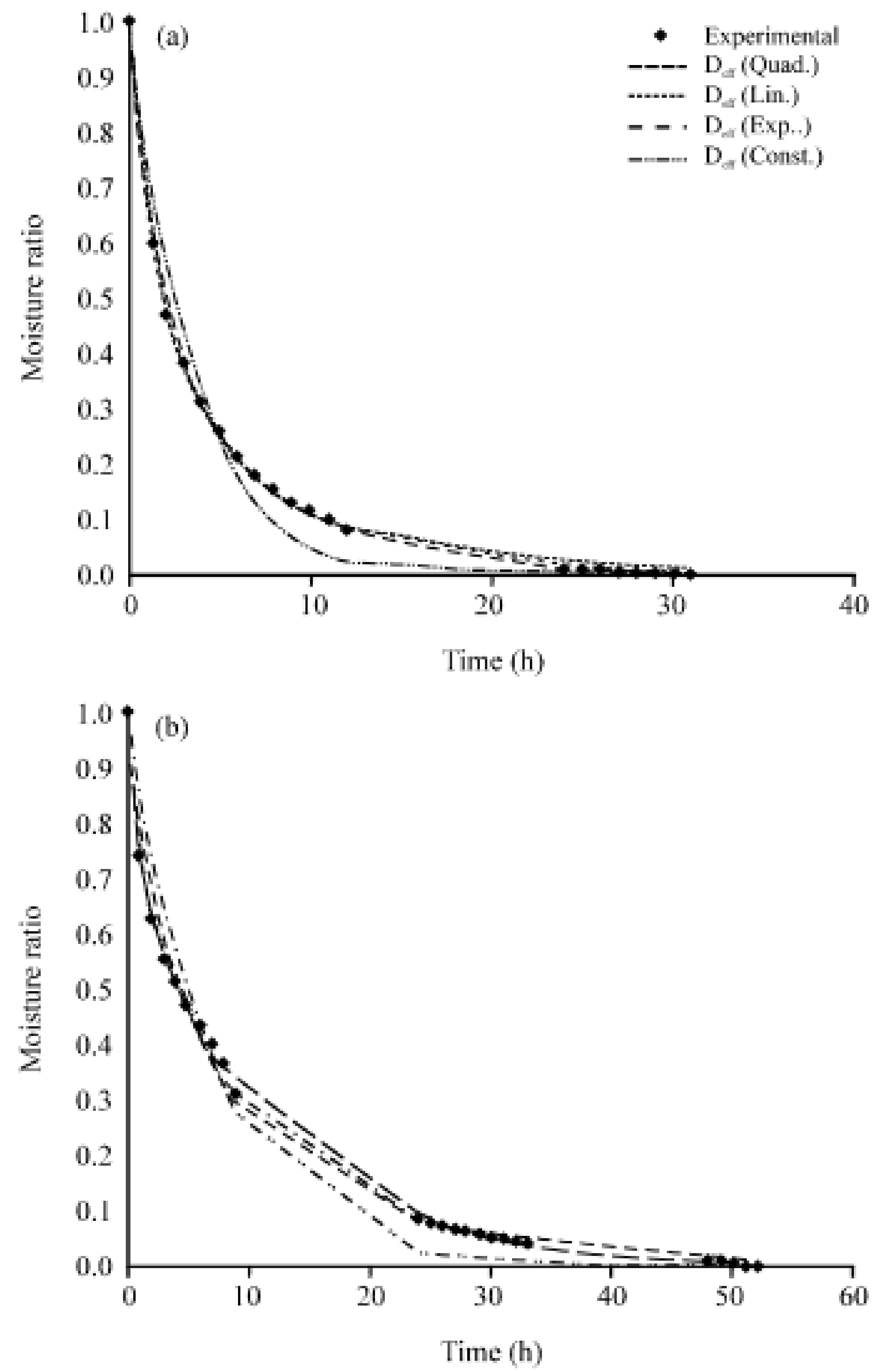

Fig. 2: Comparison between the experimental and the predicted data, (a) HHPD1 (53.3°C) and (b) HHPD2 (39.3°C)

Table 1: Comparison of R^2 and E-values (%)

Drying treatment	D_{eff} (quad.)	D_{eff} (linear)	D_{eff} (exp.)	D_{eff} (const.)
HHPD1 (53.3°C)				
R^2	0.9996	0.9947	0.9995	0.9698
E (%)	3.0100	11.1100	3.9100	18.9800
HHPD2 (39.3°C)				
R^2	0.9987	0.9935	0.9966	0.9863
E (%)	4.9300	8.1600	7.4700	22.4800

The variation of the effective diffusivity with moisture content for HHPD1 and HHPD2 are as shown in Fig. 3a and b. The effective diffusivity values are in the order of 10^{-10} to 10^{-11} which is within the range as those reported in studies (Zogzas *et al*., 1996).

It can be seen that the exponential model tend to predict a higher effective diffusivity as compared to the other models most of the time. Meanwhile, the quadratic model and slopes method predicted a sudden increase in effective diffusivity towards the final stage of drying. Comparison between the various models and the slopes method showed big difference between the predicted diffusivity values. It must be noted that the basis of the

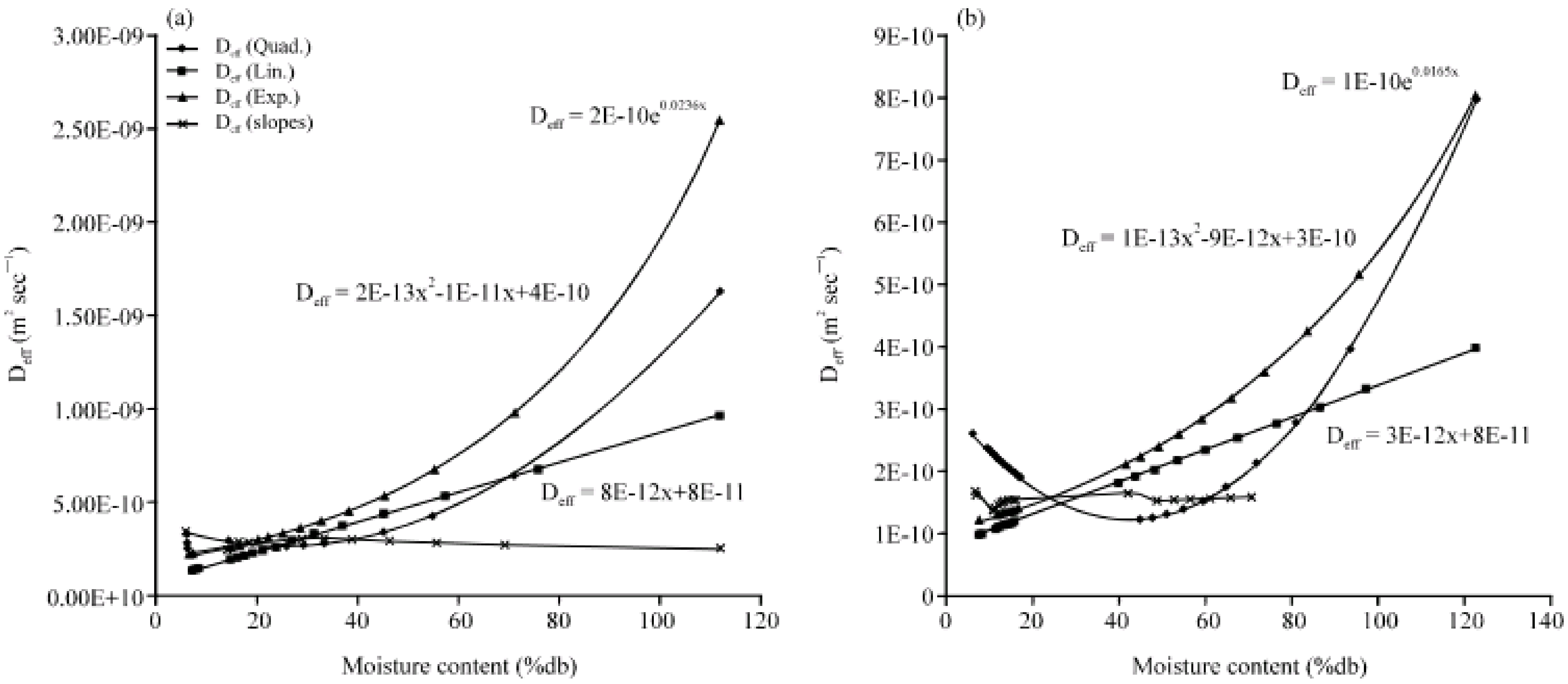

Fig. 3: Predicted variable diffusivity models, (a) HHPD1 (53.3°C) and (b) HHPD2 (39.3°C)

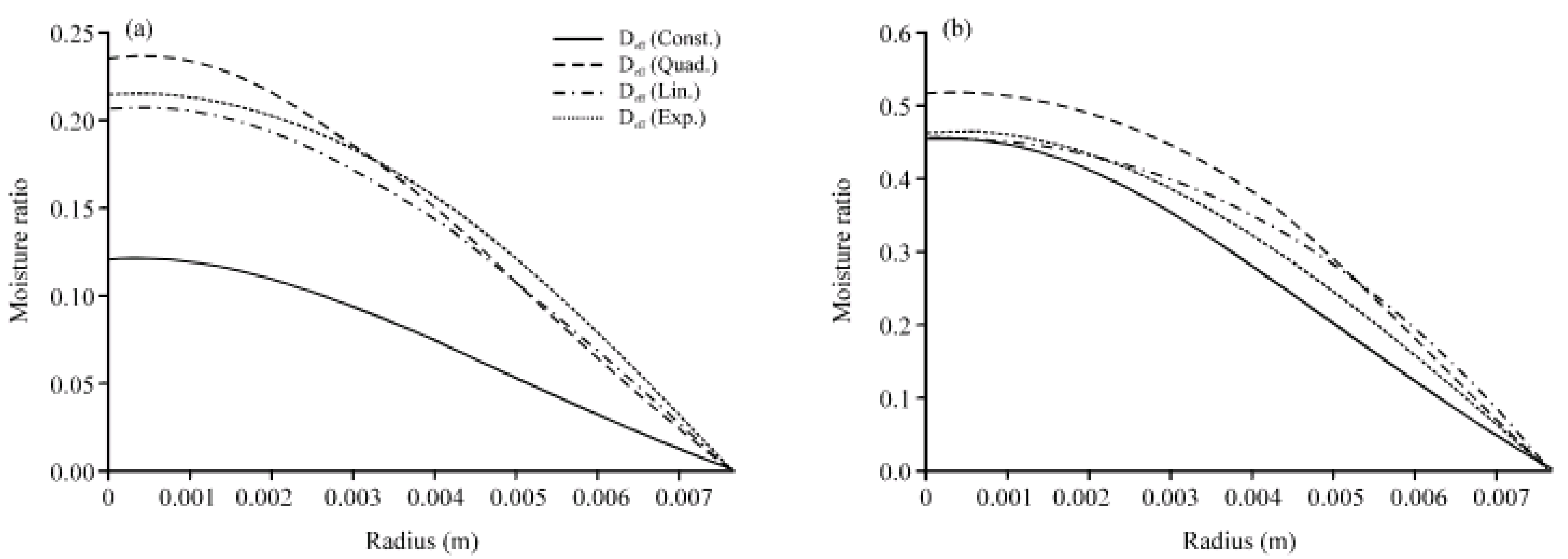

Fig. 4: Predicted moisture ratio at t = 9 h along bean radius during drying, (a) HHPD1 (53.3°C) and (b) HHPD2 (39.3°C)

slopes method is based on the constant diffusivity model of the Fick's law general solution. The current applied models could be more realistic and reasonable as compared to the slopes methods as it was predicted using the partial differential equation of the Fick's diffusional model taking into account the variation of diffusivity with local moisture content.

The drop of effective diffusivity with moisture content is apparent as cocoa bean consists of two main layers namely the external testa and the internal cotyledon. The testa will dry faster as compared to the inner part and this increases the resistance to moisture diffusion as moisture content reduces. Furthermore, the testa is covered by a thin film of slimy mucilage resulted from the fermentation process and this will add an additional layer of resistance to moisture diffusion as drying progresses. However, the quadratic model predicted a slight increase in effective diffusivity towards the later stage of drying. Such prediction may not reflect the actual mechanism, since it was purely a curve fitting analyses. Nevertheless, this could imply that some structural changes have occurred inside the beans during drying. This was observed in the drying of fresh blueberries where big changes in intercellular space created more opened structure and contribute to the higher increase of effective diffusivity (Shi *et al*., 2008). Similar observation can be observed in cocoa beans as the cotyledon starts to form crevices as moisture content is reduced.

The variation of moisture ratios inside the cocoa beans during drying are as shown in Fig. 4 and 5. It can be seen that the constant diffusivity assumption predicted a much lower profiles as compared to those predicted by the variable diffusivity models after 9 and 24 h of drying.

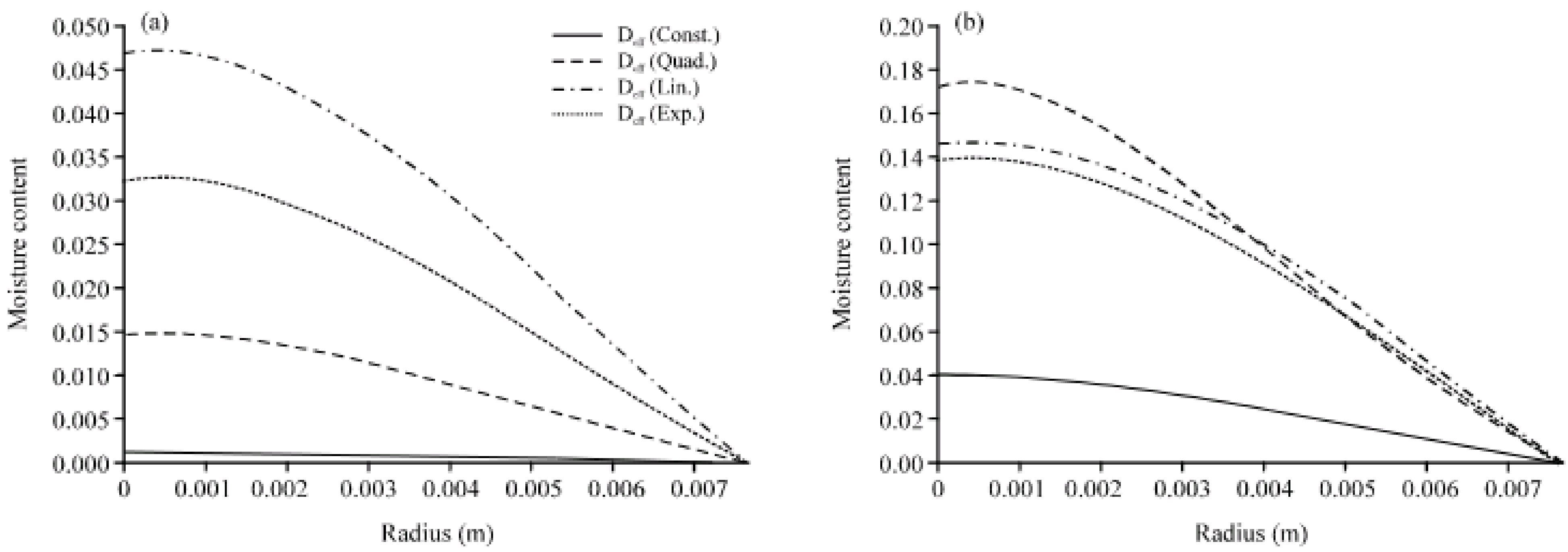

Fig. 5: Predicted moisture ratio at t = 24 h along bean radius during drying, (a) HHPD1 (53.3°C) and (b) HHPD2 (39.3°C)

In the first 9 h of drying, the quadratic model predicted higher moisture ratios in the middle section of the beans in both treatments (Fig. 4a, b). The quadratic model predicted about 99 and 24% higher in HHPD1 and HHPD2, respectively, compared to the constant diffusivity model based on average moisture ratio at this specific hour of drying. The drop in moisture ratio is slower from the center and gradually increases towards the surface of the beans.

Towards the end of drying, after 24 h in HHPD1 (Fig. 5a), the linear model shows higher moisture ratios profile followed by the exponential and the quadratic models. The linear model predicted a much higher average moisture profile at about 42% higher than the constant diffusivity model. In HHPD2 (Fig. 5b), the quadratic model predicted the highest average moisture ratio (4% higher) as compared to the constant diffusivity model. Modelling showed that there is no specific trend among the models either in over or under predicting the moisture ratios throughout the drying process and it solely depends on the variation of effective diffusivity at the specific drying time.

CONCLUSION

Modelling showed good fitting in the entire variable diffusivity model between the experimental and predicted data. The quadratic model showed excellent fitting with E (%) values of less than 5. The effective diffusivity values are in the order of 10^{-10} to 10^{-11} which is within the range reported in literatures. The quadratic model predicted possible structural changes within the beans which could be due to the formation of crevices within the cotyledon as moisture content is reduced. Modelling showed that the prediction of the moisture contents throughout the drying process solely depends on the variation of effective diffusivity at the specific drying time.

ACKNOWLEDGMENTS

The study was made possible through the Research Assistantship Grant from the School of Chemical and Environmental Engineering, University of Nottingham, Malaysia Campus and also the support given by the Ministry of Science, Technology and Innovation through the e-Science research Grant (05-02-12-SF0014).

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