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Modeling using a new thin layer drying model and product quality of cocoa

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ABSTRACT

A new semi-theoretical thin layer model for modeling the air drying of cocoa beans with overnight tempering at ambient temperature was developed. The new model was a combination of the Page and two-term drying model. Results showed that the new model was found best described the drying process under the conditions tested (60, 70 and 80 °C). Effective diffusivities were found between 7.46×10^{-11} and 1.87×10^{-10} m^2/s. The Arrhenius constant and activation energy were estimated at 8.43×10^{-4} m^2/s and 44.92 KJ/mol, respectively. Analyses of pH and cut test for bean quality showed that beans dried at 60 °C had lower acidity and good flavour quality as compared to other drying treatments.

1. Introduction

Cocoa beans are the seeds of a tropical tree botanically known as *Theobroma cacao* (Family Sterculiaceae). It is grown mostly in the wet tropical forest climate which is within 20° of latitude of the equator at countries such as Cote d'Ivoire, Ghana, Nigeria, Cameroon, Brazil, Equador, Papua New Guinea, Indonesia and Malaysia (Beckett, 1994). Upon harvesting of ripe cocoa pods, fresh cocoa beans are fermented for 5–7 days and dried immediately after fermentation to safe moisture level of 7.5% (w.b.). During these stages the cocoa beans undergo various chemical and biochemical changes that form the necessary flavour precursors needed during processing. Drying is usually carried out using natural sun drying and artificial hot air techniques. Cocoa smallholders produce in small quantity would prefer sun drying while for the bigger plantation the hot air (artificial) method is preferred.

Mathematical modeling using thin layer drying models has been studied in drying of fruits, vegetables, seafood and other agriculture or crop products (Akpinar et al., 2003; Jain and Pathare, 2007; Jayas et al., 1991; Karathanos and Belessiotis, 1999; Midilli et al., 2002; Thuwapanichayanan et al., 2008; Yaldiz et al., 2001). The models fall into three categories namely the theoretical, semi-theoretical and empirical. Semi-theoretical models offer a compromise between theory and ease of application (Akpinar, 2006a). Examples of semi-theoretical models are such as the Newton model (O'Callaghan et al., 1971), Page model (Akpinar et al., 2003), Henderson and Pabis model (Karathanos and Belessiotis, 1999), logarithmic model (Yaldiz et al., 2001), two-term model (Togrul and Pehlivan, 2004), two term exponential model (Akpinar et al., 2003), Verma et al. model (Verma et al., 1985) and the Midilli–Kucuk model (Midilli et al., 2002) are used widely. In empirical modeling a direct relationship between the moisture content and drying time is derived. The fundamentals of the drying process are neglected and the Wang and Singh model (Wang and Singh, 1978) is an example of empirical model used in literatures.

Studies of the modeling of cocoa drying are relatively scarce and only few published literatures are available (Wan Daud et al.,1996, 2007; Nganhou et al., 1992; Bravo and Mc Gaw, 1974). No work has been done to model the drying process with the inclusion of the tempering period that resembles the actual commercial practice. Most of the cocoa drying literatures are focused mostly in flavour development, quality and bean acidity (Hii et al., 2006; Bart-Plange and Baryeh, 2003; Bonaparte et al., 1998; Jinap et al., 1994; Meyer et al., 1989; Biehl et al., 1989). Based on these reasons, the present study was conducted to model the artificial drying process of cocoa beans with the inclusion of tempering using a new semi-theoretical model. Product quality attributes were investigated for appearance, pH and cut test as these are the basic parameters used by chocolate manufacturer to assess incoming bean quality. These quality attributes contribute significantly towards the quality of the finished products.

2. Materials and methods

2.1. Sample preparation

Fresh cocoa beans were obtained from Jengka, Pahang and fermented using wooden boxes for five days. The fermenting mass weighed about 25 kg based on the fresh beans weight using box

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Nomenclature

a, b, c	coefficients in thin layer models	m_i	moisture content at time i (% wet basis)
k, g, n	constants in models	R^2	coefficient of determination
D_{eff}	effective diffusivity (m^2/s)	R_g	gas constant in Eq. (10) (8.314 J/mol K)
D_o	Arrhenius constant (m^2/s)	RMSE	root mean square error
dm/dt	drying rate (g H_2O/g wet solid h)	R	radius (m)
E_a	activation energy (KJ/mol)	r_o	radius of object (m)
K	Kelvin (K)	t	time (h)
MR	moisture ratio (dimensionless)	TP1	first tempering period
MR_{exp}	experimental moisture ratio (dimensionless)	TP2	second tempering period
MR_{pre}	predicted moisture ratio (dimensionless)	T	temperature (°C)
M	moisture content (% wet basis)	W_i	weight at $t = t_i$ (g)
m_o	initial moisture content (% wet basis)	W_{bd}	bone-dry weight (g)
m_e	equilibrium moisture content (% wet basis)	χ^2	chi-square

dimension measuring 30.5 cm × 30.5 cm × 30.5 cm as used by Hii and Tukimon, (2002). The beans were turned every 48 h to ensure uniformity during fermentation.

2.2. Drying procedure

The fermented beans (about 700 g) were dried using an air-ventilated oven (Memmert, DO6836, Germany) at temperature of 60, 70 and 80 °C with natural convective airflow of 0.01 m/s (Fig. 1). The relative humidity was 6%, 4.7% and 2.9% at these temperatures, respectively. The beans were spread thinly in single layer (about 1.05 cm thick) on a meshed sample tray with square openings measuring 0.4 × 0.4 cm. Heat was generated by the heater integrated into the walls of the oven and the distributor fan was not switched on in order to simulate the natural convective environment of the commercial cocoa dryer. The exhaust air escaped through a ventilation hole (diameter = 4 cm) at the back of the oven. Drying was conducted for 8 h daily and the beans were let tempered at room temperature overnight. The purpose of this step is for the moisture within the beans to redistribute from the internal to the outer layer of the beans (testa) because the testa will generally dry faster than the cotyledon layer in hot air drying. Drying was terminated when the moisture content of the beans reached 7.5% wet basis. The experiment at each drying temperature was conducted in three replicates.

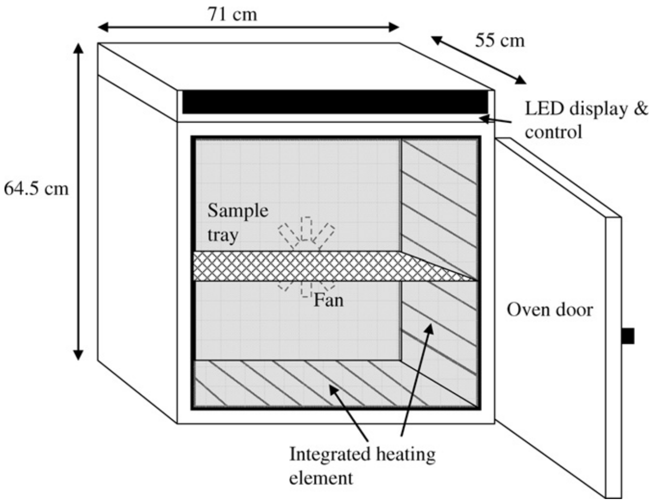

Fig. 1. Schematic of the oven drying equipment.

2.3. Moisture content

The beans used in each experiment were weighed every two hours during drying by using an analytical balance (AND Instrument, MX50, USA). The moisture content of the beans was determined with reference to the bone-dry weight of the beans using the formula below as according to AOAC (2000)

$$\text{Moisture content} = \frac{(W_i - W_{bd}) \times 100}{W_i} (\%\ \text{wetbasis}), \tag{1}$$

where the subscripts i and bd refer to the initial 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. The EMC values determined were 6.3%, 5.74% and 3.6% for the oven drying at 60, 70 and 80 °C, respectively.

2.4. pH

Ground nibs (5 g) were homogenised in 45 ml boiled distilled water. The mixture was filtered with Whatman No. 4 filter paper and cooled to 20–25 °C. The resulting filtrate was measured for pH using a pH meter (Schott Instruments, D-55122, Germany) which had been calibrated with buffers at pH 4 and 7. This measurement was performed in triplicates.

2.5. Cut test

Cut test was carried out according to the Malaysian Standard MS 293 (Anon, 1995). Hundred pieces of dried cocoa beans were cut lengthwise through the middle using a penknife. Both halves of each bean were examined in full daylight according to the cross sectional colour of the beans namely fully brown, partly purple–brown, fully purple and slaty according to a set of reference pictures by Malaysian Cocoa Board. As according to the standard, beans with more than 60% fully brown colour is considered as good flavour beans. The test was performed in triplicates.

2.6. Drying rates

The drying rates were calculated based on the following formula as used by Guine and Fernandes (2006) in their drying studies.

At $t = t_0$,

$$\frac{dm}{dt} = \frac{m_1 - m_0}{t_1 - t_0} \quad \text{First order forward finite difference.} \tag{2}$$

At $t = t_i$ ($i = 1, \ldots, N - 1$),

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{m_{i+1} - m_{i-1}}{t_{i+1} - t_{i-1}} \quad \text{Second order centered finite difference.} \tag{3}$$

At $t = t_N$,

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{m_N - m_{N-1}}{t_N - t_{N-1}} \quad \text{First order backward finite difference.} \tag{4}$$

2.7. Mathematical modeling

A total of nine thin layer models were used for modeling including a newly developed model (Table 1). This new model was developed based on the Page and the two term models. It was encountered by previous experience that these two models when used individually often produced reasonable fitting for drying data with inclusion of tempering.

The moisture ratio (MR) is defined as $(m_\mathrm{i} - m_\mathrm{e})/(m_\mathrm{o} - m_\mathrm{e})$ where the subscripts i, e and o denote at time t_i, equilibrium and initial, respectively. Statistical parameters such as the chi-square (Eq. (5)), root mean square error (Eq. (6)) and coefficient of determination (R^2) were used to assess the goodness of fitting

$$\text{Chi-square}: \ \chi^2 = \frac{\sum_{i=1}^{N}(\mathrm{MR}_{\mathrm{exp},i} - \mathrm{MR}_{\mathrm{pre},i})^2}{N - z}, \tag{5}$$

$$\text{Root mean square error}: \ \mathrm{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}(MR_{\mathrm{pre},i} - MR_{\mathrm{exp},i})^2\right]^{1/2}. \tag{6}$$

Modeling was carried out using the least square method and the Microsoft Excel spreadsheet (Microsoft Office 2003, USA) was used to perform this task using the SOLVER tool based on the Generalized Reduced Gradient (GRG) method of iteration.

2.8. Effective diffusivity

The cocoa beans are assumed in the form of spherical and the Fick's second law of diffusion for spherical object is defined as follow:

$$\frac{\partial m}{\partial t} = D_\mathrm{eff}\left[\frac{\partial^2 m}{\partial r^2} + \frac{2}{r}\frac{\partial m}{\partial r}\right], \tag{7}$$

where m can be defined as the moisture content (dry or wet basis), moisture ratio, weight ratio and density. By using appropriate initial and boundary conditions, Crank (1975) gave the analytical solutions for various geometries and the solution for spherical object with constant diffusivity is given as

$$\mathrm{MR} = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\cdot \exp^{-\frac{D_\mathrm{eff} n^2 \pi^2 t}{r_o^2}}. \tag{8}$$

The effective diffusivity was estimated by using ten terms of the analytical solution (Eq. (9)) of the Fick's equation by using non-linear regression analyses. The Microsoft Excel SOLVER tool was used for this purpose

$$\mathrm{MR} = \frac{6}{\pi^2}\exp^{-\frac{D_\mathrm{eff}\pi^2 t}{r_o^2}} + \frac{6}{4\pi^2}\exp^{-\frac{D_\mathrm{eff} 4\pi^2 t}{r_o^2}} + \cdots + \frac{6}{100\pi^2}\exp^{-\frac{D_\mathrm{eff} 100\pi^2 t}{r_o^2}}. \tag{9}$$

2.9. Experimental design and analyses

The experiments were conducted as a completely randomized single factor experiment. All the experimental treatments were conducted in three replicates. The experimental data were analysed by using one-way ANOVA and mean comparison using Duncan's Multiple Range Test at 95% confidence level. The statistical software used was SAS for Window (Version 9.1, SAS Institute, USA).

3. Results and discussion

3.1. Drying kinetics and modeling

The drying kinetics of the cocoa beans dried artificially inside the oven are as shown in Figs. 2 and 3. The initial moisture content before drying was about 52% ± 0.928 w.b. (mean ± std. deviation). As expected, the drying temperature had a significant effect on the drying kinetics of the samples. The moisture content decreased continuously with time and an increase in temperature resulted in reduced drying time. The longest and shortest drying time were recorded at 52 h (60 °C) and 30 h (80 °C), respectively. Two separate tempering periods (TP1 and TP2) were present in the 60 °C treatment while only one was present (TP1) in the 70 and 80 °C treatments. The drying rate curves showed falling trend beyond moisture content of 45%, 42% and 52.7% at drying temperatures of 60, 70 and 80 °C, respectively. A short initial warming up period was observed in the early stage of the 60 and 70 °C treatments but the length of this period was unable to be determined due to the short time interval used (2 h). Bravo and Mc Gaw (1974) have reported occurrence of this period in cocoa drying at the initial 0.3 h of the drying process and followed by a constant rate period thereafter that last for not more than 2 h (drying temperatures range 55–86 °C). This is quite similar to those observed in the 60 and 70 °C treatments.

The 80 °C treatment showed the highest drying rates curve as compared to the other two treatments (Fig. 3). The highest drying rate achieved in 80 °C was 0.0797 (g water/g wet solid h) while at 70 °C and 60 °C were 0.047 (g water/g wet solid h) and 0.0389 (g water/g wet solid h), respectively. It can be seen that at higher moisture content the increase in temperature has more considerable effect on the drying rates as compared to lower temperature

Table 1
Thin layer drying models tested for modeling

Model no.	Model name	Model equation	References
I	Newton	$MR = \exp^{(-kt)}$	Ayensu (1997)
II	Henderson and Pabis	$MR = a\exp^{(-kt)}$	Akpinar et al. (2003)
III	Page	$MR = \exp^{(-kt^n)}$	Karathanos and Belessiotis (1999)
IV	Logarithmic	$MR = a\exp^{(-kt)} + c$	Yaldiz et al. (2001)
V	Two term model	$MR = a\exp^{(-kt)} + c\exp^{(-gt)}$	Togrul and Pehlivan (2004)
VI	Two-term exponential	$MR = a\exp^{(-kt)} + (1 - a)\exp^{(-kat)}$	Akpinar et al. (2003)
VII	Verma et al.	$MR = a\exp^{(-kt)} + (1 - a)\exp^{(-gt)}$	Verma et al. (1985)
VIII	Midilli–Kucuk	$MR = a\exp^{(-kt^n)} + bt$	Midilli et al. (2002)
IX	New model	$MR = a\exp^{(-kt^n)} + c\exp^{(-gt^n)}$	This paper

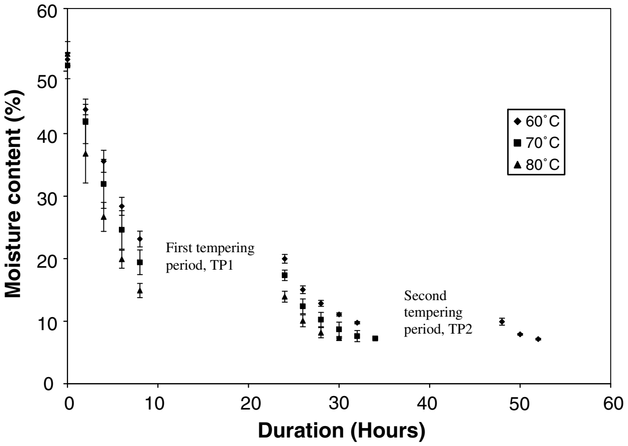

Fig. 2. Experimental moisture contents of the cocoa beans during drying.

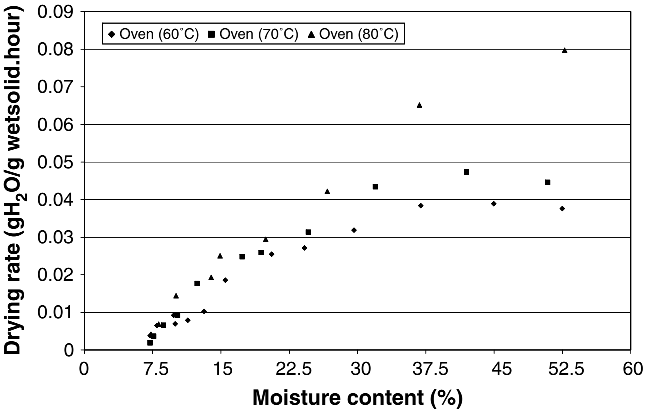

Fig. 3. Drying rates versus the experimental moisture contents of cocoa beans.

Table 2
Effect of tempering on reduction in moisture content

Treatment (°C)	Moisture content before TP1 (%)	Moisture content after TP1 (%)	Total reduction in moisture content (%)	
			TP1	TP2
Oven 60	24.18	20.57	3.61	0.15
Oven 70	19.42	17.34	2.08	–
Oven 80	14.90	13.92	0.98	–

which is almost negligible towards the end of drying. The availability of free water at this stage is getting lesser. In general, too high drying rate was not recommended for cocoa drying as this will retain most of the acids inside the beans and cause excessive acidity in the finished chocolate products (Mc Donald et al., 1981; Jinap et al., 1994). Excessive bean acidity will cause improper flavour development during roasting and the sour note cannot be removed even in the subsequent chocolate conching process.

By having a closer look at the effect of overnight tempering at ambient during the first tempering period (TP1) moisture reduction was greatest in the 60 °C as compared to those at 70 °C and 80 °C (Table 2). The reduction in moisture content during TP2 was about 0.15% and not as significant as compared to TP1 in the 60 °C treatment. The drop in moisture content was due to two factors namely the residual heat inside the beans still sufficient to evaporate small amount of moisture and also due to the driving force (moisture gradient) exist between the inner core and the drier outer surface. Table 2 shows that the higher the moisture content before TP1 (e.g. 24.18% at temperature 60 °C), the greater is the moisture content reduction and vice versa. Thakur and Gupta (2006) reported similar observation in paddy grain drying with intervening rest period where moisture diffusivity was higher when the grain was rested at higher moisture content as compared to those at lower moisture content. The diffusivity at this stage is a function of both residual grain temperature and moisture content. The higher moisture diffusivity at this stage results in greater moisture reduction during the tempering period.

The best model describing the thin layer drying characteristic was chosen as the one with the highest R^2 values, the lowest χ^2 and RMSE values. In all cases, the R^2, χ^2 and RMSE values range from 0.9462 to 0.9887, 0.0017 to 0.0178 and 0.0309 to 0.1153, respectively. The new model was able to present the highest R^2 values (0.9837–0.9887), the lowest χ^2 (0.0022–0.0057, except in the 80 °C treatment) and the lowest RMSE (0.0309–0.0591) values in all three drying temperature treatments as compared to other thin layer models (Tables 3–5). Based on these figures, the new model (Model IX) was found to be the best fitted model to describe the drying curves in all the temperatures tested.

Fig. 4 shows the comparison of the predicted and experimental values. The new model was able to describe the drying process quite closely especially for the first eight hours of drying. Deviation between the experimental and predicted data occurred thereafter in the second (60–80 °C) and third period (60 °C) of drying. However, the new model was able to produce smaller deviation as compared to the other models tested (Models I–VIII) in these periods. The deviation is due to the inclusion of the tempering period which creates a discontinuity in the drying curve due to the absence of heating. Nevertheless, the application of semi-theoretical models to describe the kinetics of combined drying-tempering process has been reported by researchers previously (Togrul and Pehlivan, 2004; Doymaz, 2005a; Cihan et al., 2007; Akpinar and Bicer, 2008). The Page equation was found in several literatures to be able to fit drying curves of various food products (Jayas et al., 1991) while the two-term model is basically derived from the first two terms of the analytical solution of the diffusion equation. By combining the advantages of these two factors the new model was found able to outperform other models tested.

3.2. Effective diffusivities

The estimated effective diffusivities are as shown in Table 6. The values range from 7.46×10^{-11} to 1.87×10^{-10} m^2/s and fall within the range of values reported in many drying literatures. The effective diffusivities increased with temperature as expected.

The relationship between the effective diffusivities and temperature is assumed in the Arrhenius form of the type:

$$D_{\mathrm{eff}} = D_{\mathrm{o}} \exp\left[-\frac{E_{\mathrm{a}}}{R_{\mathrm{g}}(T + 273.15)}\right]. \tag{10}$$

This equation can be linearized by applying natural log at both sides and a plot of $\ln D_{\mathrm{e}}$ versus $1/T$ will produce a straightline. A plot from the present work is as shown in Fig. 5 and confirmed the proposed relationship between the effective diffusivities and temperatures ($R^2 = 0.997$). The activation energy and the Arrhenius constant can be determined from the slope and the y-intercept, respectively. The Arrhenius constant is a diffusivity constant equivalent to the diffusivity at infinitely high temperature. The activation energy is the energy barrier that must be overcome in order

Table 3
Results of the fitting statistics of various thin layer models at 60 °C drying temperature

Model no.	Model name	Coefficients and constants	R^2	χ^2	RMSE
I	Newton	$k = 0.082386$	0.9555	0.0178	0.1280
II	Henderson and Pabis	$a = 0.917682$, $k = 0.071243$	0.9462	0.0157	0.1153
III	Page	$k = 0.158067$, $n = 0.745418$	0.9710	0.0091	0.0875
IV	Logarithmic	$a = 0.900112$, $k = 0.10995$, $c = 0.084583$	0.9584	0.0091	0.0839
V	Two term model	$a = 0.555364$, $k = 0.045333$, $c = 0.468222$, $g = 0.248672$	0.9771	0.0083	0.0760
VI	Two-term exponential	$a = 0.23213$, $k = 0.270112$	0.9775	0.0106	0.0948
VII	Verma et al.	$a = 0.443208$, $k = 0.237069$, $g = 0.045492$	0.9679	0.0078	0.0775
VIII	Midili–Kucuk	$a = 1.018874$, $k = 0.173383$, $n = 0.707331$, $b = -0.00036$	0.9652	0.0107	0.0859
IX	New model	$a = 0.555446$, $k = 0.072361$, $n = 1.817112$, $c = 0.433171$, $g = 0.002186$	**0.9857**	**0.0057**	**0.0591**

Table 4
Results of the fitting statistics of various thin layer models at 70 °C drying temperature

Model no.	Model name	Coefficients and constants	R^2	χ^2	RMSE
I	Newton	$k = 0.12145$	0.9562	0.0069	0.0794
II	Henderson and Pabis	$a = 0.953477$, $k = 0.109947$	0.9494	0.0075	0.0781
III	Page	$k = 0.213312$, $n = 0.700557$	0.9619	0.0042	0.0584
IV	Logarithmic	$a = 0.895623$, $k = 0.178257$, $c = 0.128645$	0.9658	0.0030	0.0469
V	Two term model	$a = 0.251672$, $k = 0.023791$, $c = 0.775421$, $g = 0.209632$	0.9704	0.0033	0.0460
VI	Two-term exponential	$a = 0.278931$, $k = 0.297019$	0.9709	0.0050	0.0641
VII	Verma et al.	$a = 0.758529$, $k = 0.19855$, $g = 0.022611$	0.9615	0.0030	0.0469
VIII	Midili–Kucuk	$a = 1.009444$, $k = 0.12383$, $n = 1.121868$, $b = 0.004706$	0.9548	0.0037	0.0486
IX	New model	$a = 0.639781$, $k = 0.086176$, $n = 1.788652$, $c = 0.350367$, $g = 0.002534$	**0.9837**	**0.0022**	**0.0349**

Table 5
Results of the fitting statistics of various thin layer models at 80 °C drying temperature

Model no.	Model name	Coefficients and constants	R^2	χ^2	RMSE
I	Newton	$k = 0.177839$	0.9673	0.0084	0.0857
II	Henderson and Pabis	$a = 0.971189$, $k = 0.169838$	0.9618	0.0094	0.0857
III	Page	$k = 0.344168$, $n = 0.575384$	0.9654	0.0037	0.0539
IV	Logarithmic	$a = 0.881435$, $k = 0.239859$, $c = 0.123062$	0.9855	0.0018	0.0351
V	Two term model	$a = 0.201999$, $k = 0.01865$, $c = 0.806089$, $g = 0.273835$	0.9864	0.0021	0.0339
VI	Two-term exponential	$a = 0.308366$, $k = 0.384677$	0.9864	0.0074	0.0757
VII	Verma et al.	$a = 0.801588$, $k = 0.269514$, $g = 0.018033$	0.9636	0.0017	0.0341
VIII	Midili–Kucuk	$a = 1.002818$, $k = 0.218615$, $n = 0.938837$, $b = 0.004185$	0.9819	0.0027	0.0392
X	New model	$a = 0.729654$, $k = 0.220349$, $n = 1.270623$, $c = 0.267136$, $g = 0.011612$	**0.9887**	0.0022	**0.0309**

to activate moisture diffusion. By increasing the temperature and hence the drying rate this energy barrier can be overcome easier relatively but there should be a compromise between high temperature and acceptable product quality (Kashaninejad et al., 2007). Too high temperature is also not recommended for cocoa drying as the resulting product is often associated with high acidity (Jinap et al., 1994).

The values of D_o and E_a were estimated at 8.43×10^{-4} m^2/s and 44.92 KJ/mol, respectively. These values are actually within the range as reported in literatures for other agriculture materials (Table 7).

3.3. Product quality

All the dried beans produced were noted to have medium dark brown colour of typical commercial grade A cocoa beans and free from surface mould. Surface moulding is usually associated with very high humidity and low air movement during drying. The typical sour odour was detected which is due to the acetic acids contained within the beans. Acetic acid is mainly produced through oxidation of ethanol in the presence of oxygen by acetic acid bacteria. During drying, this acid is evaporated off along with the moisture removal process due to its volatile nature. However, the lactic acids contained inside cannot be evaporated off since it is not a volatile compound. None of the beans produced unpleasant putrid odour since all the beans were fermented and dried in a proper manner. All the beans were able to dry in not more than 2 or 3 days in all the treatments. Beans dried under unfavourable condition (e.g. prolong drying due to low temperature and humid air) will appear to be dark and mouldy and stained with putrid odour. The dark appearance was due to the presence of phlobaphenes, tanning-containing macromolecules and quinone-amino acid adducts and the putrid odour was mainly due to the production of ammonia nitrogen through amino acid oxidase enzyme (Jinap et al., 1994).

Table 8 shows the pH of the dried cocoa beans from each treatment. Comparison was also made against the sun dried beans obtained from other experiments. The oven dried beans pH ranged from 5.16 to 5.26 while for the fermented beans the registered pH was 4.97. Generally, these pH values falls within the values reported for most dried cocoa beans. High acidic beans are always associated with pH of less than 5.2 while the best flavoured beans from West Africa usually have pH values around 5.5 (Jinap et al., 1994).

Statistical analyses showed that the pH of the sun dried beans was significantly different ($p < 0.05$) from the oven dried and the fermented samples. The pH value for sun dried beans is usually higher (less acidic) than artificially dried beans due to the slow and gentle drying process that enable the evaporation of more acetic acid. Oven dried samples at higher temperature (70 and 80 °C) showed no significant different ($p > 0.05$) from the fermented beans due to the high drying rate. High drying rate will cause the

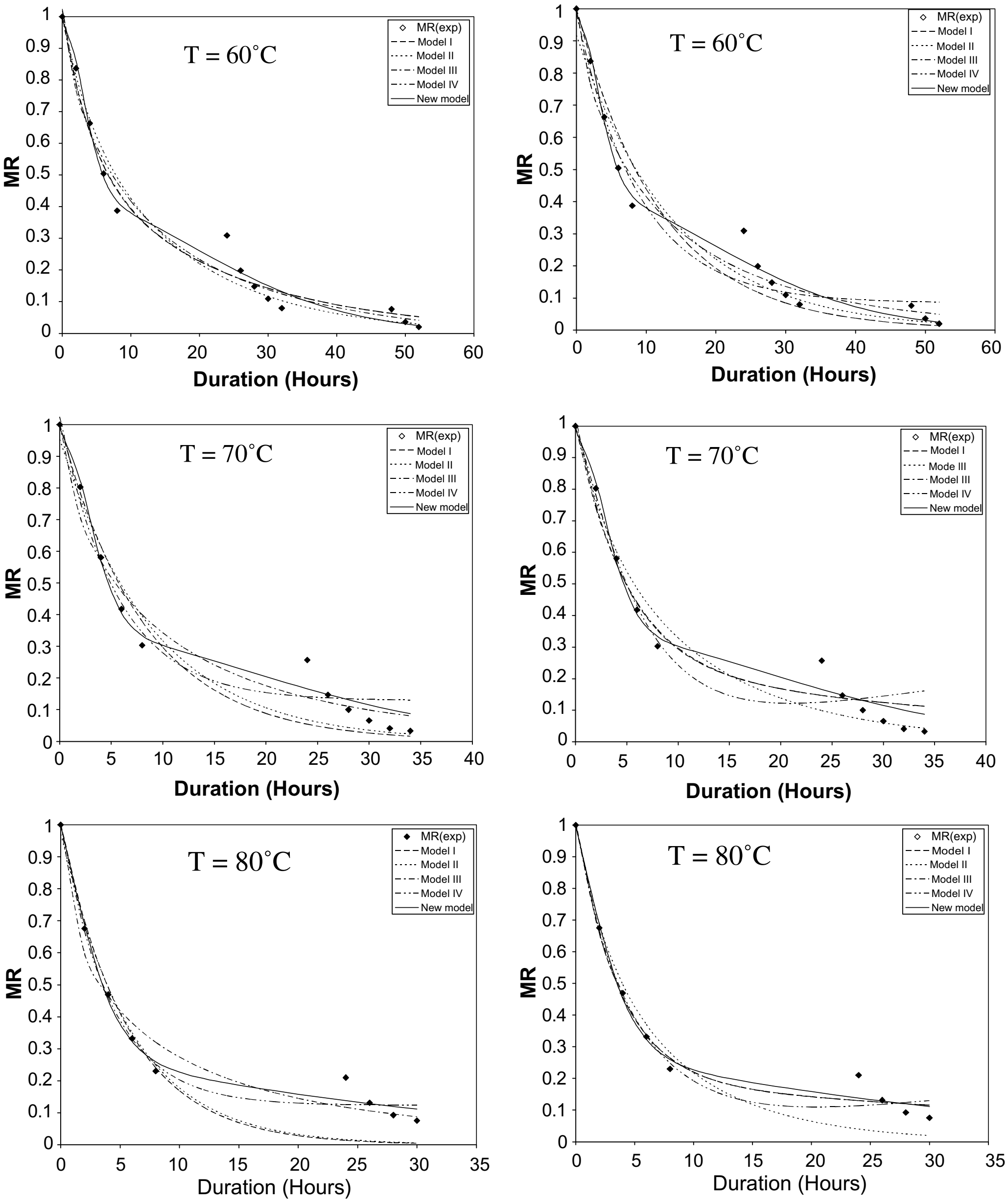

Fig. 4. Comparison between the experimental and the predicted data.

Table 6
Effective diffusivities of cocoa beans and other crop products

Materials	Effective diffusivity, D_e (m^2/s)	References
Cocoa		
60 °C	7.46×10^{-11}	Present work
70 °C	1.25×10^{-10}	
80 °C	1.87×10^{-10}	
Figs	2.47×10^{-10}	Doymaz (2005a)
Apricot	8.90×10^{-10}–1.30×10^{-9}	Mahmutoglu et al. (1995)
Mulberry	2.32×10^{-10}–2.76×10^{-9}	Maskan and Gogus (1998)
Prune	4.30×10^{-10}–7.60×10^{-10}	Sabarez and Price (1999)
Mint	7.04×10^{-12}	Akpinar (2006b)
Parsley	4.53×10^{-12}	Akpinar (2006b)
Basil	6.44×10^{-12}	Akpinar (2006b)

testa layer of the beans to dry faster and break the diffusion path of the acetic acid during moisture removal. Hence, most of the acids remain inside the beans and cause excessive sourness note to the

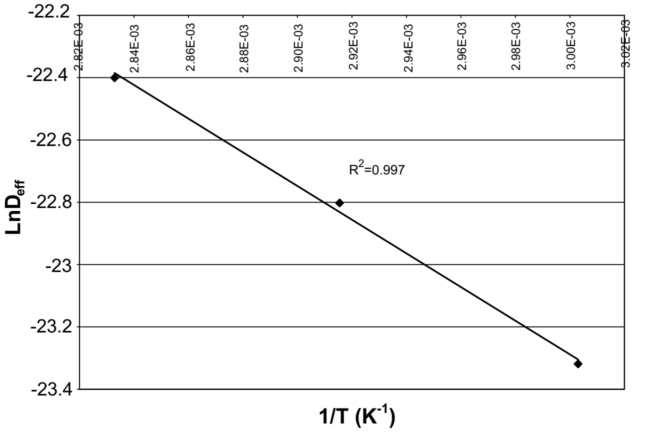

Fig. 5. The Arrhenius relationship between the effective diffusivities and temperature.

Table 7
Comparisons of activation energy (E_a) and Arrhenius constant (D_o)

Materials	E_a (KJ/mol)	D_o (m^2/s)	References
Okra	51.26	–	Doymaz (2005b)
Red Chili	41.95	–	Gupta et al. (2002)
Beans	39.47–39.41	7.983×10^{-3}–4.5×10^{-10}	Senadeera et al. (2003)
Potato	12.32–14.34	1.59×10^{-7}–2.314×10^{-7}	Senadeera et al. (2003)
Peas	42.35	9.633×10^{-2}	Senadeera et al. (2003)
Chestnuts	20.46–22.58	6.7×10^{-6}–1.21×10^{-5}	Guine and Fernandes (2006)
Red apple	19.957–22.624	3.01–7.095×10^{-7}	Kaya et al. (2007)
Baggase	19.47	2.43×10^{-7}	Vijayaraj et al. (2007)
Cocoa	44.92	8.43×10^{-4}	Present work

Table 8
The pH of dried and fermented cocoa samples

Dried cocoa samples	pH[*]
Sun	5.53 ± 0.058^a
Oven (60 °C)	5.26 ± 0.142^b
Oven (70 °C)	5.16 ± 0.202^{bc}
Oven (80 °C)	5.20 ± 0.001^{bc}
Fermented beans	4.97 ± 0.119^c

[*] Means (value ± std. deviation) within the same column with the same following letter are not significantly different ($p > 0.05$).

beans. It is generally recommended that drying should be performed at bean temperature not exceeding 60 °C to avoid retention of excessive acids.

Results of the cut test analyses are as shown in Fig. 6. No significant was found among all the colour attributes assessed ($p < 0.05$). This could be due to the high temperature range used (60–80 °C) used where complete browning was able to achieve just before the beans dried at the desired moisture content (7.5%, w.b.). The analyses showed that no slaty beans were observed in all treatments. Slaty beans are non-fermenting beans and this indicates that the fermentation process during sample preparation was conducted properly. The presence of too high percentage of slaty and purple beans will cause excessive astringency to the finished products that can mask the cocoa flavour. Results also showed that the percentage colour ranged from 57.78 to 68.89, 31.11 to 37.78 and 0.00 to 5.56 for the brown, purple–brown and purple colours attributes, respectively. It can be seen that the 60 °C oven drying treatment showed the highest percentage of brown colour, lowest percentage of purple–brown and purple colour beans as compared to beans produced from the 70 and 80 °C treatments. In the 60 °C treatment the percentage brown colour was more than 60% which indicates beans with good flavour quality. Nevertheless, the beans from the other two treatments showed brown colour slightly below 60%.

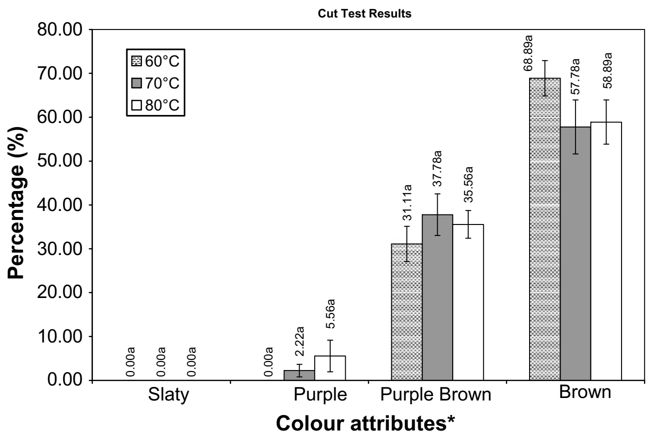

Fig. 6. Results of cut test analyses of dried cocoa samples.

4. Conclusion

Drying kinetics and modeling of the artificial drying process of cocoa beans were investigated. Initial warm up period was observed in the 60 and 70 °C treatments. However, these periods were short and subsequent drying only took place in the falling rate period. From the present work it was possible to conclude that the proposed new model can be used to describe the drying kinetics of cocoa drying at 60, 70 and 80 °C with inclusion of overnight tempering. The calculated effective diffusivities ranged from 7.46×10^{-11} to 1.87×10^{-10} m^2/s. The effective diffusivities increased with temperature following the Arrhenius type relationship. The values for D_o and E_a were estimated at 8.43×10^{-4} m^2/s and 44.92 KJ/mol, respectively. All the beans were found to be acceptable in terms of physical appearance which resemble grade A beans. Dried beans obtained from the 60 °C treatment were found to have lower acidity and good flavour quality as assessed by cut test.

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