Original article

The kinetics of polyphenol degradation during the drying of Malaysian cocoa beans

Tin Mar Kyi,[1] Wan Ramli Wan Daud,[2]* Abu Bakar Mohammad,[2] Mohd. Wahid Samsudin,[3] Abdul Amir Hassan Kadhum[2] & Meor Zainal Meor Talib[2]

1 Department of Industrial Chemistry, Yangon University, Myanmar
2 Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
3 Department of Chemistry, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

(Received 20 September 2001; Accepted in revised form 25 June 2003)

Summary The main objective of the study was to determine the kinetics of the polyphenol oxidation reaction in cocoa beans during air drying at various air temperatures and humidities. The temperatures used were between 40 and 60 °C and the relative humidities were between 50 and 80%. The higher the temperature and relative humidity of the drying air, the lower the amount of polyphenol residue in the cocoa beans, because of enzymatic oxidation of polyphenols. At higher drying temperatures, non-enzymatic oxidation of polyphenols could also occur. Computer simulation results gave rate constants for the polyphenol oxidation reaction (k_1) and the condensation reaction (k_2), at various air conditions, in the range of 0.055–0.200 and 0.136–0.155 h^{-1} respectively. The activation energies obtained for the polyphenol oxidation reaction were in the range of 27 800–30 312 J K^{-1} mol^{-1}. The reaction kinetics of the enzymatic browning reaction fitted a pseudo first-order reaction.

Keywords Activation energy, browning, oxidation, rate constant, relative humidity.

Introduction

Fermented cocoa beans are dried in order retain the 'chocolate' flavour developed during fermentation and to reduce the moisture content of the cocoa bean to about 7% (Akhir & Said, 1984; Said, 1993; Said *et al*., 1988). However, the drying process is not simply a removal of moisture for it also involves a residual fermentation process as well. The chemical changes that take place inside the beans during fermentation continue during drying, either until the moisture content drops to below 7% or until the enzymes are inactivated. During fermentation and drying, the polyphenols in cocoa beans undergo complex chemical changes that are known collectively as browning, these changes affect the flavour and colour of chocolate (Danehy, 1986). Although most polyphenols are reduced during fermentation and drying, they are still present in cocoa beans and impart astringent and bitter tastes (Jalal & Collin, 1977). The reduction of bitterness and astringency is because of the oxidation of polyphenols to insoluble tannins, which are the flavour precursor for chocolate processing (Jinap & Dimick, 1990; Haslam & Lilley, 1992; Lee, 1992). More recently, Misnawi *et al*. (2002) investigated the addition of crude cocoa polyphenol oxidase and purified tyrosinase from mushrooms to partially fermented cocoa beans to degrade polyphenols in order to reduce astrigency and bitterness, finding the latter enzyme to be more effective. In a recent paper (Wollgast & Anklam, 2000b), the importance of polyphenols as antioxidants to human health was highlighted.

There has been no extensive study on the kinetics of the browning reaction in cocoa beans,

*Correspondent: Fax: + 603 89252546;
e-mail: wramli@eng.ukm.my

doi:10.1111/j.1365-2621.2005.00959.x

especially under drying conditions. Previous research on the drying of cocoa beans has not considered these browning reactions at all (Bravo & McGaw, 1974; Daud *et al*., 1994, 1996; Fotso *et al*., 1994; Talib, 1994; Talib *et al*., 1995). As the browning reaction involves a complex reaction mechanism with many different molecules, it has probably proved too difficult to study previously.

Reactions can be classified as either enzymatic or nonenzymatic browning. The nonenzymatic browning (Maillard) reactions involve the carbonyl groups of reducing sugars and the amino groups of proteins which undergo chain reactions to produce coloured polymeric products (Hodge, 1953; Gooding, 1960; Sharp, 1960; Hodge & Osman, 1976; Eichner & Ciner-Doruk, 1981; Labuza, 1981). Enzymatic browning involves the transformation of phenolic compounds first to quinones and then to brown or black polymers under the catalytic influence of the polyphenol oxidase enzyme (McEvily *et al*., 1992).

Fermentation of cocoa beans, prior to drying, is necessary to ensure the formation of flavour precursors (Dimick, 1993). During fermentation, sucrose, the dominant sugar in cocoa beans, is hydrolysed to fructose and glucose by invertase present in the testa of the bean. Yeast, which proliferates in the presence of sugar, citric acid and anaerobic conditions, converts most of the sugar in the pulp to alcohol and carbon dioxide. Citric acid is lost, either in the 'sweating' stage or through microbial breakdown. As a result, a rise in pH and a small rise in temperature favours growth of lactic acid bacteria which convert glucose to lactic acid, alcohol and acetic acid. Bean death occurs at this time due to the heat generated, and the diffusion of ethanol and acetic acid into the bean (Wood & Loss, 1989). After bean death polyphenols diffuse from their storage cells and polymerize, oxidize and interact with proteins. The anaerobic changes occur mainly in fermentation, followed by aerobic oxidative changes, which continue during drying. During the aerobic phase, oxygen diffuses into tissue and the oxidase enzyme becomes active (Dimick, 1993). The oxidation of several complex polyphenolic substrates occurs by enzyme-catalysed coupled oxidation in which a simple phenolic molecule acts as the initial enzyme substrate and the *o*-quinone generated then participates in a coupled redox system with complex polyphenol (Haslam & Lilley, 1992).

Polyphenol oxidase catalyses the hydroxylation of mono-phenols to diphenols such as hydroquinone, and in a second step, the oxidation of colourless diphenols to highly coloured *o*-quinone, which is an extremely reactive intermediate. Ortho-quinone, formed by enzymatic oxidation, can react with a hydroquinone to yield a condensation product. In cocoa beans, anthocyanins are hydrolysed enzymatically to anthocyanidins, which polymerize with simple catechins to form high-molecular-weight procyanidins or complex tannins during fermentation (Roelofsen, 1958; Forsyth & Quesnel, 1963; Kim & Keeney, 1983).

(−)-Epicatechin polymerizes with (+)-catechin to form complex tannins during fermentation and is the major substrate for enzymatic browning during drying (Kim & Keeney, 1983). During the drying stage both (−)-epicatechin and procyanidins are oxidized enzymatically and the final result of polyphenol oxidation is the production of polymeric brown pigments (Dimick, 1993). Said *et al*. (1988) observed experimentally that there was a significant reduction in the content of polyphenolic compounds, especially (−)-epicatechin, in the pod storage period and degradation of the (−)-epicatechin and (+)-catechin was significant after a 5-day fermentation period, indicating that polyphenol degradation was already occurring during fermentation.

The objective of this paper was to investigate polyphenol degradation, which is one of the principal browning reactions, during the drying of Malaysian cocoa beans.

Kinetic model of enzymatic browning in cocoa beans

Reactions in foods have been found to generally follow either pseudo zero- or first-order kinetics. Labuza (1971), Labuza & Saltmarch (1981) and Franzen *et al*. (1990) found that the Maillard reaction (nonenzymatic browning) could be typically described by zero-order reaction kinetics. This is true in the sense that the concentration of the brown pigment products is negligible compared with the concentration of reactants present. The term pseudo is added to the order of the reaction

in biological materials, such as foods because the actual reaction mechanism and its kinetics are far more complex. The pseudo reaction orders in foods are therefore semi-empirical in nature and are not to be taken as reflecting actual reaction mechanism (Leahy & Reineccius, 1989).

The enzymatic browning can be represented by (Kyi *et al*., 1996):

$$\text{Polyphenol} + \text{Oxygen} \xrightarrow{k_1} o\text{-Quinone}$$

$$o\text{-Quinone} + \text{Hydroquinone} \xrightarrow{k_2} \text{Melanin} + \text{Water}$$

The kinetics of the oxidation of polyphenol is represented by:

$$-r_A = k_1 C_A^a, \tag{1}$$

$$r_{H_2O} = k_2 C_{H_2O}^b, \tag{2}$$

where r_A is the rate of polyphenol oxidation (kg kg^{-1} dry cocoa h^{-1}), $r_{H_2}O$ is the rate of water production (kg kg^{-1} dry cocoa h^{-1}), C_A is the concentration of polyphenol (kg kg^{-1} dry cocoa), $C_{H_2}O$ is the concentration of water (kg kg^{-1} dry cocoa), k_1 and k_2 are the rate constants (h^{-1}) for reactions 1 and 2 respectively, and a and b are the orders of reactions 1 and 2 respectively. Orthoquinone, formed by enzymatic oxidation of polyphenol in the first reaction, is an extremely reactive intermediate compound that immediately reacts in the second reaction. Hence it can be assumed that the rate of polyphenol oxidation and condensations are of the same order. The browning reaction can then be described sufficiently by the first reaction. If this reaction is assumed to be first order, then the kinetics of polyphenol oxidation reaction can be estimated by

$$\ln C_A = \ln C_{A_0} - k_1 t, \tag{3}$$

where C_{A_0} is the initial concentration of polyphenol (kg kg^{-1} dry cocoa). The determination of the the parameter k_2 in the second equation is much more complex. Free moisture in the cocoa beans and water from the condensation reaction is removed during drying. The model for drying with a chemical reaction could be written as:

$$\frac{\partial X}{\partial t} = K_1 \nabla^2 X + K_2 \nabla^2 T - \frac{r_{H_2O} M_{H_2O}}{\rho_S}, \tag{4}$$

$$\frac{\partial T}{\partial t} = K_3 \nabla^2 X + K_4 \nabla^2 T + \frac{r_{H_2O} \Delta H M_{H_2O}}{\rho_S C_{p_S}}, \tag{5}$$

where $K_1 = D$, $K_2 = D_d$, $K_3 = D\varepsilon\Delta H/C_{p_s}$, $K_4 = (\lambda_S/\rho_S C_{p_s}) + (D\delta\varepsilon\Delta H/C_{p_s})$, D is the moisture diffusivity, D_d is the thermal diffusivity coefficient, $M_{H_2}O$ is the molecular weight of water, λ_S is the thermal conductivity of cocoa, ε is the phase conversion factor, δ is the thermal gradient coefficient, ΔH is the latent heat of evaporation, ρ_S is the density of cocoa, C_{p_S} is the specific heat of cocoa, X is the dry basis moisture content of the sample and T its temperature. Assuming that the second reaction is first order, then substituting eqn 2 into eqns 4 and 5, we get:

$$\frac{\partial X}{\partial t} = K_1 \nabla^2 X + K_2 \nabla^2 T - \frac{k_2 C_{H_2O} M_{H_2O}}{\rho_S}, \tag{6}$$

$$\frac{\partial T}{\partial t} = K_3 \nabla^2 X + K_4 \nabla^2 T + \frac{k_2 C_{H_2O} \Delta H M_{H_2O}}{\rho_S C_{p_S}}. \tag{7}$$

The temperature, absolute humidity and air velocity of the surrounding fluid is assumed uniform and the dominant modes for heat and mass transfer to the environment are by convection and evaporation. The cocoa bean is assumed to be a spherical body and there is no significant shrinkage during the drying period. The amount of moisture produced and heat evolved from the polyphenol oxidation reaction is very small compared with the original moisture content of cocoa bean and the temperature of the environmental chamber. The mass flux at the boundary condition is expressed as:

$$-\rho D(\nabla X + \delta \nabla T) = K_G \sigma (Y_S - Y_G) = J, \tag{8}$$

whereas the heat flux equation is given by:

$$\begin{aligned} &-\varepsilon \Delta H \rho D(\nabla X + \delta \nabla T) - \lambda \nabla T \\ &\quad = h_t (T_S - T_a) + \Delta H J, \end{aligned} \tag{9}$$

where h_t is heat transfer coefficient, J is the mass flux, K_G is the mass transfer coefficient, T_S and T_a are the surface and ambient air temperatures respectively, Y_G is the humidity of surrounding air, Y_S is the saturated humidity of surrounding air and σ is the psychrometric coefficient.

The value of the parameter k_2 in the second equation is determined by simulating the drying using eqns 6–9 and a known value of moisture diffusion in cocoa beans (Talib, 1994), and comparing the experimental and the simulated drying moisture profiles. This is achieved by using a simple explicit method (LSE) with a modified implicit

Crank Nicholson (LCN) finite difference algorithm based on a parabolic equation in spherical polar coordinates (Ibrahim & Daud, 1989; Ibrahim, 1994).

Materials and methods

Sample preparation of cocoa beans

Cocoa beans samples were obtained from Sungai Ruan, Temerloh, Pahang, Malaysia. The freshly harvested cocoa pods were stored for 10 days in a shady place and fermented for 5 days with single turning after 48 h. The fermented cocoa beans were kept in a deep freezer at a temperature of −20 °C. The sample solutions for the analysis of polyphenols were prepared hourly after withdrawal of the cocoa seed sample from the environmental chamber. A sensitive HPLC method (Kim & Keeney, 1983) was used for the analysis of polyphenols in cocoa beans.

Drying of cocoa beans

An environmental chamber (Isuzu model μ2501, Isuzu, Isuzu, Japan) was used for drying, air flowed at approximately 1 m s^{-1}, at a fixed relative humidity (RH) and temperature around the sample for about 5 h (Talib, 1994; Daud *et al*., 1996). The working range for air RH and temperature was 50–80% and 40–60 °C respectively. The average bean weight suitable for processing is equivalent to 83–100 beans per 100 g (Wood & Loss, 1989). The sample weight used was 20 g.

Preparation of polyphenol sample solutions for HPLC analysis

The (−)-epicatechin and (+)-catechin were determined and quantified by the modified method of Kim & Keeney (1983). Dried cocoa samples were ground in a blender. Pieces of dry ice were added to the beans to prevent melting of cocoa lipids because of the frictional heating of grinding. After grinding the powder was sieved through a 710-μm screen. Powdered samples were defatted for 16–18 h using petroleum ether (B.P. 35–60 °C) as solvent. The samples were dried in a vacuum oven at 65 °C for 5 min and stored in the dark inside a desiccator over silica gel prior to the extraction procedures.

For the extraction of polyphenols, 0.5 g of defatted cocoa powder and 80 mL of 80% aqueous acetone in a 125-mL Erlenmeyer flask were sonicated for 30 min in a sonic cleaning device filled with ice water. A clear filtrate was obtained by vacuum filtration through Whatman No. 1 filter paper. Glassware and residue were washed with 80% aqueous acetone and the total filtrate was made up to 100 mL in a volumetric flask. A measured 5 mL portion, was dried in a freeze dryer. The residue was resuspended into 10 mL aliquots of distilled water by swirling for 2 min in a 45 °C water bath. The solutions were pooled and injected through a C18 reverse-phase SEP-PAK (Waters Assoc., Milford, MA, USA) that had been pre-conditioned with 2 mL of methanol followed by 5 mL of distilled water. The chemical compounds (+)-catechin and (−)-epicatechin were retained by the SEP-PAK, and eluted with about 10 mL of 40% aqueous CH_3OH. The final volume of eluant was made up to 10 mL in a volumetric flask. A 10 μL volume of this final solution was injected into the HPLC analytical column. Separation of polyphenol was done in a C18 column (Restek Corporation, Bellefonte, PA, USA) using a mobile phase of water:methanol:acetic acid (87:8:5 by volume). Polyphenols were detected at 280 nm and quantified by comparing peak area of the sample to those of standards (Kyi, 2001).

HPLC apparatus and operating conditions

Measurement of browning is a difficult analytical problem. Toribio & Lozano (1984) used colour measurement to follow the kinetics of nonenzymatic browning in an apple juice concentrate during storage. The complexity of the reactions and the various compounds involved (Hodge, 1953; Spark, 1969; Toribio & Lozano, 1984) make it difficult to study the reactions by means of a simple analytical chemical method; however, Wollgast & Anklam (2000a) reviewed analytical methods for analysis, quantification, isolation, purification and structural elucidation of polyphenols in cocoa and they recommended the use of HPLC with a variety of detectors. Wollgast *et al*. (2000) developed a very accurate method for separation and identification of procyanidins using reverse phased HPLC with electrospray ionization mass spectrometric and tandem mass

spectrometric detection, but a good, rapid, HPLC method for the determination of polyphenols in cocoa beans developed by Kim & Keeney (1983), was used in this study.

An analytical column (Restek Corp.) equipped with a pump (Gilson pump 305, Villiers-le-Bel, France) and an ultravoilet detector (Gilson UV detector model 116) set at 280 nm wave length was used. The chromatographic column was 25 cm × 4.6 mm i.d. (C18 Waters Assoc.) and was preceded by a Restek pre-column (Restek Corp.). The mobile phase was prepared with distilled water, methanol and acetic acid (87:8:5 by volume). This mobile phase was filtered through a 0.45 μm pore size filter and deaerated by vacuum. The flow rate of the mobile phase was set at 1.5 mL min^{-1} during the measurement of polyphenol. At the end of each day, the chromatographic system was flushed with distilled, filtered and deaerated water for 30 min followed by flushing overnight with methanol (HPLC grade), as recommended by the supplier, ensuring removal of lipophilic substances from the column. The system was again flushed with distilled, filtered and deaerated water for 30 min before separating another sample solution.

Results and discussions

Degradation of polyphenols

The HPLC method successfully separated (+)-catechin, and (−)-epicatechin, and the rate of degradation of the latter was found to be greater than that of the former. However, in this study, total polyphenol degradation was used because the proposed reaction kinetics model was based on the total polyphenols. Figures 1 and 2 show the degradation of the total polyphenol content (catechin and epicatechin) with time, during cocoa drying at different air temperatures and relative humidities. The concentration of total polyphenol declined rapidly during drying because of the enzymatic oxidation of polyphenols. The experimental results show that the higher the temperature and RH of the drying air, the lower the residual amount of polyphenol in the cocoa beans during drying. The logarithm of total polyphenols vs. time at 40 °C and different relative humidities is shown in Fig. 2. Polyphenol degradation fitted a

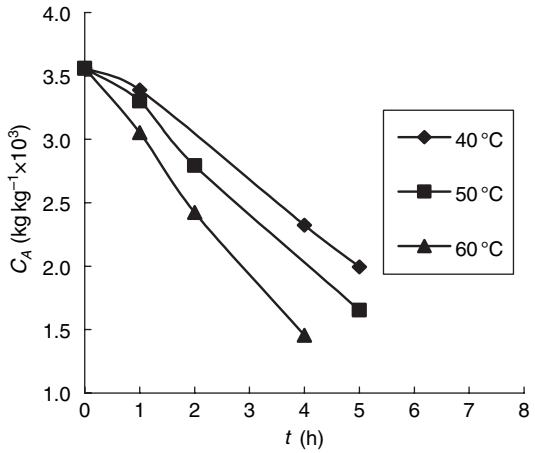

Figure 1 Total polyphenols degradation in cocoa beans with time during drying at 50% RH.

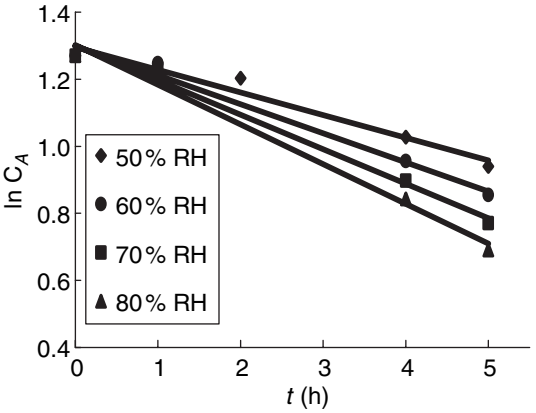

Figure 2 Correlation of the logarithm of total polyphenol with time at 40 °C.

pseudo first-order reaction with a coefficient of correlation, $r^2 > 0.95$. The rate constants and activation energies are presented in Tables 1 and 2. These result are consistent with those reported by Franzen *et al.* (1990).

Table 1 Reaction rate constant, k_1 at different air temperatures and relative humidities

	k_1 (h^{-1})		
Air relative humidity (%)	**40 °C**	**50 °C**	**60 °C**
50	0.0555	0.0815	0.1053
60	0.0713	0.0939	0.1365
70	0.0863	0.1136	0.1693
80	0.0991	0.1303	0.1999

Table 2 Activation energy E_{a_1} for polyphenol degradation in cocoa beans at different air relative humidities

Air relative humidity (%)	E_{a_1} (J K^{-1} mol^{-1})	r^2
50	27 800	0.9906
60	28 085	0.9889
70	29 135	0.9847
80	30 324	0.9793

Effect of temperature and RH on polyphenol degradation

The results in Table 1 show that the polyphenol degradation rate increases with increasing temperature and RH. This is consistent with previous studies on browning in fruits, potatoes and cabbage (Legault *et al.*, 1951; Hendel *et al.*, 1955; Reynolds, 1965; Mizrahi *et al.*, 1970a,b; Labuza *et al.*, 1972b; Waletzko & Labuza, 1976; Kanner *et al.*, 1982). As with the results of Legault *et al.* (1951) and Resnik & Chirife (1979) for fruit, potato and cabbage, the temperature dependence of cocoa browning followed the Arrhenius Law as shown in Fig. 3. The activation energy of polyphenol oxidation reaction, calculated from the slope of $\ln k_1$ vs. $1/T$, increased with RH (Table 2).

Determination of k_2

The experimental drying data at various air temperatures and RHs were compared with the simulated drying data obtained using eqns 6–9 for the same conditions, using known values of the moisture diffusivity (D) in cocoa (Talib, 1994), with various k_2 values. For example, Fig. 4 shows the moisture content profiles of the experimental drying data and the simulated data for 40 °C, 50% RH, $D = 8.09 \times 10^{-5}$ m^2 s^{-1} and $k_2 = 0.1364$ h^{-1}, and Fig. 5 shows both the simulated temperature profile for the same condition. The values of the rate constant k_2 which best fit the simulated data to the experimental drying data are shown in Table 3. The results in Table 3 show that the condensation reaction rate increased with increasing temperature and decrease with increasing RH.

Correlation of k_1 and k_2

The correlations between the polyphenol oxidation reaction rate constant k_1 and the

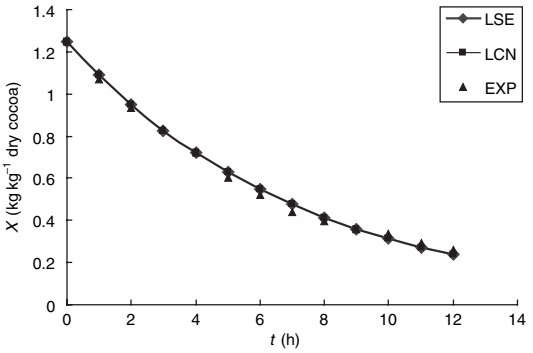

Figure 4 Moisture content (X) profiles of the experimental drying data (EXP) and the simulated data (LSE, LCN) for 40 °C, 50% RH, $D = 8.09 \times 10^{-5}$ m^2 s^{-1} and $k_2 = 0.1364$ h^{-1}.

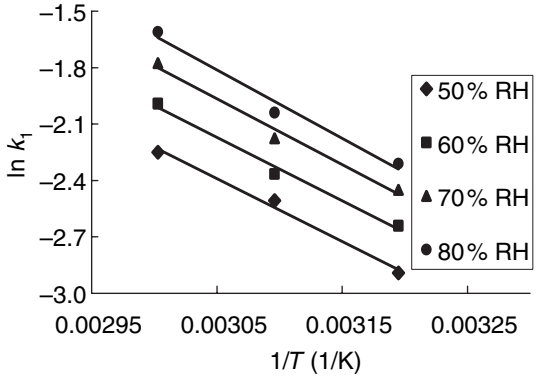

Figure 3 Correlation of $\ln k_1$ with $1/T$ at different air relative humidities.

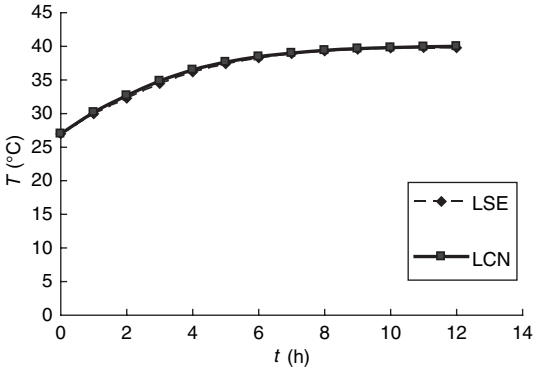

Figure 5 Temperature profiles (T) of the simulated data (LSE, LCN) for 40 °C, 50% RH, $D = 8.09 \times 10^{-5}$ m^2 s^{-1} and $k_2 = 0.1364$ h^{-1}.

Table 3 Reaction rate constant, k_2, at different air temperatures and relative humidities

	k_2 (h^{-1})		
Air relative humidity (%)	**40 °C**	**50 °C**	**60 °C**
50	0.1364	0.1592	0.2081
60	0.1201	0.1490	0.1824
70	0.1124	0.1391	0.1664
80	0.1001	0.1280	0.1548

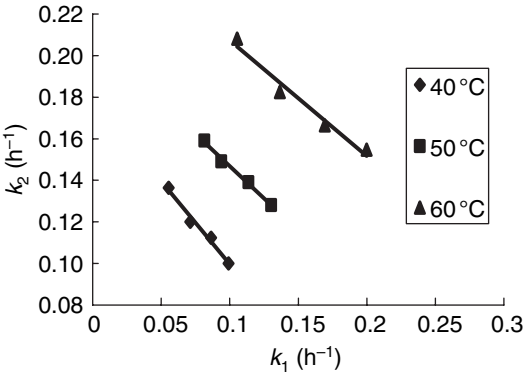

Figure 6 Correlation of k_1 with k_2 at different air temperatures.

condensation reaction rate constant k_2 at different temperatures (Fig. 6) are straight lines, with $r^2 > 0.96$. The rate constant k_1 increased with both increasing temperature and RH, whereas k_2 increased with increasing temperature but decreased with increasing RH. The linear equations of the correlations shown in Fig. 6 are as follows:

$$k_2 = 0.801k_1 + 0.1798 \quad r^2 = 0.9839 \text{ at } 40\,\text{C}$$
$$k_2 = 0.6176k_1 + 0.2086 \quad r^2 = 0.9928 \text{ at } 50\,\text{C}.$$
$$k_2 = 0.5562k_1 + 0.2629 \quad r^2 = 0.96 \text{ at } 60\,\text{C}$$

This linear relationship validates the earlier assumptions that both reactions are of the same order.

Conclusions

The concentration of polyphenol in cocoa beans declines rapidly during drying under air conditions of 40–60 °C and 50–80% RH. The higher the temperature and RH of the drying air, the faster the chemical reactions inside the cocoa beans during drying. The reaction kinetics of polyphenol oxidation and condensation reactions fit a pseudo first-order reaction. Linear correlation between k_1 and k_2 gave straight lines with $r^2 > 0.96$.

Acknowledgments

The authors thank the Malaysian Ministry of Science, Technology and Environment for sponsoring this work under project IRPA 03-02-02-0028.

References

Akhir, H. & Said, M. (1984). *The Importance of Drying For Producing Good Quality Beans*. Pp. 34–48. Serdang, Malaysia: Cocoa/Coconut Research Division, Malaysian Agricultural Research & Development Institute.

Bravo, A. & McGaw, D.R. (1974). Fundamental artificial drying characteristics of cocoa beans. *Tropical Agriculture (Trinidad)*, **51**, 395–406.

Danehy, P.J. (1986). Maillard reactions: nonenzymatic browning in food systems with special reference to the development of flavour. *Advances in Food Research*, **30**, 77–100.

Daud, W.R.W., Talib, M.Z.M. & Ibrahim, M.H. (1994). Drying of cocoa beans. *Drying*, **94**, 1129–1135.

Daud, W.R.W., Talib, M.Z.M. & Ibrahim, M.H. (1996). Characteristic drying curves of cocoa beans. *Drying Technology*, **14**, 2387–2396.

Dimick, P.S. (1993). *Penn State Chocolate Manufacture Short Course*. Pp. 29–465. University Park, PA: Penn State University.

Eichner, K. & Ciner-Doruk, M. (1981). Formation and decomposition of browning intermediates and visible sugar-amine browning reactions. In: *Water Activity: Influences on Food Quality* (edited by L.B. Rockland & G.F. Stewart). Pp. 567–572. New York: Academic Press, Inc.

Forsyth, W.G.C. & Quesnel, V.C. (1963). The mechanism of cocoa curing. *Advances in Enzymology*, **25**, 457–463.

Fotso, P.J., Lecomte, D., Pomathios, L. & Nganhou, J. (1994). Convective drying of cocoa beans: drying curves for various external condition. *Drying*, **94**, 937–944.

Franzen, K., Singh, R.K. & Okos, M.R. (1990). Kinetics of nonenzymatic browning in dried skim milk. *Journal of Food Engineering*, **11**, 225–239.

Gooding, E.G.B. (1960). The storage behaviour of dehydrated foods. In: *Recent Advances in Food Science*, Vol. 2 (edited by J. Hawthorn & J.M. Leitch). Pp. 22–40. London: Butterworths.

Haslam, E. & Lilley, T.H. (1992). Polyphenol complexation: a study in molecular recognition. In: *Phenolic Compounds in Food and their Effects on Health 1* (edited by C.T. Ho, C.Y. Lee & M.T. Huang). Pp. 8–47. ACS Symposium Series 506, 202nd National Meeting of the American Chemical Society. Washington, DC: American Chemical Society.

Hendel, C.E., Silveira, V.G. & Harrington, W.O. (1955). Rates of nonenzymatic browning of white potato during dehydration. *Food Technology*, **9**, 433–438.

Hodge, J.E. (1953). Dehydrated foods: chemistry of browning reactions in model systems. *Journal of Agricultural and Food Chemistry*, **1**, 928–943.

Hodge, J.E. & Osman, E.M. (1976). Carbohydrates. In: *Food Chemistry* (edited by O.R. Fennema). Pp. 91–97. New York: Marcel-Dekker Inc.

Ibrahim, M.H. (1994). Drying of oil palm kernels. PhD Thesis, Universiti Kebangsaan Malaysia, Bangi, Selangor.

Ibrahim, M.H. & Daud, W.R.W. (1989). Drying of a porous sphere in an air stream. In: *Proceedings of the Sixth International Conference on Numerical Methods in Thermal Problems*, 3–7 July 1989, Swansea, UK, Part 2 (edited by R.W. Lewis & K. Morgan). Pp. 938–947. Swansea, UK: Pine Ridge Press.

Jalal, M.A.F. & Collin, H.A. (1977). Polyphenols of mature plant, seedling and tissue cultures of theobroma cacao. *Phytochemistry*, **16**, 1377–1380.

Jinap, S. & Dimick, P.S. (1990). Acidic characteristics of fermented dried cocoa beans from different countries of origin. *Journal of Food Science*, **55**, 547–550.

Kanner, J., Fishbein, J., Shalom, P., Harel, S. & Beb-Gera, I. (1982). Storage stability of orange juice concentrate packaged aseptically. *Journal of Food Science*, **47**, 429–432.

Kim, H. & Keeney, P.G. (1983). Method of analysis for (−) epicatechin in cocoa beans by high performance liquid chromatography. *Journal of Food Science*, **48**, 548–551.

Kyi, T.M. (2001). Drying with chemical reaction in cocoa bean drying. PhD Thesis, Universiti Kebangsaan Malaysia, Bangi, Selangor.

Kyi, T.M., Daud, W.R.W., Mohammad, A.B., Samsuddin, W. & Kadhum, A.A.H. (1996). Drying with chemical reaction. In: *Proceedings of the 12th Symposium of Malaysian Chemical Engineers*. Pp. 15–21. Bangi, Selangor: Universiti Kebangsaan Malaysia.

Labuza, T.P. (1971). Kinetics of lipid oxidation in foods. *CRC Critical Review of Food Technology*, **2**, 355–405.

Labuza, T.P. (1981). The nonenzymatic browning reactions as affected by water in foods. In: *Water Activity: Influences on Food Quality* (edited by L.B. Rockland & G.F. Stewart). Pp. 605–650. New York: Academic Press.

Labuza, T.P. & Saltmarch, M. (1981). Kinetics of browning and protein quality loss in whey powders during steady state and nonsteady state storage conditions. *Journal of Food Science*, **47**, 92–95.

Labuza, T.P., McNally, L., Gallangher, D., Hawkes, J. & Hurtado, F. (1972b). Stability of intermediate moisture foods, 1. Lipid oxidation. *Journal of Food Science*, **37**, 154–159.

Leahy, M.M. & Reineccius, G.A. (1989). Kinetics of formation of alkyl pyrazines: effect of type of amino acid and type of sugar. In: *Flavor Chemistry: Trends and Developments* (edited by R. Teranishi, R. Buttery & F. Shahidi). Pp. 76–91. ACS Symposium Series No. 388. Washington, DC: American Chemical Society.

Lee, C.Y. (1992). Enzymatic oxidation of phenolic compounds in fruits. In: *Phenolic Compounds in Food and Their Effects on Health 1* (edited byC.T. Ho, C.Y. Lee & M.T. Huang). Pp. 305–316. ACS Symposium Series 506, 202nd National Meeting of the American Chemical Society, Washington, DC: American Chemical Society.

Legault, R.R., Hendel, C.E., Talburt, W.F. & Pcol, M.F. (1951). Browning of dehydrated sulfited vegetables during storage. *Food Technology*, **5**, 417–423.

McEvily, A.J., Iyengar, R. & Gross, A.T. (1992). Inhibition of polyphenol oxidase by phenolic compounds. In: *Phenolic Compounds in Food and Their Effects on Health 1* (edited by C.T. Ho, C.Y. Lee & M.T. Huang). Pp. 318–325. ACS Symposium Series 506, 202nd National Meeting of the American Chemical Society, Washington, DC: American Chemical Society.

Misnawi, Selamat, J., Bakar, J. & Saari, N. (2002). Oxidations of polyphenols in unfermented and partly fermented cocoa beans by cocoa polyphenol oxidase and tyrosinase. *Journal of Science of Food and Agriculture*, **82**, 559–566.

Mizrahi, S., Labuza, T.P. & Karel, M. (1970a). Computer aided predictions of extent of browning in dehydrated cabbage. *Journal of Food Science*, **35**, 799–803.

Mizrahi, S., Labuza, T.P. & Karel, M. (1970b). Feasibility of accelerated tests for browning in dehydrated cabbage. *Journal of Food Science*, **35**, 804–807.

Resnik, S. & Chirife, J. (1979). Effect of moisture content and temperature on some aspect of nonenzymatic browning in dehydrated apple. *Journal of Food Science*, **44**, 601–605.

Reynolds, T.M. (1965). Chemistry of nonenzymatic browning. *Advances in Food Research*, **14**, 167–283.

Roelofsen, P.A. (1958). Fermentation, drying, and storage of cocoa beans. *Advances in Food Research*, **8**, 225–296.

Said, M.B. (1993). Over fermentation of cocoa beans and its effect on quality. In: *Fermentation* (edited by N. Ramli). Pp. 49–52. Bangi, Selangor: Malaysian Cocoa Board.

Said, M.B., Musa, M.J. & Biehl, B. (1988). An integrated approach towards quality improvement of Malaysian cocoa beans. In: *The Proceedings of the 10th International Conference on Cocoa*, Santo Domingo. Pp. 767–773.

Sharp, J.G. (1960). Nonenzymatic browning deterioration in dehydrated meat. In: *Recent Advances in Food Science*, Vol. 2 (edited by J. Hawthorn & J. Leitch). Pp. 65–73. London: Butterworths.

Spark, A.A. (1969). Role of amino acids in nonenzymatic browning. *Journal of Science in Food and Agriculture*, **20**, 308–316.

Talib, M.Z.M. (1994). Ciri-Ciri Pengeringan Biji Koko. MSc Thesis, Universiti Kebangsaan Malaysia, Bangi, Selangor.

Talib, M.Z.M., Daud, W.R.W. & Ibrahim, M.H. (1995). Moisture desorption isotherms of cocoa beans. *Transaction of the American Society of Agricultural Engineers*, **38**, 1153–1155.

Toribio, J.L. & Lozano, J.E. (1984). Nonenzymatic browning in apple juice concentrate during storage. *Journal of Food Science*, **49**, 889–892.

Waletzko, P. & Labuza, T.P. (1976). Accelerated shelf-life testing of an intermediate moisture food in air and in an

oxygen-free atmosphere. *Journal of Food Science*, **41**, 1338–1344.

Wollgast, J. & Anklam, E. (2000a). Review on polyphenols in theobroma cacao: changes in composition during the manufacture of chocolate and methodology for identification and quantification. *Food Research International*, **33**, 423–447.

Wollgast, J. & Anklam, E. (2000b). Polyphenols in chocolate: is there a contribution to human health. *Food Research International*, **33**, 449–459.

Wollgast, J., Pallaroni, L., Agazzi, M.-E. & Anklam, E. (2000). Analysis of procyanidins in chocolate by reversed-phase high performance liquid chromatography with electrospray ionisation mass spectrometric and tandem mass spectrometric detection. *Journal of Chromatography A*, **926**, 211–220.

Wood, G.A.R. & Loss, R.A. (1989). *Cocoa*, 4th edn. Pp. 450–520. London: Longmans.

