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Thin layer drying kinetics of cocoa and dried product quality

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Studies were carried out to investigate the cocoa drying kinetics and compare the quality of the dried beans produced from sun and artificial hot air drying. Currently, these are the methods commonly used by cocoa farmers and plantations to dry cocoa beans. Drying trials were conducted in thin layer using natural sun light and by hot air inside an air-ventilated oven at air temperatures of 60 °C, 70 °C and 80 °C. Comparison was also made against freeze-dried cocoa beans for quality assessment. The quality attributes assessed were colour (L^*, a^*, b^* and hue angle), texture (hardness and fracturability) and polyphenol content (total polyphenols, epicatechin and catechin contents). Theoretical modelling was performed on the drying kinetics using Fick's law of diffusion and to determine the effective diffusivity values. Reasonable values were obtained for the coefficient of determination (R^2) between the experimental and predicted moisture ratio data (range 0.9845–0.9976). Effective diffusivity values were found within the range reported in literatures (range 1.61×10^{-10} m^2 s^{-1}–8.01×10^{-11} m^2 s^{-1}). Quality assessment showed significant differences ($p < 0.05$) among the sun dried, freeze-dried and oven dried samples in texture, colour and polyphenol content.

1. Introduction

Cocoa (*Theobroma cacao* L.) is native to the Amazonia region and typically grown in tropical countries such as Ivory Coast, Ghana, Nigeria, Indonesia, Brazil, Venezuela and Malaysia (Beckett, 1994). World production of cocoa beans was about 3,888,000 t in 2006/07 crop year and nearly 70% of this quantity was produced in West Africa (World Cocoa Foundation, 2008). Cocoa is consumed widely in the form of chocolates and consumption rate is rising due to the increasing popularity of chocolate confectioneries worldwide. The application of cocoa can also be found in beverages, cosmetics, pharmaceuticals and toiletries products. Cocoa is also associated with various health benefits especially due to its polyphenol contents. The benefits of polyphenols are well known such as anti-carcinogenic, anti-atherogenic, anti-ulcer, anti-thrombotic, anti-inflammatory, immune modulating, anti-microbial, vasodilatory and analgesic effects (Porter, 2006). Cocoa polyphenols also exhibit higher antioxidant activity than teas and red wines (Lee *et al.*, 2003).

The processing of cocoa beans consists of two major steps namely fermentation and drying. Fresh cocoa beans are usually fermented using the heap or box methods for 5–7 days depending on the condition of the beans. During fermentation the temperature of the beans will rise from ambient to about 50–55 °C due to the exothermic oxidation reaction (Wood and

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Nomenclature

D_{eff}	effective diffusivity ($m^2 s^{-1}$)
dm	dry matter
MR	moisture ratio (dimensionless)
m_0	initial moisture content (% dry basis)
m_i	local moisture content (% dry basis)
m_e	equilibrium moisture content (% dry basis)
R^2	coefficient of determination
r	radius (m)
R	radius of object (m)
t	time (h)
t_0	initial time (h)
t_i	time at the ith step (h)
t_N	end of drying time (h)
dm/dt	drying rate (g [H_2O] g^{-1} [dm] h^{-1})
EMC	equilibrium moisture content (% dry basis)
w_i	weight (g)
w_d	dry weight (g)
L^*	brightness (dimensionless)
a^*	colour redness/greenness (dimensionless)
b^*	colour yellowness/blueness (dimensionless)
h^*	hue angle

Lass, 1985). Fermentation is the initial step needed in the development of various flavour precursors in the beans. After fermentation, the beans are dried immediately to avoid over fermentation, which could lead to product deterioration. Drying can be carried out using natural or artificial hot air methods. The flavour development process continues during drying and the browning process is the most important reaction occuring at this stage (McDonald *et al.*, 1981). Drying is usually terminated when the dried beans' moisture content reaches 7.5% (wet basis).

Modelling of the drying kinetics can be carried out using Fick's theoretical model (Gastón *et al.*, 2004; Jain and Pathare, 2007; Janjai *et al.*, 2008), semi-theoretical (Verma *et al.*, 1985; Midilli *et al.*, 2002; Doymaz, 2005; Demir *et al.*, 2007; Kaya *et al.*, 2007; Karaaslan and Tunçer, 2008) and fully empirical models (Wang and Singh, 1978; Abalone *et al.*, 2006). Crank (1975) reported extensive studies on the general solutions of Fick's diffusional model and Jayas *et al.* (1991) presented a review of the various thin layer drying models used. Studies on the kinetics of cocoa drying are scarce especially in the area of sun drying. In the past, various studies have mainly been concerned with the design and performance of driers (Wood, 1961; Allison and Kenten, 1964). The earliest studies related to the fundamental characteristics of cocoa drying were carried out by Bravo and McGaw (1974). In their studies the constant and falling rate periods were identified and were fitted with empirical functions. Fotso *et al.* (1994) and Wan Daud *et al.* (1996) reported the characteristic drying curves of cocoa beans at various external conditions with critical moisture contents identified in their studies. The interaction of water and acetic acid in the cocoa bean during drying was studied by Nganhou *et al.* (2003) using one-dimensional diffusion model. However, these studies did not take into account the tempering period and quality attributes such as texture, colour and polyphenol content of the dried product. In the past, reported studies on cocoa quality were mainly in the area of acidity and sensory evaluation (Powell, 1958; Meyer *et al.*, 1989; Biehl *et al.*, 1989; Jinap *et al.*, 1994; Hii *et al.*, 2006). The analyses of total polyphenols as affected by drying temperatures are scarce and in most studies the analyses were performed on beans sourced from various warehouses and from different varieties and geographical locations (Kim and Keeney, 1984; Niemenak *et al.*, 2006; Tomas-Barberan *et al.*, 2007). Kyi *et al.* (2005) studied the reaction kinetics of the browning process at temperature of 40–60 °C and presented pseudo-first order mechanisms. However, in real on-farm processing much higher temperatures are used in order to increase the output of the drier although this will have an adverse effect on flavour.

The objectives of the current studies were to investigate the drying kinetics of cocoa beans based on Fick's theoretical model and the effect of drying on dried product quality (texture, colour, total polyphenol content) obtained from sun and artificial hot air drying.

2. Materials and methods

2.1. *Sample preparation*

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 (Hii and Tukimon, 2002). 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 30–50 °C) and that no mould growth was observed.

2.2. *Drying methods*

2.2.1. *Sun drying*

The beans were spread thinly on a meshed wooden tray with area about 30 cm × 90 cm and raised 1 m above ground level. The beans were mixed every 1 h to ensure uniformity. Ambient temperature and relative humidity were measured using a datalogger (Rotronic HW3, USA). Drying was conducted from 9 am till 6 pm daily.

2.2.2. *Artificial hot air drying*

The fermented beans (about 700 g) were artificially dried using an air-ventilated oven (Memmert DO6836, Germany) at temperature of 60 °C, 70 °C and 80 °C (Fig. 1). 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. The relative humidities were 6%, 4.7% and 2.9% at drying temperatures of 60 °C, 70 °C and 80 °C, respectively. Heat was generated by the heater integrated into the side walls of the oven and the hot air flowed through the samples. The exhaust air escaped through a ventilation hole (diameter 4 cm) at the back of the oven. The beans were mixed every 2 h to ensure uniformity. Drying was conducted for 8 h daily and the beans were left to temper at room temperature overnight. The tempering step is a common routine in cocoa drying and the purpose is to redistribute the internal moisture to the outer bean layer (testa) after each drying cycle.

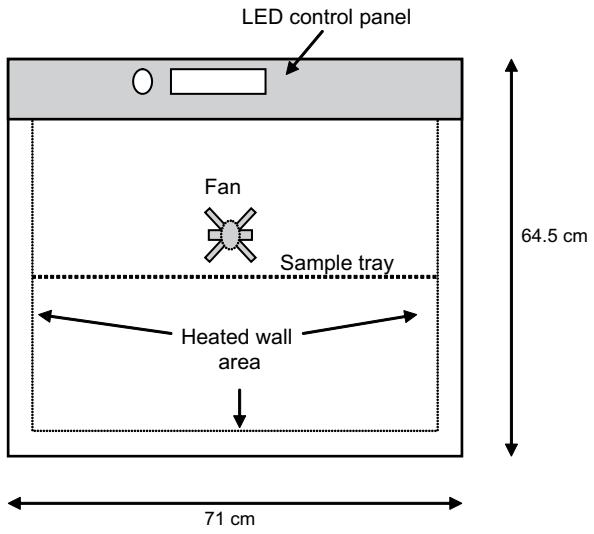

Fig. 1 – Schematic of the oven drying equipment.

2.2.3. *Freeze drying*

Freeze drying was conducted by using a laboratory freeze drier (CHRIST Alpha 1-2 LDplus, Germany) to obtain samples for quality analyses. About 50 pieces of cocoa beans were chilled in the freezer (−5 °C) overnight. The chilled cocoa beans were then dried in the freeze drier at −30 °C for 24 h (main drying) and −50 °C for 6 h (final drying). Previous experience showed that by using this drying profile the beans were dried to the desired moisture content of 7.5% (wet basis).

2.3. *Physical and chemical analyses*

2.3.1. *Moisture content*

The beans used in each experiment were weighed prior to mixing during drying by using an analytical balance (AND MX50, USA). The moisture content (m_i) of the beans was determined with reference to the dry weight of the beans using Eq. (1).

$$m_i = \frac{w_i - w_d}{w_d} \times 100\% \quad (1)$$

where the terms w_i and w_d refer to the initial and dry weight, respectively. The equilibrium moisture contents (EMCs) were determined by drying until no further change in weight was observed for the beans in each treatment. The EMC values determined were 7.26%, 6.72%, 6.09% and 3.74% (dry basis) for the sun and oven drying at 60 °C, 70 °C and 80 °C, respectively.

2.3.2. *Colour test* (L*, a*, b*)

The ground cocoa nibs were placed into a clear petri dish. The sensor of the colour meter was pointed directly at the ground nibs and care was taken to avoid any interference from ambient light sources. This measurement was made using a handheld colour meter (Accuprobe HH06, USA) and measurement was performed in triplicate. The colour of the ground cocoa nibs was measured for L^* (light–dark spectrum), a^* (green–red spectrum) and b^* (blue–yellow spectrum) values. Hue angles (h^*) were calculated using Eq. (2).

$$h^* = \tan^{-1}\left(\frac{b^*}{a^*}\right) \quad (2)$$

2.3.3. *Bean texture*

Bean texture was tested using a texture analyzer (Stable Microsystems TA.XT TEE32, UK) by using a 2 mm cylindrical probe at test speed of 0.5 mm s^{-1} with penetration distance of 2 mm. Trigger force was set to auto (5 g) with data acquisition rate of 40 Hz. The probe penetrated the flatter side of the beans at stable position. The hardness and fracturability were measured from the force deformation curve (force *versus* time). The area under the curve was taken as an indication of the hardness and the linear distance along the curve as an indication of fracturability. This measurement was performed in triplicate.

2.3.4. *Total polyphenols, epicatechin and catechin contents*

The analyses were carried out at Malaysian Cocoa Board (Selangor, Malaysia) using the methods developed by Kim and Keeney (1984). Defatted cocoa samples of 0.1 g were extracted with 80 ml of 70% aqueous acetone using sonication for 30 min in ice water. The mixture was then centrifuged (5000 rpm) at 4 °C for 15 min. The analysis was carried out by taking 100 ml of filtered extract, diluted with 7.9 ml of distilled water. Then 500 ml of Folin-Ciocalteau reagent was added to the mixture, mixed well and left for 8 min. After 8 min, 1.5 ml of 20% sodium carbonate was added and the mixture was allowed to stand for 2 h for colour development. The absorbance of the extract was measured at 765 nm using a spectrophotometer (Shimadzu UV-2501PC, Japan).

For the analysis of catechin and epicatechin contents, 0.5 g of defatted samples were sonicated with 80 ml of 80% aqueous acetone in a 125 ml conical flask for 30 min. Iced water was added into the sonicator vessel to prevent possible browning. The extract was then filtered through a Whatman no. 4 filter paper. The residue and glassware were washed with 80% aqueous acetone and the filtrate was made up to 100 ml in a volumetric flask. Ten millilitre of the extract was dried using a rotary evaporator at 45 °C. The resulting residue was resuspended with 5 ml distilled water by swirling the flask in a 45 °C water bath. A SPE cartridge (Alltech, Illinois USA) C18 (300 mg) was preconditioned with 1 ml of MeOH followed by 5 ml of distilled water. The pool extract from the resuspended residue was then injected through the SPE cartridge. The epicatechin and catechin retained by the SPE cartridge were eluted with 10 ml of 40% aqueous MeOH into a 10 ml volumetric flask. Ten millilitre of this final solution was injected into the HPLC (Agilent, 1100 series, USA). A Genesis C18 column (Jones Chromatography, USA) was used with mobile phase flowrate of 1.5 ml min^{-1}. The mobile phase used was a mixture of water, MeOH and acetic acid (87:8:5). UV detection was set at 280 nm using a diode array detector.

2.4. *Drying kinetics analysis*

2.4.1. *Drying rates*

The drying rates were calculated based on the following Eqs. (3)–(5) as used by Guine and Fernandes (2006) in their drying studies.

At $t = t_0$,

$$\frac{dm}{dt} = \frac{m_1 - m_0}{t_1 - t_0} \quad \text{First order forward finite difference} \quad (3)$$

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

$$\frac{dm}{dt} = \frac{m_{i+1} - m_{i-1}}{t_{i+1} - t_{i-1}} \quad \text{Second order centred finite difference} \quad (4)$$

At $t = t_N$,

$$\frac{dm}{dt} = \frac{m_N - m_{N-1}}{t_N - t_{N-1}} \quad \text{First order backward finite difference} \quad (5)$$

2.4.2. *Mathematical modelling*

Fick's second law of diffusion for spherical geometry (Eq. (6)) was used for modelling of the drying process based on the local moisture content (m_i) with the following boundary conditions (Eqs. (7)–(9)) used:

$$\frac{\partial m_i}{\partial t} = D_{eff}\left[\frac{\partial^2 m_i}{\partial r^2} + \frac{2}{r}\frac{\partial m_i}{\partial r}\right] \quad (6)$$

$$m_i = m_0 \quad t = 0 \;\; 0 < r < R \quad (7)$$

$$m_i = m_e \quad t > 0 \;\; r = R \quad (8)$$

$$\partial m/\partial r = 0 \quad t > 0 \;\; r = 0 \quad (9)$$

The general solution for a one-dimensional unsteady state diffusion (Eq. (10)) can be written as follows (Crank, 1975):

$$MR = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp^{D_{eff}n^2\pi^2 t/R^2} \quad (10)$$

The moisture ratio (MR) is defined as

$$MR = \frac{m_i - m_e}{m_0 - m_e} \quad (11)$$

Due to the presence of the tempering period, modelling was carried out for each drying day individually at different estimated effective diffusivities by using 10 terms ($n = 10$) of the general solution. Modelling 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.

2.5. *Statistical analyses*

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 ($p < 0.05$). The statistical software used was SAS for Windows (SAS Institute Version 9.1, USA).

3. Results and discussion

3.1. *Drying characteristics*

The moisture ratio *versus* time curves for the sun and oven (artificial hot air) drying treatments are shown in Fig. 2. In general the curves show a decreasing trend as drying progressed. The durations to complete the drying process were 75 h, 52 h, 34 h and 30 h in the sun drying and all the oven drying treatments (60 °C, 70 °C and 80 °C), respectively. It is obvious that sun drying recorded the longest drying time as temperatures fluctuated according to the ambient which is very much lower than the temperature used in artificial hot air drying (60–80 °C). This results in slower drying rates and longer drying duration. Typical temperature and relative humidity profiles of ambient conditions are shown in Fig. 3. Nevertheless, sun dried cocoa beans are often associated with high quality and good cocoa flavour (Jinap, 1994).

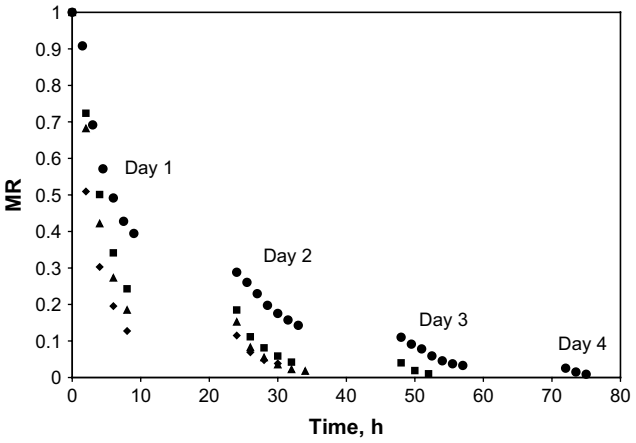

Fig. 2 – Drying curves of the sun and oven drying treatments (● Sun; ■ 60 °C; ▲ 70 °C; ◆ 80 °C).

The drying rate curves are presented in Fig. 4. In the oven drying treatments only falling rate period was observed as indicated by the curves. The decrement in drying rates was greater starting from the initial moisture contents (103.87–111.86% d.b.) to about moisture content of 25% (d.b.) in the oven drying treatments. Beyond this moisture content (25% d.b.), drying rates only deviated slightly from each other even at different drying temperatures and this continued until the end of drying. At such low drying rates only a small amount of free water is available and the diffusion of bound water is the

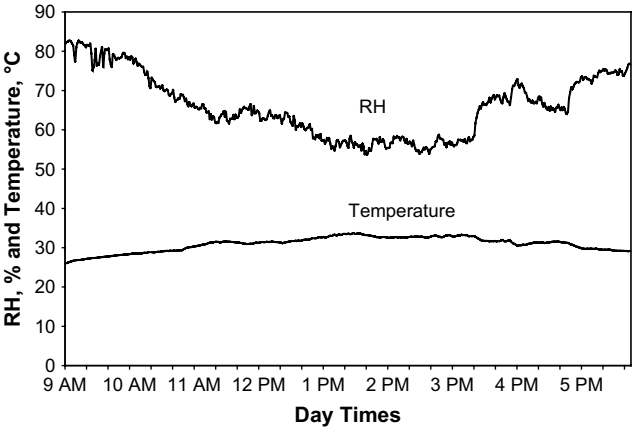

Fig. 3 – Ambient temperature and relative humidity during a typical day in sun drying.

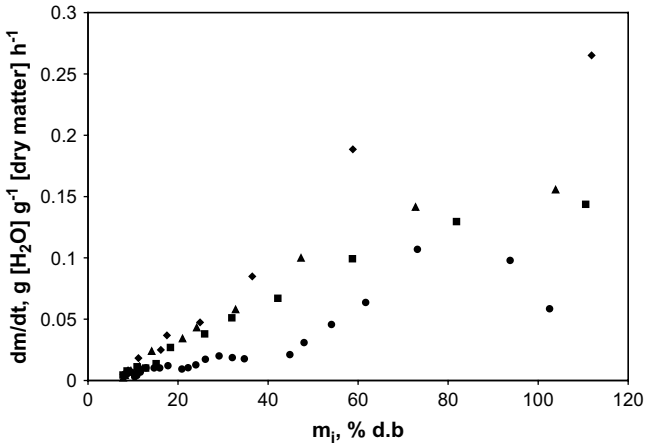

Fig. 4 – Drying rates *versus* moisture contents of cocoa beans during drying (● Sun; ■ 60 °C; ▲ 70 °C; ◆ 80 °C).

main mechanism controlling the water transport (Thuwapanichayanan *et al.*, 2008). The highest drying rates were registered at the initial stage of drying with values of 0.2652 g $[H_2O]$ g^{-1} [dm] h^{-1}, 0.1556 g $[H_2O]$ g^{-1} [dm] h^{-1}, 0.1436 g $[H_2O]$ g^{-1} [dm] h^{-1}at drying temperatures of 80 °C, 70 °C and 60 °C, respectively. The sun drying treatment showed a mixture of initial warm up, constant rate and falling rate periods due to the fluctuating ambient conditions (temperature and relative humidity). The highest drying rate was registered in the first day of drying at 0.1069 g $[H_2O]$ g^{-1} [dm] h^{-1}. Overall, the drying rates of the sun drying treatment were much lower than the oven drying treatments for most of the times.

Results of the modelling by using 10 terms of the general solution of Fick's theoretical model for various temperatures are shown in Fig. 5. Overall, it can be seen that in the oven drying treatments the model predicted the drying process quite well except in the first day of drying. The model under and over predicted the moisture reduction process at the initial and final stage of the oven drying process, respectively, in the first day. Other than that the model predictions were quite close to the experimental data in the second and third day of oven drying. Calculation of the coefficients of determination (R^2) showed values of 0.9871, 0.9845 and 0.9976 for oven drying treatments at 60 °C, 70 °C and 80 °C, respectively. In the sun drying treatment, greater deviation was observed between the experimental and predicted data in the initial stage of drying in all days. This could be due to the initial warm up period resulting from the wetter bean surface and the low ambient temperature (typically < 30 °C) at the start of the drying process on each drying day. Nevertheless, the calculated coefficient of determination was 0.9852, good considering that the drying process is highly unsteady due to the fluctuating ambient conditions.

There are various reasons for the lack of fit to the actual experimental data when using the theoretical model. This could be due to several key assumptions made in the derivation of the general solution of Fick's second law of diffusion such as no product shrinkage, effective diffusivity is independent of moisture content and isothermal drying

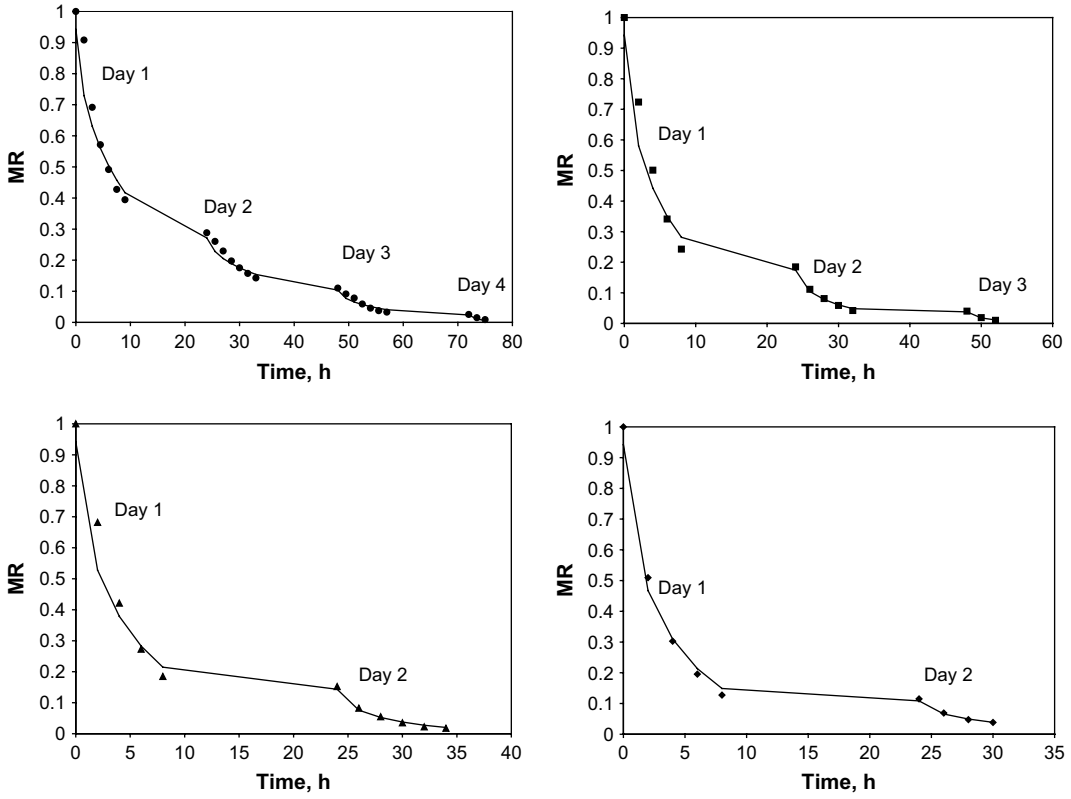

Fig. 5 – Comparison between the experimental and predicted data using the Fick's theoretical model (— Predicted; ● Sun; ■ 60 °C; ▲ 70 °C; ◆ 80 °C).

conditions. It is apparent that for most biological products, shrinkage due to drying is unavoidable and affects greatly the diffusion path of the moisture inside the product. Incorporation of volume shrinkage into the theoretical model has been proven able to model the drying process effectively in several studies (e.g. Hernández *et al.*, 2000; Tuwapanichayanan *et al.*, 2008). In the theoretical model, effective diffusivity is assumed as a constant and it is usually expressed as a function of temperature only in the form of the Arrhenius equation. For products exhibiting constant diffusivity, the effective diffusivity can be determined by using the first term of the general solution of Fick's second law by linearization using natural logarithms. However, some products fail to provide a straight line graph with reasonable R^2 value and exhibit non-linearity. The non-linearity characteristic indicates variation of effective diffusivity with moisture content (Tuwapanichayanan *et al.*, 2008). A drying temperature gradient exists between the product and the drying air and this has significant impact on the proper determination of the effective diffusivity based on the drying data. Srikiatden and Roberts (2008) used apparatus capable of providing isothermal drying condition and was reported able to obtain more accurate effective diffusivity and better fitting using the Fick's diffusional model in experiments carried out using potato and carrot.

3.2. *Effective diffusivities*

During drying the effective diffusivities in the sun and oven drying treatments were found to range from 8.01×10^{-11} to $4.84 \times 10^{-10}\ m^2\ s^{-1}$ and 1.61×10^{-10} to $3.23 \times 10^{-10}\ m^2\ s^{-1}$, respectively (Fig. 6). These values are within the range of diffusivities reported for most agricultural crop materials (Table 1). The lowest and highest values of effective diffusivities were recorded by sun drying in the second day ($4.57 \times 10^{-11}\ m^2\ s^{-1}$) and fourth day ($4.84 \times 10^{-10}\ m^2\ s^{-1}$), respectively. It can be seen that there was an increasing trend in the effective diffusivities in all treatments as drying progressed except in the 80 °C oven drying treatment where a drop was observed.

Table 1 – Effective diffusivities of cocoa beans and other crop products.

Materials	Effective diffusivity, D_{eff} ($m^2\ s^{-1}$)	References
Cocoa		
Sun drying	8.01×10^{-11}–4.84×10^{-10}	Present work
Oven (60 °C)	1.61×10^{-10}–3.23×10^{-10}	Present work
Oven (70 °C)	2.14×10^{-10}–2.47×10^{-10}	Present work
Oven (80 °C)	1.69×10^{-10}–2.86×10^{-10}	Present work
Wheat	2.976×10^{-7}–8.0×10^{-7}	Gastón *et al.* (2004)
Cashew	0.948×10^{-9}–2.2×10^{-9}	Hebbar and Rastogi (2001)
Chestnut	5.1×10^{-11}	Cletus and Carson (2008)
Mint	7.04×10^{-12}	Akpinar (2006)
Parsley	4.53×10^{-12}	Akpinar (2006)
Basil	6.44×10^{-12}	Akpinar (2006)

The effective diffusivities of the oven drying treatments can be described by an Arrehnius relationship on the first drying day. The relationship is presented in Fig. 7 with diffusivity constant and activation energy estimated at $4.08 \times 10^{-6}\ m^2\ s^{-1}$ and 28.11 kJ mol^{-1}, respectively. The estimated activation energy is within the range reported for various agricultural crops ranging from 12.32 kJ mol^{-1} to 51.26 kJ mol^{-1} (Senadeera *et al.*, 2003; Doymaz, 2005). However, this relationship cannot be used to describe the effective diffusivities in the second day of oven drying. The reason could be due to the fact that the initial moisture content on each drying day (apart from day 1) varied and that the diffusion process did not start from a common initial moisture content. Furthermore, the initial moisture gradient between the centre and surface of the partially dried beans varied after tempering. Hence, the effective diffusivity is not a function of temperature anymore after this stage and the moisture content should be taken into

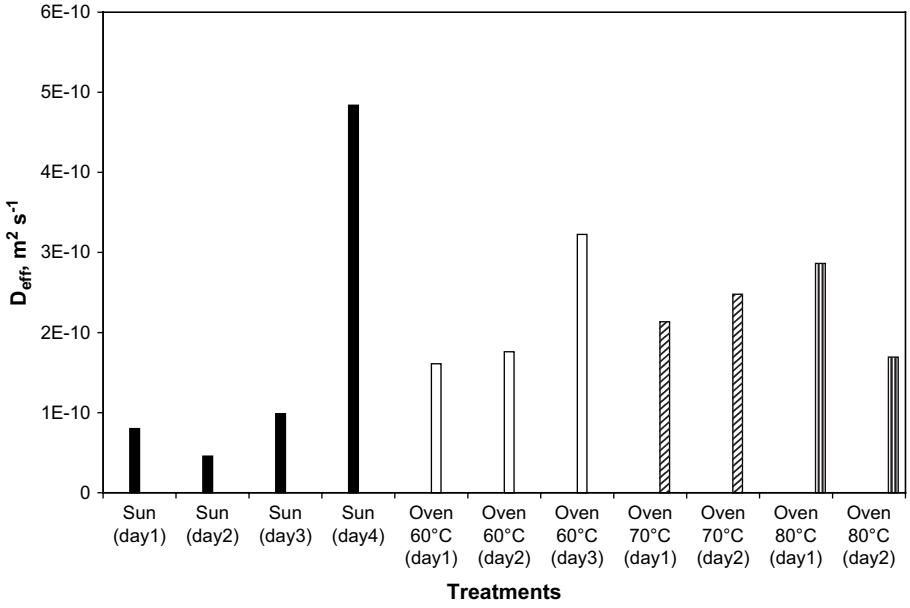

Fig. 6 – Effective diffusivities during sun and oven drying of cocoa beans.

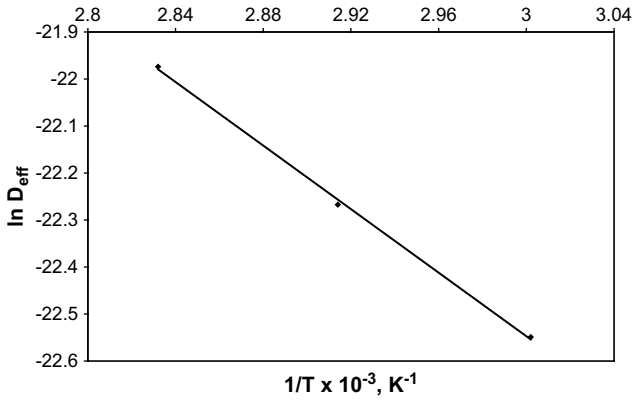

Fig. 7 – Plot of ln D_{eff} *versus* 1/T for first day of oven drying.

account. Various authors have reported the dependence of diffusion coefficient on initial moisture content (e.g. Hustrulid, 1963) and as a function of moisture content and temperature (e.g. Pabis, 1982; Steffe and Singh, 1982; Garau *et al.*, 2006). The relationship can be described in a parabolic or exponential form.

3.3. *Effect of drying on hardness and fracturability*

Results of the hardness and fracturability of the dried cocoa samples are as shown in Table 2. The hardness values ranged from 3.28 to 7.81 kg s and the fracturability values ranged from 4268.90 to 7902.10 (unit = dimensionless). Freeze-dried beans showed the lowest hardness and fracturability values since freeze-dried product will tend to be porous and fragile.

Statistical analyses showed that the hardness of the sun dried samples was significantly different ($p < 0.05$) from the 80 °C oven dried samples. All the oven dried samples were also found significantly harder ($p < 0.05$) than the freeze-dried beans. No significant difference ($p > 0.05$) was found in terms of hardness among the oven drying treatments but the 80 °C oven dried beans showed the highest hardness value. This could be due to the shell that was observed crinkly and stuck tightly to the nib. The hardness values also showed an increasing trend as the drying temperatures increased (from freeze to 80 °C oven drying).

In terms of fracturability, the sun dried and freeze-dried beans were found significantly different ($p < 0.05$) from the oven dried beans (for all temperatures). No significant difference ($p > 0.05$) was found among the oven drying treatments but fracturability was the highest from the 60 °C oven dried beans among all the drying treatments. The fracturability values also showed an increasing trend as the drying temperatures increased.

3.4. *Effect of drying on colour*

Table 3 shows the colour parameters L^*, a^*, b^* values and the calculated hue angles (h) of the dried ground cocoa nibs from all the drying treatments. The parameters L^*, a^* and b* values represent light–dark spectrum with a range from 0 (black) to 100 (white), the green–red spectrum with a range from −60 (green) to +60 (red), and the blue–yellow spectrum with a range from −60 (blue) to +60 (yellow), respectively. The colour parameters are related to the browning reaction where a decrease in L^* values, an increase in a^* values and a decrease in hue angles (h^*) indicate more browning (Rocha and Morais, 2003; Hawlader *et al.*, 2006). The range of values recorded were 38.35–49.14, 4.86–7.96, 10.02–12.51 and 52.62–68.22 for the L^*, a^*, b^* and h^* values, respectively.

The L^* values of the freeze-dried cocoa beans showed significant differences ($p < 0.05$) from the oven and sun dried beans. The freeze-dried samples showed the highest L^* values where browning is less likely to occur due to the sub-zero temperature used. This is confirmed by the lowest a^* value and highest hue angle recorded as compared to other dried beans. All the a^* values showed no significant difference ($p > 0.05$) among the drying treatments. However, the 60 °C oven dried cocoa beans showed the highest a^* value which could indicate more browning. The L^* and a^* values showed an increasing and decreasing trend, respectively, as drying temperature increased in the oven treatments.

No significant difference ($p > 0.05$) between the freeze-dried and other dried samples was observed in terms of the b^* values. The b^* values merely showed that all the dried samples were more yellow in colour (+60) and they are not an indicator of browning (Rocha and Morais, 2003). Nevertheless, the sun dried and the 70 °C oven dried samples showed the highest and lowest b^* values, respectively. Comparison of the hue angles showed that the freeze-dried samples were significantly different ($p < 0.05$) from the oven dried samples at 60 °C and 70 °C. The lowest hue angle was recorded by the 60 °C

Table 2 – Hardness and fracturability of dried cocoa samples from drying treatments.

Drying method	Hardness (kg s)	Fracturability
Sun	5.03 ± 0.17^{bc}	5098.60 ± 270.56^{b}
Oven (60 °C)	7.02 ± 0.37^{ab}	7902.10 ± 114.23^{a}
Oven (70 °C)	6.59 ± 0.56^{ab}	6633.70 ± 427.0^{a}
Oven (80 °C)	7.81 ± 0.60^{a}	6926.60 ± 65.48^{a}
Freeze dried	3.28 ± 1.50^{c}	4268.90 ± 1142.04^{b}

Mean value ± standard deviation ($n = 3$ replicates) within the same column with the same following letter are not significantly different ($p > 0.05$).

Table 3 – The L^*, a^*, b^* values and hue angle of dried cocoa samples.

Drying method	L^*	a^*	b^*	h^*
Sun	39.44 ± 1.34^{b}	7.06 ± 2.37^{a}	12.51 ± 0.17^{a}	60.95 ± 7.91^{ab}
Oven (60 °C)	37.74 ± 1.62^{b}	7.96 ± 0.83^{a}	10.40 ± 0.02^{a}	52.62 ± 2.82^{b}
Oven (70 °C)	38.35 ± 1.24^{b}	7.61 ± 0.86^{a}	10.02 ± 1.14^{a}	52.80 ± 0.02^{b}
Oven (80 °C)	40.49 ± 0.88^{b}	5.73 ± 0.33^{a}	11.94 ± 1.84^{a}	64.11 ± 4.72^{ab}
Freeze dried	49.14 ± 0.62^{a}	4.86 ± 0.87^{a}	12.11 ± 0.18^{a}	68.22 ± 3.25^{a}

Mean value ± standard deviation ($n = 3$ replicates) within the same column with the same following letter are not significantly different ($p > 0.05$).

Table 4 – Total polyphenol, catechin and epicatechin contents of dried cocoa samples.

Drying method	Total polyphenols ($mg\,g^{-1}$)	(−)-Epicatechin ($mg\,g^{-1}$)	(+)-Catechin ($mg\,g^{-1}$)
Sun	61.81 ± 2.43^{c}	4.08 ± 0.04^{a}	0.00 ± 0.00^{b}
Oven (60 °C)	77.20 ± 13.30^{abc}	5.69 ± 0.33^{a}	0.15 ± 0.21^{ab}
Oven (70 °C)	82.68 ± 3.42^{ab}	7.76 ± 2.11^{a}	0.08 ± 0.11^{ab}
Oven (80 °C)	71.42 ± 0.48^{bc}	3.06 ± 1.13^{a}	0.35 ± 0.02^{a}
Freeze dried	88.45 ± 0.07^{a}	8.08 ± 5.32^{a}	0.18 ± 0.05^{ab}

Results are expressed as gallic acid equivalents. Mean value ± standard deviation ($n = 3$ replicates) within the same column with the same following letter are not significantly different ($p > 0.05$).

oven dried beans which could indicate more browning as compared to other samples. The hue angle showed increasing trend as the drying temperature increased in the oven treatment.

3.5. *Total polyphenols, epicatechin and catechin contents*

Table 4 shows that the values obtained ranged from 61.81 to 88.45 $mg\,g^{-1}$, 3.06–8.08 $mg\,g^{-1}$ and 0.00–0.35 $mg\,g^{-1}$ for the total polyphenols, (−)-epicatechin and (+)-catechin contents, respectively. The (+)-catechin was present in smaller amounts since this compound is consumed more by the enzyme during the browning reaction. In terms of total polyphenol content, statistical analyses showed that the freeze-dried samples contained significantly more polyphenols ($p < 0.05$) as compared to the sun and 80 °C oven dried samples. The freeze-dried samples contained the highest polyphenol content due to the inactive enzymatic activity and hence the impeded browning reaction. The sun dried samples showed the lowest total polyphenol content due to the lower temperature profile and longer drying process. There was no significant difference ($p > 0.05$) among the oven dried samples and this could be due to the high temperature used. The enzyme was reported to have an optimum pH and temperature at 6.0 and 35.5 °C, respectively, but it is rapidly destroyed at 70–75 °C (McDonald *et al.*, 1981).

No significant difference ($p > 0.05$) was found in terms of (−)-epicatechin content among all the drying treatments. Nevertheless, the values showed that the 80 °C oven dried and freeze-dried samples had the lowest and highest (−)-epicatechin content, respectively. In terms of (+)-catechin content, the sun dried samples showed significant difference ($p < 0.05$) as compared to the oven dried samples at 80 °C. The 80 °C oven dried samples also showed the highest (+)-catechin content among all the treatments. The oven dried samples showed no significant differences ($p > 0.05$) for (−)-epicatechin or (+)-catechin contents.

4. Conclusion

Cocoa drying trials were carried out using sun and artificial hot air drying in an oven (air temperatures 60 °C, 70 °C and 80 °C). Drying time was the longest in sun drying due to the lower drying temperature which fluctuated according to the ambient conditions. Only falling rate drying periods were observed in the oven drying treatments at the drying temperatures tested. Mixture or initial warm up, constant rate and falling rate periods were observed in sun drying due to the fluctuating temperature profiles. Modelling using Fick's diffusion model showed reasonable agreement between the experimental and predicted moisture ratio data with coefficient of determination ranging from 0.9845 to 0.9976. Estimated effective diffusivities were ranged from 4.57×10^{-11} $m^2\,s^{-1}$ to 4.84×10^{-10} $m^2\,s^{-1}$. The diffusivities during the first drying day could be approximated by the Arrhenius temperature dependency relationship. Statistical analyses showed that the hardness of the sun dried samples was significantly different ($p < 0.05$) from the 80 °C oven dried samples. Fracturability of the sun dried and freeze-dried beans was significantly different ($p < 0.05$) from the oven dried beans (in all temperatures). Colour analyses showed no significant difference ($p > 0.05$) in terms of L^*, a^*, b^* and h^* values between the sun dried and oven dried samples. However, an increasing trend was observed in the L^*, b^* and h^* values and a decreasing trend for the a^* values as drying temperature increased in the oven drying treatments. Analyses of polyphenols showed no significant difference ($p > 0.05$) in terms of total polyphenols, (+)-catechin and (−)-epicathechin contents among the oven dried samples. Sun drying showed the lowest total polyphenols and (+)-catechin contents due to the longer drying duration at ambient temperature.

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