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Effect of hot-air drying temperature on the polyphenol content and the sensory properties of cocoa beans

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Abstract

Several studies have been reported on the potential health benefits of cocoa polyphenols. However, heat treatment on cocoa beans during drying has an inhibitory effect on the retention of its polyphenols. The polyphenol degradation mechanism due to heating is scarcely reported in literatures for cocoa beans. This paper aims to provide substantial evidence to prove that temperature and heating time has a negative effect on cocoa polyphenols. The study measured total polyphenols content of cocoa beans dried at 60°C, 70°C and 80°C respectively, at relative humidity (RH) level of 50% for heating time ranging from 0 to 40 h. Results showed that the total polyphenols content was found to be a maximum at 70°C drying temperature and reduced as the heating time for drying increased. This experiment confirmed the thermal degradation of polyphenols due to high temperature and exposure time with little effect from enzymatic activity especially at very low moisture content level. Sensory evaluation showed that astringency taste was rated higher for sample dried at 70°C.

Introduction

Cocoa (*Theobroma cacao* L.) is a widely consumed commodity and its application can be found in the manufacturing of chocolates, beverages, cosmetics, pharmaceuticals and toiletries products. Recent studies have revealed several positive health implications of cocoa polyphenols ranging from preventing cardiovascular disease, lowering blood pressure, improving endothelial function, inhibiting platelet aggregation and reducing inflammatory responses (Dillinger *et al.*, 2000; Maleyki *et al.*, 2008; Kothe *et al.*, 2013). Typically, the cocoa polyphenols contents are about 6 to 8% by weight of a dried fermented cocoa bean (Crozier *et al.*, 2011). The composition and amount of polyphenols in cocoa beans vary strongly with bean type, origin and the methods of processing. It has been reported that fermentation, drying and alkalization can lead to substantial decrease in cocoa polyphenols after processing in the range of nearly 60% total flavonoids (Wollgast and Anklam, 2000; Hii *et al.*, 2009; Jolic *et al.*, 2011).

Drying after fermentation is a very important step as it has a huge role in determining the final quality of dried cocoa beans. Conventionally, cocoa farmers use sun and hot air to dry cocoa beans to the desired moisture content. The drying process ensures various chemical and bio-chemical changes that are necessary to form the flavour and aroma precursors are produced for the subsequent roasting process in secondary processing (Misnawi *et al.*, 2003; Garcia-Alamilla *et al.*, 2007). However, drying degrades polyphenols in cocoa beans via a complex reaction known as browning and also due to thermal effect. Although polyphenols in bean degrades considerably during drying, the remaining amount present will still impart an astringent taste to the chocolate products after processing (Kyi *et al.*, 2005). The thermal degradation reaction of polyphenols can be explained as the oxidation of phenolic compounds due to both enzymatic reaction and non-enzymatic process which leads to the browning reaction. The high temperature drying processes usually leads to non-enzymatic oxidation of polyphenols. The precursor for the degradation reaction, polyphenol-oxidases enzymes are activated during fermentation and drying.

The objective of the current study was to investigate the effects of heat treatment during drying on the total polyphenols content of cocoa beans.

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Label	Temperature (°C)	Exposure times (h)	Relative Humidity (%)
H60	60		
H70	70	12, 24, 32, 40	50
H80	80		

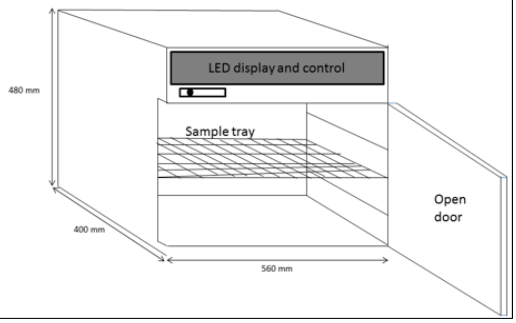


Figure 1. Schematic diagram of humidity chamber with the operating conditions

This area of study is scarcely reported in literatures for cocoa beans except for those due to enzymatic browning as reported by Kyi *et al*. (2005) where the author studied polyphenols degradation of cocoa beans in the initial 5 h of drying.

Materials and Methods

Sample preparation

Mixed clone varieties of fermented cocoa beans were obtained from Malaysia Cocoa Board (Pahang, Malaysia). The average sizes of the beans were of ~2.7 x 1.5 x 1.0 cm (length x width x breadth). The fermentation process was carried out by leaving the cocoa beans in a wooden fermentation box of 1.2 x 1.2 x 1.2 m for a period of five days. The fermented samples were stored in deep freezer at -18°C to stop fermentation and to preserve the beans. In each experiment, 100 g of frozen samples were allowed to defrost sufficiently at room temperature before drying. The samples were spread thinly on a meshed tray for subsequent drying.

Humidity controlled drying chamber

Drying experiments were carried out using a humidity controlled drying chamber (Memmert HCP 108, Germany) with an overall dimension of 48×56×40 cm. The beans were spread thinly on a meshed tray with square openings measuring 0.4 × 0.4 cm. Heat was generated by heaters integrated into the walls of the chamber. The equipment was allowed to pre-heat for more than 10 h prior to experiment to achieve stable drying temperature and relative humidity. Figure 1 shows the schematic sketch of the humidity controlled drying chamber.

Drying procedure

Trials were conducted based on the experimental treatments as indicated in Figure 1. The relative humidity was set constant at 50% and air flow rate was fixed at 0.01m/s inside the drying chamber. After the completion of drying at each temperature and heating time, the samples were analysed for total polyphenol content.

Moisture content

Moisture content (X_i) in dry basis was determined hourly based on the weight of the whole beans (M_i) using Eq. (1) (Hii *et al*., 2009). Dry solid weight of the beans (M_{ds}) was determined by using the oven method at 105°C by heating for at least 24 h.

$$X_i = \frac{M_i - M_{ds}}{M_{ds}} \times 100 \quad (\%) \tag{1}$$

Drying rates

The drying rates was calculated by approximation of the derivatives of finite differences (Guine and Fernandes, 2006) based on the following Eq. (2-4)

At $t = t_0$ (initial time),

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

At $t = t_i$ (i= 1, … , N-1), where X denotes the moisture content.

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

At, $t = t_N$ (final time),

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

Effective diffusivity

Effective diffusivity maybe defined as the transport of moisture within solid which may occur by any one or more of the following mechanisms (Mujumdar, 2008): Liquid diffusion, if the wet solid being dried is at a temperature below the boiling point of water; vapour diffusion if the liquid vaporizes within the material; Knudsen diffusion when the liquid vaporizes within the material; surface diffusion during drying; diffusion due to hydrostatic pressure differences when internal vaporization rates exceed the rate of vapour transport through the solid to the surroundings and due to combinations of a few or all the mechanisms mentioned above. Effective diffusivity Deff was determined by using the general solution of the Fick's law for spherical object as shown in Eq. (5) below;

$$MR = \frac{6}{\pi^2} \sum_{n=1}^{n=\infty} \frac{1}{n^2} \exp\left[\frac{-n^2 \pi^2 D_e t}{R^2}\right] \tag{5}$$

Where MR is the moisture ratio, which can be calculated from the equation given below,

$$MR = \frac{M_i - M_e}{M_o - M_e} \tag{6}$$

Where, subscripts i, e and o denote at time t_i, equilibrium and initial, respectively.

Only the first term of the equation was used and upon linearization by applying natural logarithm at both sides, a straight line graph can be plotted (ln MR vs t) using Eq. (7). The slope of the graph was used to obtain the values of D_{eff} (Hii *et al*., 2009).

$$LnMR = Ln(\frac{6}{\pi^2}) - (\frac{\pi^2 D_e t}{r^2}) \quad (7)$$

The dependence of effective diffusivity on temperature can be further described using the Arrhenius equation as shown in Eq. (8):

$$D_{eff} = D_o \exp\left[-\frac{E_a}{R_g(T+273.15)}\right] \quad (8)$$

Where, D_0 is Arrhenius constant, Ea is Activation energy and R is Gas constant (8.314 J $mol^{-1}K^{-1}$). This equation can be linearized by applying natural logarithm on both sides of ln D_{eff} versus 1/T will produce a straight line. The activation energy and Arrhenius constant can be determined from the slope and y-intercept respectively.

Total polyphenols content

Polyphenols analyses were carried out according to the method by Kim & Keeney (1984). Dried cocoa beans were peeled to separate the nibs from the shells for analyses. The samples were ground in a dry mill and then sieved through a 600 µm screen to obtain the fine powders. Five gram of ground samples were defatted for 2 hours using petroleum ether in Soxtherm (Gerhadt, Germany). The samples were filtered through Whatman No. 1 filter papers (Sigma-Aldrich, USA) and the residues were oven dried at 60°C for 6 hours to allow the traces of petroleum ether to evaporate. For extraction of polyphenols, 10 ml of 70% acetone solution was added to 0.1 g of dried defatted samples and sonicated (Elmasonic P, Germany) for 30 minutes in ice water. The samples were then centrifuged (Eppendorf, Germany) at 5000 rpm for 10 minutes.

Subsequent steps were carried out by diluting 100 µl of the supernatant liquid with 7.9 ml of distilled water. Then, 500 µl of Folin-Ciocalteau (Sigma-Aldrich, USA) reagent was pipette into the test tube, shaken to allow it to mix well and left for 8 minutes. Next, 1.5 ml of 20% sodium carbonate solution was pipette into the mixture and left to stand for 2 hours for colour development. This was repeated for the standard Gallic acid solutions. The absorbance of the standards and polyphenols extracts was measured with a UV/Vis spectrophotometer (PerkinElmer, USA) at 765nm. The results are reported as Gallic acid equivalents (GAE) per gram dry cocoa. The study measured total polyphenol content of cocoa samples for H60, H70 and H80 for 12, 24, 32 and 40 hours respectively.

Sensory evaluation

Sensory evaluation was carried cut for cocoa beans dried at 60°C, 70°C and 80°C respectively for a period of 24 h. Around 200 grams of cocoa beans were then broken with the shells removed manually to obtain the inner nibs for roasting. Roasting was carried out by heating the nibs at thin layer on a flat aluminium dish at 140°C for 35 minutes inside a hot-air oven (Hii *et al*., 2009). Upon roasting, the nibs were ground using an end runner mill into paste form (cocoa liquor). Sensory evaluation was carried out by five trained panels from Malaysian Cocoa Board (Nilai, Malaysia) and Ghanaian cocoa liquor was used as the reference sample. Rating was carried out by using a descriptive scales ranging from 1 to 10 and flavour notes assessed were cocoa, bitterness, astringency and sourness, where a score of 1 indicates extremely low flavour intensity and a score 10 indicates extremely high flavour intensity.

Statistical analysis

The statistical analyses were carried out in SPSS version 10 (IBM, USA), all th3e experimental data were performed for three replicates. The experimental data were analysed using one-way ANOVA and mean comparison using Duncan's Multiple Range Test at 95% confidence level.

Results and Discussion

Drying kinetics

Figure 2(A) shows that moisture ratios decreased exponentially with time as reported for most agricultural products (Waewsak *et al.*, 2006; Hii *et al*., 2009; Ndukwu *et al*., 2009) and the moisture ratio for samples dried from H80 is lower than samples dried at H70 and H60 during drying. Figure 2 (B) shows the drying rate curves for H60, H70 and H80, respectively. The initial drying rates were estimated at 0.15, 0.16 and 0.21 g H_2O g^{-1} dry solid.hr for H60, H70 and H80, respectively. The higher drying rate for H80 was due to the higher temperature which initiates greater driving force for drying to occur. Only falling rate period was observed in H80 but for H70 and H60 the initial period showed a rather reasonable existence of constant rate period due to the lower drying temperatures and the saturated surface moisture which is evaporating away from the samples. The rates of drying for all the experiments reduce significantly as the moisture content approaches 0.2 g H_2O g^{-1} dry solid.

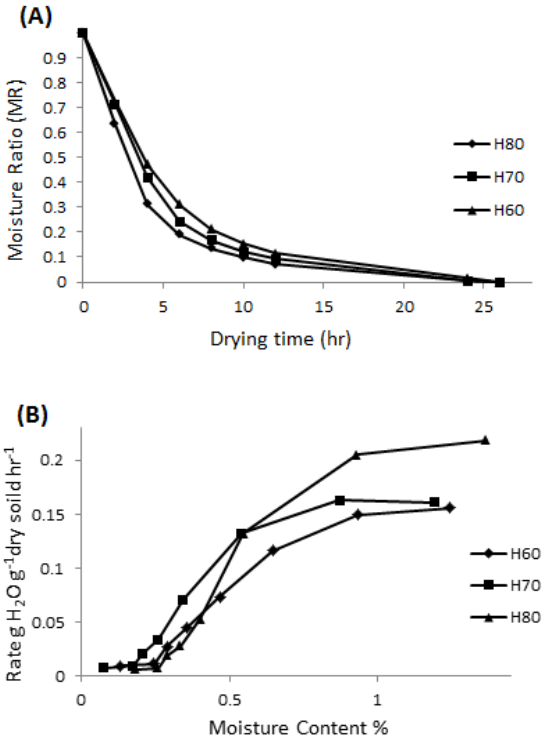


Figure 2. (A) Moisture ratio curves for cocoa beans dried for trials H60, H70 and H80; (B) Drying Rate curves of cocoa for trial H60, H70 and H80 respectively

Effective diffusivities

The effective diffusivities determined are in the range of 2.36 x 10^{-10} to 2.86 x 10^{-10} m^2s^{-1} (Figure 3) which are within the order of magnitudes reported for drying of food materials (10^{-12} - 10^{-8} m^2s^{-1}) (Doymaz *et al*., 2005; Waewsak *et al*, 2006). Comparing with published values for cocoa beans show similar observation where most of the values are in the order of 10^{-10} $m2s^{-1}$ (Hii *et al*., 2009). Artificial drying methods usually lead to higher activation energy values as opposed to sun drying due to the lower driving force under ambient air condition. The plot as shown in Figure 3 explains the relationship between effective diffusivity and temperature. The Arrhenius constant is a diffusivity constant equivalent to the diffusivity at infinitely high temperatures (Hii *et al*., 2009). The values of D_0 and E_a were calculated to be 7.16 x $10^{-9}m^2/s$ and 9.43 k J/mol respectively. The activation energy indicates the minimum barrier that needs to be overcome to initiate the moisture diffusion process during drying. The Arrhenius equation is interpreted in Equation (9) with the experimental results obtained.

$$D_{eff} = 7.16X10^{-9} \exp\left[-\frac{9.43}{R_g(T+273.15)}\right] \quad (9)$$

Total polyphenol content

Figure 4 shows the total polyphenols content of cocoa beans from H60, H70 and H80 trials analysed for 12, 24, 32 and 40 hours of drying, respectively.

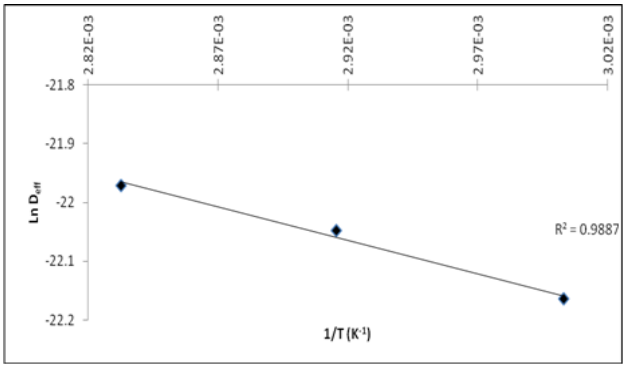
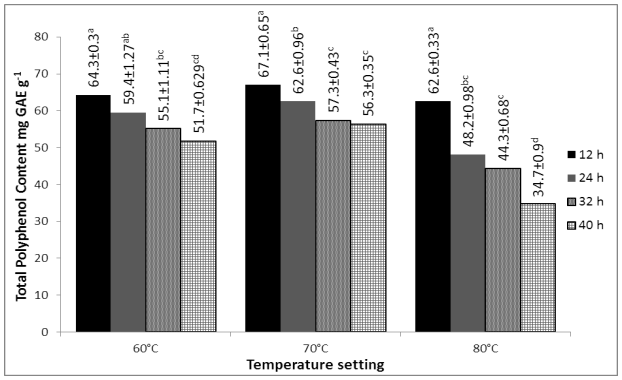


Figure 3. The Arrhenius relationship between the effective diffusivities and temperature

General trend shows reduction of total polyphenol content with increasing exposure time during drying. Significant difference ($p < 0.05$) was also noted for the polyphenol content between drying at 12 h and 40 h in all temperature treatments. Figure 4 shows maximum value of total polyphenol recorded at 70°C which indicates a higher retention of cocoa polyphenols at this temperature. Comparison between the samples dried at 60°C and 80°C show that the retention of cocoa polyphenols is higher at the lower temperature (60°C). The high polyphenol retention trend at low temperature cocoa drying as opposed to high temperatures have been noted in several literatures due to the thermal degradation of volatile phenolic constituents at higher temperatures (Ndukwu, 2009; Hii *et al*., 2011). This shows that thermal decomposition could play a more critical role in polyphenols degradation at higher drying temperature range (70°C - 80°C) whereas at the lower temperature range (70°C and below), the mechanism could be mainly attributed to enzymatic degradation during drying (Kyi *et al*., 2005).

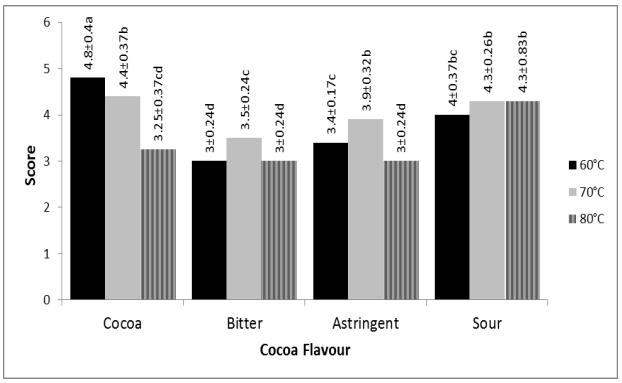
Sensory evaluation

Figure 5 shows results from the sensory evaluation carried out for the cocoa samples. Cocoa flavour is a desired attribute and ideally it should be preserved through proper fermentation and drying techniques. The sourness scores should be low with astringency and bitterness maintained at a lower level but shall not be completely removed from the overall flavour. Significant difference ($p < 0.05$) was observed for cocoa flavour attribute; this could be due to the sufficient time that the beans were provided for browning process to complete. The sourness scores were statistically non-significant ($p < 0.05$) but maintained a rather high reading as compared to the reference due to the production of acidic compounds during fermentation. Excessive sourness is not recommended as this will mask the



*Mean values having a common letter within the same temperature effect are not significant according to the Duncan's Multiple Range test at 5% Level

Figure 4. The total polyphenol contents of dried cocoa samples



*Mean values having a common letter within the same flavour attribute are not significant according to the Duncan's Multiple Range test at 5% Level

Figure 5. Flavour scores from sensory evaluation of cocoa

cocoa flavour during chocolate processing. Bitterness score is usually not influenced by processing as this is mainly due to the xanthine compounds inside the cocoa beans. Astringency showed a maximum score for H70 and significantly different from H80 ($p < 0.05$) which agreed well with the maximum total polyphenols (phenolic compounds imparts astringent taste) content recorded previously. The higher astringency flavour coupled with the higher sourness flavour has resulted in a slightly lower cocoa flavour in the dried beans but better than that from H80.

Conclusion

Results show that drying rate has a strong relationship with the drying temperature and heating time. Only falling rates were observed in H80 while constant rate period was observed in H70 and H60 due to the lower drying temperatures. The minimum energy required to initiate the drying was determined at 9.43 k J/mol. The analysis of total polyphenol content results shows a high retention of polyphenols at H70 dried samples. There is a considerable decline in amount of cocoa polyphenols as the temperature and exposure time increased. This is mainly due to the thermal degradation of cocoa polyphenols. This study is highly beneficial in understanding the fundamentals of high temperature effects and prolonged exposure times on cocoa polyphenols during drying.

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