Journal of Engineering Science and Technology
Vol. 12, No. 1 (2017) 127 - 137

MASS TRANSFER KINETICS AND EFFECTIVE DIFFUSIVITIES DURING COCOA ROASTING

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Abstract

The current studies investigated the effects of temperature and moisture addition on the mass transfer kinetics of cocoa nibs during roasting. Experiments were carried out by roasting 500 gm of cocoa nibs inside an air ventilated oven at three temperature levels (120°C, 140°C and 160°C) under medium air flowrate for one hour. Two types of samples were prepared namely the raw and soaked nib samples. The soaked nib samples were prepared by soaking the raw nibs in 200 ml of water at room temperature for 5 and 10 hours. Mathematical modelling was carried out to model the mass transfer process using semi-empirical models. Modelling showed that both Page and two-term models were able to give close fitting between the experimental and predicted values. Effective diffusivity values were estimated in the order of magnitude of 10^{-5} m^2/s for the mass transfer process. Results obtained from these studies fill the current knowledge gap on the mass transfer kinetics of cocoa roasting.

Keywords: Cocoa, Diffusivity, Mass Transfer, Modelling, Roasting.

1. Introduction

The processing of cocoa beans (*Theobroma cacao*) begins with fermentation and drying in order to develop the necessary flavour precursors for aroma development during roasting [1]. Prior to roasting, the bean is broken and the shell is removed to obtain only the nib (or known as dried cocoa cotyledon) using a winnower and breaker machine. The cocoa nibs are usually roasted inside a batch drum roaster (temperature 130-150°C) or sometimes but not widely used, inside a continuous roaster. The duration of roasting is typically 30 - 90 minutes in industrial operation depending on the recipe and the degree of roasting.

Nomenclatures

a, b, g, k, n	Constants in semi-empirical model
D_e	Effective diffusivity, m^2/s
D_o	Pre-exponential factor, m^2/s
E	Activation energy, kJ/mol
L	Half thickness, m
MR	Moisture ratio, dimensionless
N	Number of data
R	Universal gas constant, 8.314 J/mol.K
$RMSE$	Root mean square error
SD	Standard deviation
T	Temperature, K
t	Time, s
X	Moisture content, g H_2O/g dry solid
z	Number of constants

Subscripts

Exp	Experimental
e	Equilibrium
o	Initial
Pre	Prediction

Upon roasting, the roasted nibs are ground into paste form inside a grinding machine. The paste is commonly known as cocoa liquor and this is one of the major ingredients used in chocolate manufacturing. The cocoa liquor can be further processed into cocoa powder and cocoa butter which are also used in chocolate making [1]. The flavour of cocoa liquor and powder is greatly affected by roasting but not for cocoa butter as it is usually deodorized upon butter pressing.

Roasting is a simultaneous heat and mass transfer operations whereby heat is supplied to enable moisture diffusion and evaporation from the cocoa nibs. The amount of moisture present in the nibs will affect the rate of mass (moisture) transfer and hence the processing time; which is crucial as this will affect not only the colour but also the flavour of the roasted nibs. Typically, the roasted nibs have intense chocolatey aroma and the moisture content should be less than 2 % (d.b) before grinding.

In the past, various studies have been reported for effect of roasting on nibs' colouration [2, 3]; physical/chemical changes [4-6] and flavour changes [7-9] However, reported studies on the effect of roasting on the mass transfer kinetics are relatively scarce. Schroder et al. [10] had reported the changes in moisture contents of cocoa beans and nibs during convective and microwave assisted roasting but without further attempt to model the mass transfer kinetics. In addition, effective diffusivity is a transport property which is important in the design of thermal heating equipments such as dryer and roaster. Typically, effective diffusivity is a strong function of temperature which governs the progress of moisture diffusion upon heating [11]. The diffusion process also governs the evaporation of flavour volatiles and the development of flavour compounds, i.e., in Millard reaction [1]. Therefore, this property affects greatly the processing time require to complete a roasting process which is vital not only in equipment design but also in aroma development

Hence, the objectives of the research were to investigate the effects of temperature and moisture addition on the mass transfer kinetics of cocoa nibs during roasting. The purpose of moisture addition was to imitate the conditions of the nibs which are very moist and partly rehydrated after the alkalizing process before roasting [1]. Results from these studies fill the current knowledge gap on the mass transfer kinetics of cocoa roasting which are scarcely reported in published literatures.

2. Materials and Methods

2.1. Roasting

Cocoa nibs (also known as dried cocoa cotyledons) were obtained from Malaysian Cocoa Manufacturing Sdn. Bhd. (Seremban, Malaysia). About 500 gm samples were prepared and placed on a wire meshed tray in thin layer (~1 cm nibs thickness) prior to roasting. Roasting was carried out by placing the tray in the middle section of an air ventilated oven (Memmert, Germany) with airflow adjusted to medium setting. Two types of samples were prepared namely the raw and soaked nib samples (Table 1).

Table 1. Roasting trials conducted for raw and soaked nib samples.

Sample	Temperature
Raw nibs	120,140 and 160°C
Soaked nibs (0h, 5h, 10h)	140°C

The soaked samples were prepared by soaking the raw nibs in 200 ml of water at room temperature for 5 and 10 hours. This is to imitate the partly rehydrated and moist conditions of the nibs after alkalization. In a typical processing plant, alkalization is carried out using alkaline solutions in order to achieve different degree of colourization under pressurized condition. It is therefore proposed that this can be further investigated in future research.

During roasting, the weights of the nibs were measured every 10 minutes using an analytical balance (Metler Toledo, USA) for fixed roasting duration of 60 minutes. Moisture contents of the nibs (X) were determined by using Eq. (1) with reference to the bone dry weight [12]. The bone dry samples were prepared by placing the final roasted nibs in an oven overnight at 105°C for 24 hour. All roasting trails were conducted in duplicate.

$$X = \frac{Wt.\,of\ sample(g) - Wt.\,of\ bone\ dry\ sample(g)}{Wt.\,of\ bone\ drysample(g)} \tag{1}$$

2.2. Roasting rates

Roasting rates were calculated based on the moisture content data according to Eqs. (2) to (4) [13]:

At $t = t_0$ (initial time),

$$\frac{dX}{dt} = \frac{X_1 - X_0}{t_1 - t_0} \tag{2}$$

At $t = t_i$ (intermediate points)

$$\frac{dX}{dt} = \frac{X_{i+1} - X_{i-1}}{t_{i+1} - t_{i-1}} \tag{3}$$

where $i = 1, \ldots, N\text{-}1$

At $t = t_N$ (final time),

$$\frac{dX}{dt} = \frac{X_N - X_{N-1}}{t_N - t_{N-1}} \tag{4}$$

2.3. Mathematical modelling

The mass transfer kinetics was analyzed by fitting three semi-empirical models to the experimental data as shown in Table 2. Statistical parameters such as R^2, *chi-square*, Eq. (5) and root mean square error (*RMSE*, Eq. (6)) were used to determine the goodness of fitting [12]. SOLVER was used (MS Excel, USA) for the regression analyses.

Table 2. Semi-empirical models.

Model name	Equation
Newton	$MR = exp^{-kt}$
Page	$MR = exp^{-kt^n}$
Two-term model	$MR = a\,exp^{-kt} + b\,exp^{-gt}$

where *a*, *b*, *k*, *g* and *n* are constants to be determined from regression.

$$Chi-square = \frac{\sum_{i=1}^{N}(MR_{pre\,i} - MR_{exp\,i})^2}{N - z} \tag{5}$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}(MR_{pre\,i} - MR_{exp\,i})^2\right]^{1/2} \tag{6}$$

where N = number of data, z = number of constants in model.

2.4. Effective diffusivities

This was determined by using the analytical solution of Fick's second law [11] as shown in Eq. (7). The shape of the nibs was assumed in a slab form with average thickness (*2L*) of about 3.66 mm. Five terms of the solution ($n = 5$) were used in the estimation.

$$MR = \frac{X - X_e}{X_0 - X_e} = \frac{8}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{(2n+1)^2} exp[\frac{-(2n+1)^2 \pi^2 D_e t}{4L^2} \tag{7}$$

where the term $\frac{X - X_e}{X_0 - X_e}$ is known as the moisture ratio (*MR*).

The Arrhenius equation was used to relate the effective diffusivities with temperatures for the determination of activation energy (E) in Eq. (8).

$$D_e = D_o exp^{-\frac{E}{RT}} \tag{8}$$

The activation energy was determined by taking natural logarithm at both sides, and the slope of the linear graph ($ln\ D_e$ vs. $1/T$) was used to determine this value.

2.5. Texture analyses

Texture analyses were carried out by determining the hardness of the nibs before and after soaking. The test was conducted by using texture analyser (Stable Microsystems TA.XT TEE32, UK) fitted with a circular compression probe (Diameter = 7.5 cm). About 10 g of nibs were placed on a solid metal base and compression test was carried out using the probe at test speed of 0.5 mm/s and compression distance of 2 mm. Hardness was determined as the maximum force registered from the force deformation curve (force vs time). This measurement was performed in triplicate.

2.6. Statistical analyses

Statistical analyses were carried out using one-way ANOVA and Duncan’s Multiple Range Test for mean comparison at 95% confidence level. SAS for Window software was used (SAS Institute, USA).

3. Results and Discussion

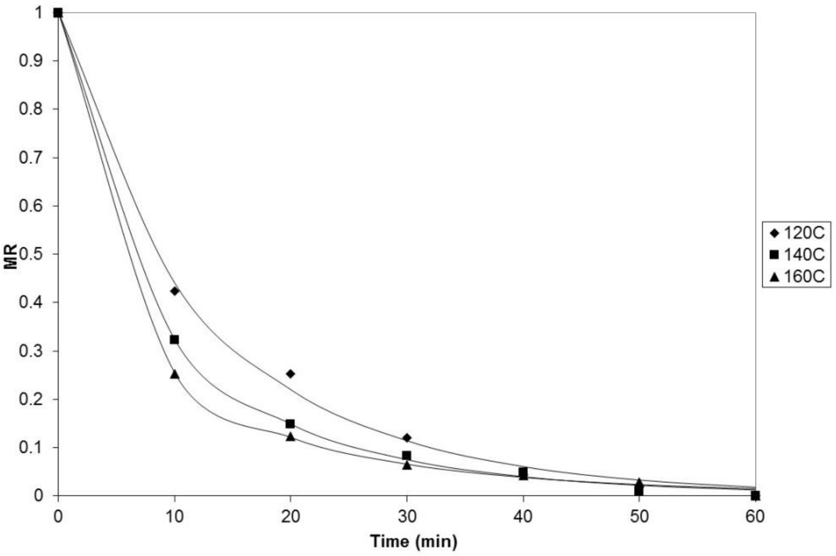
3.1. Mass transfer kinetics

Figure 1 shows the mass transfer kinetics of the cocoa nibs based on the moisture ratio profile. It can be observed that the kinetics follows exponential decay and only falling rates are observed with regards to moisture transfer.

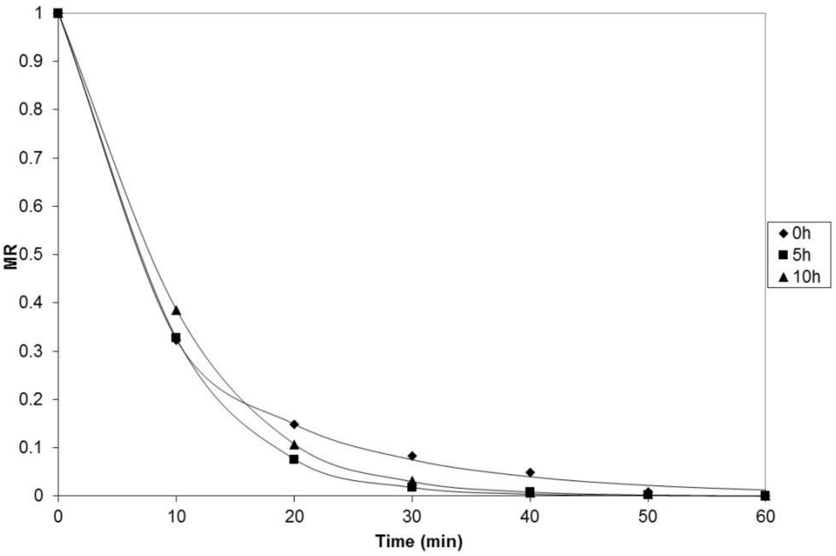
This is in agreement with the roasting rates (Fig. 2) determined from the moisture content data, where no constant rate can be observed. This shows that the mass transfer process is dominated by internal diffusion [14-16].

However, it is interesting to note that in overall the drop in moisture ratios for the soaked samples (5 h and 10 h) are faster than the raw samples (Fig. 1b). This could be due to the slightly expanded/soften structure within the solid matrix upon soaking that improves diffusion, in addition to the greater moisture gradient as the main driving force for mass transfer. This is in agreement with the hardness test carried out where the longer is the soaking duration; the softer is the nibs upon soaking (Fig. 3). It can be seen that both soaked samples are significantly softer than the raw samples ($p < 0.05$).

In addition, comparison of initial drying rates show significant different (*p* < 0.05) between the soaked and raw samples (Fig. 4). Although no significant different ($p > 0.05$) can be observed between the soaked samples (5 h and 10 h) but there is a tendency for the 5 h soaked samples to dry faster as compared to the 10 h soaked samples which could be due to the lesser amount of water rehydrated into the nibs upon soaking.

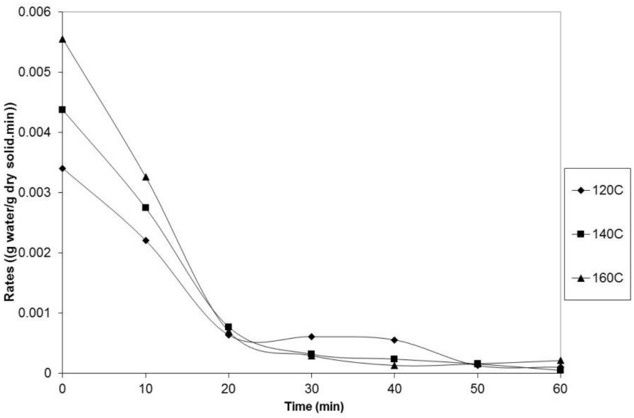


a. Raw samples

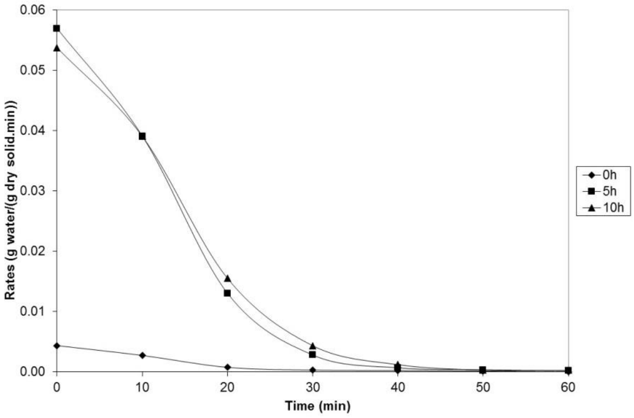


b. Soaked samples

Fig. 1. Moisture ratio profiles for raw and soaked nib samples (solid line: model prediction; marker: experimental data).

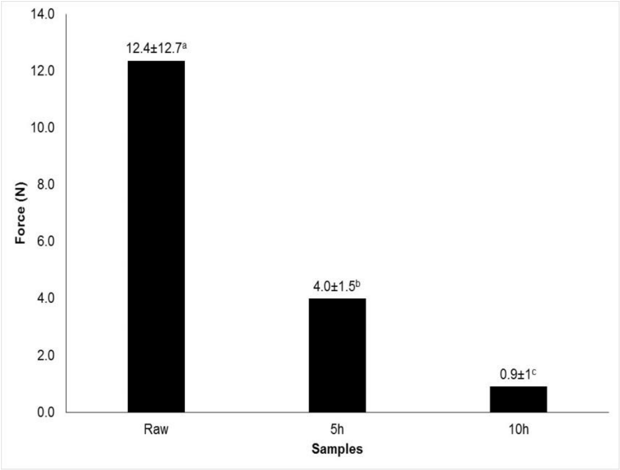


a. Raw samples



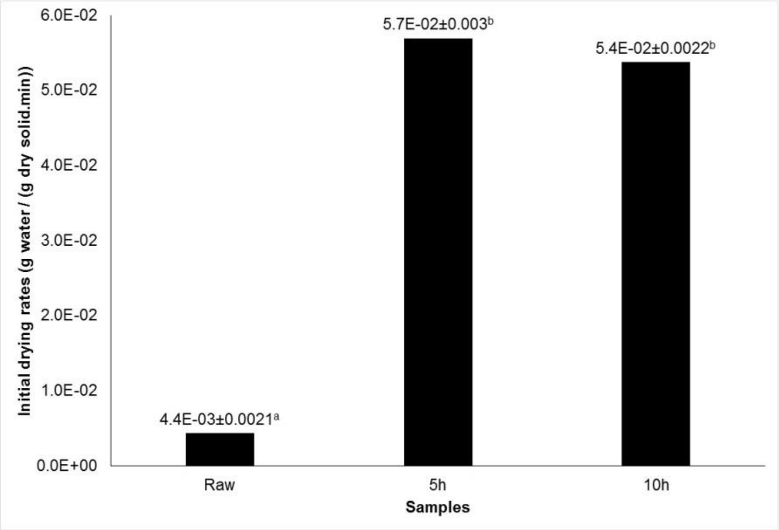
b. Soaked samples

Fig. 2. Roasting rates profiles for raw and soaked nib samples.



The readings are expressed as means ± SD

Fig. 3. Comparison of hardness between the raw and soaked nib samples.



The readings are expressed as means ± SD

Fig. 4. Comparison of initial drying rates between the raw and soaked nib samples.

3.2. Mathematical modelling

Table 3 shows that both Page and two-term models can be used to describe the experimental data during roasting depending on the experimental treatment (also as shown in Fig. 1). These samples were selected based on the model that gave the highest R^2, lowest *chi-square* and *RMSE* values. Semi-empirical models have been used widely in modelling of moisture transfer process during drying [14]. In this experiment, similar models have been used as moisture vapour is diffused and evaporated from the cocoa nibs during roasting under high temperatures.

3.3. Effective diffusivity

Table 4 shows the effective diffusivity values obtained based on the analytical solutions of Fick’s law [11]. It can be seen that diffusivity estimated from the soaked samples (5h and 10 h) are higher as compared to the raw samples. The diffusivity values estimated are generally in the order of magnitude of 10^{-5} m^2/s, which are much higher than those obtained from conventional drying at 10^{-8} - 10^{-12} m^2/s [17]. This could be due to the much higher temperature used in roasting (> 100°C) as compared to hot air drying (60°C - 80°C).

Activation energy to initiate moisture diffusion during roasting was determined at 28.6 kJ/mol, Eq. (9). This value is much lower than that determined for cocoa drying (45 kJ/mol) [18] due to the higher temperature used which corresponds to greater driving force for mass transfer. In addition to that, roasting was carried out using nib fragments instead of using whole beans as in the case of cocoa drying. Heating rate is therefore faster for the nibs due to the smaller particle size and absence of the shell layer.

$$D_e = 2.37 \times 10^{-5} exp^{-\frac{28.6}{RT}} \tag{9}$$

Table 3. Statistical results of modelling.

Effects of temperature		
120°C	140°	160°C
Newton: k = 0.0764 *Chi-square* = 0.00059 *RMSE* = 0.0224 R^2 =0.9955	Newton: k = 0.1028 *Chi-square* = 0.00069 *RMSE* = 0.0244 R^2 = 0.9958	Newton: k = 0.1235 *Chi-square* = 0.0011 *RMSE* = 0.0306 R^2 = 0.9946
Page: k = 0.1066, n = 0.8858 *Chi-square* = 0.00044 *RMSE* = 0.0177 R^2 = 0.9974	***Page:* k = 0.1976,** **n = 0.7560** ***Chi-square* = 0.0001** ***RMSE* = 0.0085** **R^2 = 0.9993**	***Page:* k = 0.3243,** **n = 0.6250** ***Chi-square* = 0.00005** ***RMSE* = 0.0064** **R^2 = 0.9996**
***Two-term:* a = 0.17,** **b = 0.83, k = 1.105,** **g = 0.064** ***Chi-square* = 0.0005** ***RMSE* = 0.0148** **R^2 = 0.9983**	Two-term: a = 0.3431, b = 0.6569, k = 1.1059, g = 0.0717 *Chi-square* = 0.00014 *RMSE* = 0.0078 R^2 = 0.9994	Two-term: a = 0.5163, b = 0.4837, k = 1.1059, g = 0.0656 *Chi-square* = 0.00011 *RMSE* = 0.007 R^2 = 0.9996
Effects of moisture addition (T = 140°C)		
0 h	5 h	10 h
Newton: k = 0.1028 *Chi-square* = 0.00069 *RMSE* = 0.0244 R^2 = 0.9958	Newton: k = 0.1169 *Chi-square* = 0.00014 *RMSE* = 0.0109 R^2 = 0.9991	Newton: k = 0.1019 *Chi-square* = 0.00025 *RMSE* = 0.0147 R^2 = 0.9985
Page: k = 0.1976, n = 0.7560 *Chi-square* = 0.0001 *RMSE* = 0.0085 R^2 = 0.9994	Page: k = 0.0724, n = 1.1892 *Chi-square* = 9.83×10^{-6} *RMSE* = 0.0026 R^2 = 0.9999	Page: k = 0.0589, n = 1.2089 *Chi-square* = 5.93×10^{-6} *RMSE* = 0.0021 R^2 = 0.9994
***Two-term:* a = 0.3431,** **b = 0.6569, k = 1.0998,** **g = 0.7172** ***Chi-square* = 7.96×10^{-6},** ***RMSE* = 0.0018** **R^2 = 0.9994**	***Two-term:* a = -0.3955,** **b = 1.3955, k = 1.1984,** **g = 0.1451** ***Chi-square* = 7.96×10^{-6},** ***RMSE* = 0.0018** **R^2 = 0.9999**	***Two-term:* a = 1.3829,** **b = 1.3955, k = 0.1277,** **g = 1.0381** ***Chi-square* = 1.09×10^{-6}** ***RMSE* = 0.00069** **R^2 = 0.9999**

Table 4. Effective diffusivities during roasting.

Effects of temperature		
120°C	140°	160°C
1.38×10^{-5} m^2/s	2.49×10^{-5} m^2/s	3.08×10^{-5} m^2/s
Effects of moisture addition (T = 140°C)		
0 h	5 h	10 h
2.49×10^{-5} m^2/s	4.37×10^{-5} m^2/s	3.42×10^{-5} m^2/s

4. Conclusion

Higher roasting rates were observed in the soaked cocoa nibs as compared to the raw nibs which could be due to the soften structure of the nibs and greater moisture gradient. Only falling rates were observed for moisture transfer during roasting. Both Page and two-term models can be used to describe the roasting kinetics for the raw and soaked nib samples. Effective diffusivity values were determined in the order of 10^{-5} m^2/s while activation energy was estimated at 28.6 kJ/mol during roasting. Results from the studies have provided an insight into the mass transfer kinetics of cocoa nibs during roasting which are beneficial to the cocoa industry especially to understand further the interaction between moisture diffusion and aroma development in future research.

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