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Effect of Roasting Time and Temperature on Volatile Component Profiles during Nib Roasting of Cocoa Beans (*Theobroma cacao*)

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Abstract: The effect of nib roasting time and temperature on volatile component profiles was studied using response surface methodology (RSM) which consisted two independent variables: time (5–65 min) and temperature (110–170°C). A steam distillation extraction (SDE) method was used to extract and gas chromatograph–mass spectrometry equipped with an ICIS data system was used to identify the volatile compounds. Tetramethylpyrazine, trimethylpyrazine, phenethyl acetate, isoamyl acetate, 3-methylbutyl acetate, phenylacetaldehyde, benzaldehyde and 2-phenylethanol were present in all treatments. Pyrazine formation increased as roasting time and temperature were increased. The number of pyrazines increased from 4 to 11 and 25, respectively, when roasting, time was increased from 5 to 35 and 65 min at 140°C. The unit area of esters increased (up to 1700–1800) when the roasting time was increased from 15 to 65 min (at 110–120°C). However, the unit area of carbonyls linearly decreased with an increasing roasting temperature at shorter time (5–25 min). The unit area of phenols was enormously reduced at the highest roasting temperature (160–170°C) with longest roasting time (45–65 min) while that of alcohol slightly decreased as roasting time and temperature were increased. © 1998 SCI.

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Key words: nib; roasting; time; temperature; pyrazines; esters; carbonyls.

INTRODUCTION

The nib of cocoa beans (*Theobroma cacao*), when roasted, gives a great impact on flavour. The quality of the roasted nib is dependent on the origin of the beans and roasting conditions. During roasting, Maillard reactions plays a major role in the formation of the cocoa flavour (Ziegleder 1991). These reactions involve two major precursors namely the free amino acids and reducing sugars which develop during fermentation (Ziegleder and Biehl 1988). The initial stage of the Maillard reaction involves the condensation of the carbonyl group of a reducing sugar with an amino compound, followed by the degradation of the condensation products to give a number of different compounds.

In the chocolate industry, whole bean roasting is still a common practice, however in the cocoa press industry nib roasting is more common (Kattenberg and Kemmink 1993). Nib roasting has been associated with several advantages such as a more uniform distribution of heat, rapid evaporation of water from the nib than from the whole bean and increase in output for the same amount of energy input (Dimick and Hoskin 1981). The nib, obtained by breaking the cocoa beans and separating the broken shells by winnowing, are usually roasted under various methods, ie batch or continuous method, direct or indirect heating and dry or wet conditions.

Since this modern technique has been introduced to the chocolate industry, the proper roasting time and temperature are still not established. Therefore, the objective of the study was to determine the effect of

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roasting time and temperature on the volatile components profile of cocoa nib.

MATERIALS AND METHODS

Cocoa samples

Fermented dried commercial beans were obtained from Malaysian Cocoa Manufacturing, Seremban, Negeri Sembilan. Upon arrival, the beans were left overnight at room temperature (27°C) before being packed and double sealed in plastic bags (5 kg per bag) the next morning. The bags were kept in a cold room (5°C) before further evaluation.

Chemicals

n-Pentane (bp 35·5–36·5°C), chloroform and petroleum-ether (bp 40–60°C) were obtained from Ajax Chemicals while methanol, sodium hydroxide and sodium sulphate anhydrous were from BDH Chemicals.

Sample preparation

Dried beans were preheated in the ventilated oven at 50°C until the moisture was reduced to 6%. The beans were then deshelled manually using cocoa breaker (Limprimita). The broken nibs were then roasted at different times and temperatures according to the central composite rotatable design (CCRD) (Cochran and Cox 1957). Two variables were used in the design: roasting time (ranged from 5 to 65 min) and temperature (ranged from 110 to 170°C). The values of the independent variables in each roasting treatment were coded as −1·414, −1, 0, +1 and +1·414. Details of actual values of the two variables are shown in Table 1.

Roasting

The oven was set at the desired temperature (110, 119, 140, 161 and 170°C) (Table 1) and was maintained for at least 1 h at that temperature to thoroughly stimulate the nib interior and reach equilibrium. About 500 g of nibs were placed in the tray (48 cm × 35 cm) and spread in a layer (3–4 mm thick). The door was opened and closed as quickly as possible before and after placing the tray of samples. The time of roasting was started immediately as the door was closed after the placement of the samples. The nib were roasted at 5, 14, 35, 56 and 65 min (Table 1). The nib were kept in a sealed container after cooling at room temperature (27°C).

TABLE 1
Central composite design for two factors and level of independent variables

Roasting treatment	*Temperature (°C)*		*Time (min)*	
	Code (X1)	*Temperature (°C)*	*Code (X2)*	*Time (min)*
1	−1	119	−1	14
2	1	161	−1	14
3	−1	119	1	56
4	1	161	1	56
5	−1·414	110	0	35
6	1·414	170	0	35
7	0	140	−1·414	5
8	0	140	1·414	65
9	0	140	0	35
10	0	140	0	35
11	0	140	0	35
12	0	140	0	35
13	0	140	0	35

Determination of volatile components

One hundred grams of ground nib were added to distilled water (200 ml) and heated for 60 min using Likens Nickerson's simultaneous distillation extraction (SDE) apparatus (Schultz *et al* 1977). The volatiles were trapped in pentane (30 ml) and concentrated (1 ml) using nitrogen flow. The volatiles were analysed on a gas chromatograph HP model 5890 Series II equipped with an FID detector. The analyses were performed on a 50 m × 0·32 m × 0·3 μm (film thickness) BPX5 column. Both injector port and detector temperatures were held at 280°C. The oven was increased from 30–250°C at 2°C min^{-1}. The effluent from the gas chromatographic column (flow rate 25 ml of He min^{-1}) was split so that 20% passed into the detector. Volatile component profiles were tentatively identified by using gas chromatograph–mass spectrometry.

Gas chromatography–mass spectrometry

Gas chromatograph–mass spectrometry, Finnigan SSQ 710 equipped with an ICIS data system operating in El mode, was used to identify the volatile compounds. The column used was BPX5 (25 m × 0·32 × 0·30 μm). The injector and column temperatures were 280°C and 300°C, respectively. The carrier gas used was helium with a flow rate of 25 ml min^{-1}; the ion temperature was 150°C which scanned from 100 to 250 Au in 1·00 ± 0·05 s with electron energy of 70 eV, emission current of 200 μV and electron multiplier of 1200 eV. Tentative quantification of volatiles was determined by using ethyl 9(*Z*)-hexadecanoate as a reference. The unit area of every single compound (fit score more than 900)

was divided to ethyl 9(*Z*)-hexadecenoat to get a unit area.

Statistical analyses

The data were statistically analysed for ANOVA and least significant different (Duncan's multiple range test) using a Statistical Analytical System (SAS 1986). The regression coefficient were used to plot three dimensional plots on the response surface which was generated by Statistical Graphics Corporation (Manugistics Inc).

RESULTS AND DISCUSSION

The number of compounds identified for different roasting time and temperatures are shown in Table 2. The total number of compounds varies depending on degree of roasting temperature and time. The results show that the number of compounds increased from 40 to 47 as the roasting time was increased from 5 to 65 min at 140°C roasting temperature. A similar trend was also observed when roasting temperature was increased from 110 to 140 and 170°C at 35 min roasting time in which the total number of compounds identified increased from 41 to 47 and 48, respectively.

Overall, about 53 compounds were identified, with pyrazines and esters being the major compounds (Table 2). In total, 14 pyrazines, 20 esters, 3 carbonyls, 3 phenols, 3 alcohols, 2 hydrocarbons, 2 ketones, 2 acids, 2 monoterpenes hydrocarbons, 1 benzenoid hydrocarbons, and 1 furan were identified.

The list of compounds identified with their unit area are shown in Table 3. The major compounds found in all samples were tetramethylpyrazine, trimethylpyrazine, phenetyl acetate, butyl acetate, isoamyl acetate, 3-methylbutyl acetate, 2 methylbutyl acetate, phenylacetaldehyde, benzaldehyde, and 2-phenylethanol (Table 3). According to Silwar (1988), the major constituents of cocoa aroma are 2-phenylacetaldehyde, tetramethylpyrazine, benzaldehyde, 2-phenylethanol and isovaleric acid.

Pyrazines

Table 2 shows that the number of pyrazines present in nib increased from 4 to 10 and 11 when roasting time was increased from 5 to 35 and 65 min (at 140°C), respectively. The number of pyrazines components also increased from 5 to 11 when the roasting temperature were increased from 119°C to 161°C (at 14 min) (Table 2). Overall, the nib treated at 170°C for 35 min produced the highest number of pyrazine derivatives (13 compounds).

For unroasted nib, 2,3-dimethylpyrazine, 2,3,5-trimethylpyrazine and 2,3,5,6 tetramethylpyrazine were detected at lower unit area (Table 3). These results agree with those obtained by Hashim and Chaveron (1994). However, Reineccius *et al* (1972) reported that only 2,3,5,6-tetramethylpyrazine was present in unroasted beans. Our results showed that 2,3,5,6-tetramethylpyrazine was the major pyrazine (1138 unit) present in unroasted nib. To date the 2,3,5-trimethylpyrazine and 2,3,5,6-tetramethylpyrazine are the two naturally occuring pyrazines formed in substantial quantity in unroasted nib (Hashim and Chaveron 1994).

2,5-Dimethylpyrazine was generated at the highest unit area of 60·5 when the nib were heated at 161°C for

TABLE 2
Number of compounds identified in the SDE extract after roasting of nib at different temperatures and times

Compound	*Number of compound*[a]											
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*
Pyrazines	4	6	5	8	4	10	11	11	13	13	12	11
Esters	20	19	20	18	19	20	20	20	17	19	20	19
Carbonyls	2	3	2	3	2	3	3	3	2	3	3	3
Phenols	2	2	1	2	3	3	3	2	3	2	2	3
Alcohols	3	2	3	3	3	3	3	3	2	2	3	3
Ketones	1	1	2	2	1	2	1	1	2	2	1	2
Hydrocarbons	2	2	2	2	2	2	2	2	2	2	2	2
Monoterpene hydrocarbons	2	2	2	2	2	2	2	2	2	2	2	2
Benzenoid hydrocarbons	1	1	1	1	1	1	1	1	1	1	1	1
Furans	1	1	0	0	1	0	0	1	1	1	0	0
Acids	2	2	2	1	2	1	1	2	1	1	1	2
Total	40	41	40	42	40	47	47	48	46	48	42	48

[a] a, Unroasted nib; b, 110°C, 35 min; c, 119°C, 14 min; d, 119°C, 56 min; e, 140°C, 5 min; f, 140°C, 35 min; g, 140°C, 65 min; h, 161°C, 14 min; i, 161°C, 56 min; j, 170°C, 35 min; k, Ghana bean (140°C, 35 min); l, whole bean (140°C, 35 min).

TABLE 3
Unit area of volatile compounds in the SDE extract after roasting of nib at different temperatures and times

Compound	*Unit area*[a]													*Ref*[b]
	Fit	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*j*	*k*	*l*	
Pyrazines														
2,3,5,6-Tetramethylpyrazine	993	1138·0	922·0	1210·0	1129·0	1147·0	1033·0	835·0	777·0	1034·0	943·0	1479·0	868·0	1
2,3,5-Trimethylpyrazine	959	106·0	94·0	11·50	187·0	83·5	250·0	282·0	186·0	461·0	366·0	226·0	198·0	1
3,5-Diethyl-2-methylpyrazine[c]	986	23·5	31·0	17·0	5·1	22·5	4·5	17·0	7·5	20	33·0	11·5	5·0	1
2,3-Dimethylpyrazine	936	6·0	2·0	2·0	32·0	7·0	18·5	58·0	26·5	47·5	51·0	34·5	20·0	1
2,3-Diethyl-6-methylpyrazine[c]	970	—	—	—	—	—	59·0	166	18·5	237·5	26·5	5·0	13·0	
2,6-Dimethyl-3-propylpyrazine[c]	949	—	—	—	14·0	—	52·0	68·5	13·5	39·5	152·5	17·0	23·5	
2-Ethyl-3-methylpyrazine	962	—	—	—	—	—	20·5	15·0	8·0	32·0	37·5	12·5	0·5	1
2,5-Dimethyl-3-propylpyrazine	935	—	—	—	—	—	13·0	6·0	4·5	9·0	17·0	—	18·0	1
2,5-Dimethylpyrazine	995	—	7·0	—	14·5	—	4·0	7·5	12·5	60·5	36·5	21·5	12·0	1
Methylpyrazine	951	—	—	—	—	—	1·5	1·5	—	6·5	4·5	9·0	1·5	1
Ethyl-3-propylpyrazine[c]	907	—	—	—	—	—	—	5·0	1·0	1·5	13·0	9·0	—	
2-Methyl-5-propylpyrazine	952	—	—	—	1·0	—	—	—	—	46·0	35·5	2·5	1·0	1
2,6-Dimethylpyrazine	961	—	0·5	0·5	—	—	—	—	—	—	—	—	—	1
2,5-Dimethyl-3-ethylpyrazine	952	—	—	—	21·0	—	—	—	36·0	142·5	0·5	66·0	—	1
Total		1274	1057	1247	1404	1260	1456	1457	1091	2138	1717	1890	1161	
Esters														
Butyl acetate[c]	921	541·5	184·5	262·0	471·5	167·5	625·0	341·0	394·5	241·5	204·0	503·5	85·0	
3-Methylbutyl acetate	984	383·0	181·5	8·0	345·5	295·5	628·0	342·0	435·0	361·5	450·5	374·5	2·5	4
Phenethyl acetate	995	5·2	10·98	9·31	4·92	11·35	3·23	5·89	7·59	6·16	8·09	5·46	9·04	5
Iso-amyl acetate	939	330·5	216·5	241·5	245·5	177·0	321·0	257·5	303·0	187·0	183·0	155·5	87·0	6
Ethyl hexadecanoate	968	25·5	198·5	176·5	106·0	207·5	37·5	80·5	146·0	82·5	95·5	64·5	181·0	5
2-Methylbutyl acetate	976	86·5	65·5	69·5	85·0	52·0	94·5	63·0	74·0	62·5	180·5	113·0	2·5	4
Ethyl 9-octadecenoate[c]	980	1·0	113·0	98·0	61·0	114·0	20·0	47·0	73·0	34·5	48·0	25·5	125·0	
Ethyl decanoate	922	42·0	78·0	60·0	—	75·0	3·0	27·5	35·5	9·5	0·5	23·0	63·0	3
Ethyl dodecanoate	923	21·5	34·0	30·0	17·0	39·5	3·0	16·5	35·3	15·0	18·0	9·5	38·5	5
Ethyl octanoate	980	2·0	64·0	56·5	39·0	68·0	18·0	42·5	45·5	39·5	92·0	34·0	94·5	5
Isobutyl acetate	991	153·0	52·0	73·5	140·0	46·0	141·0	111·0	105·5	69·5	58·0	71·0	24·5	7
Ethyl 9,12-octadecadienoate	969	0·5	59·5	46·5	29·5	55·5	7·0	23·5	0·5	13·5	23·0	21·5	68·5	5
Ethyl octadecanoate	940	1·0	47·0	40·0	24·5	49·0	8·5	18·0	29·5	17·0	21·5	11·0	66·0	5
Ethyl benzoate	988	33·0	36·0	289·0	26·5	39·5	8·5	15·5	35·5	12·5	23·0	15·5	31·0	6
Benzyl acetate	988	28·5	26·0	23·0	20·0	27·0	4·0	17·5	23·5	—	29·0	6·5	34·5	5
Ethyl tetradecanoate	966	9·5	25·0	25·5	11·5	22·0	1·5	10·5	18·5	8·5	10·5	5·5	26·0	5
Ethyl 3-methylbutanoate[c]	981	13·5	19·5	8·0	—	18·0	9·5	7·5	9·0	7·0	—	8·0	—	
Ethyl 3-phenylpropanoate[c]	938	7·5	6·5	5·0	5·0	7·0	0·5	3·0	4·0	—	4·0	1·0	10·0	
Isopropenyl acetate[c]	945	152·5	—	151·0	151·5	—	106·0	108·0	153·5	—	119·5	150·5	215·0	
Total		1858	1615	1413	1779	1513	2039	1539	1928	1169	1568	1404	1163	

Carbonyls														
Phenylacetaldehyde	997	258·0	394·5	114·5	353·5	384·0	287·5	214·0	27·5	325·5	141·5	283·5	57·0	5
Benzaldehyde	998	116·0	142·0	109·5	90·5	127·5	99·0	109·0	151·5	97·0	94·5	51·0	125·5	5
2-Phenylbul-2-enal	977	—	21·5	—	56·5	—	18·5	53·0	15·5	—	45·5	34·5	121·0	5
Total		374·0	558·0	224·0	480·5	511·5	405·0	376·0	194·5	422·5	281·5	375·0	297·5	
Phenols														
Methoxyphenol[c]	995	107·0	99·0	—	123·0	127·0	110·5	71·0	—	40·5	57·0	37·5	110·5	
4-Ethyl 2-methoxyphenol[c]	980	54·5	56·5	48·5	46·5	63·5	9·0	29·5	35·0	21·5	36·0	—	78·5	
p-Cresol	915	—	—	—	—	44·0	8·0	14·0	7·5	13·0	—	6·0	8·0	8
Total		161·5	155·5	44·5	189·5	234·5	127·5	114·5	42·5	79·0	93·0	43·5	197·0	
Alcohols														
Linalool	983	124·5	135·5	130·5	90·5	128·0	86·0	57·0	97·5	55·0	73·5	57·5	115·0	5
2-Phenylethanol	983	89·0	53·0	29·5	55·5	103·5	9·0	32·5	28·8	—	—	20·0	41·5	3
2-Heptanol	989	55·0	—	79·0	43·0	2·0	30·0	18·0	62·5	41·0	25·5	42·5	12·0	5
Total		274·0	188·5	239·0	189·0	235·5	145·0	107·5	188·8	100·0	99·0	120·0	168·5	
Ketones														
Acetophenone	992	3·0	9·5	22·0	4·0	27·0	18·0	2·5	—	14·5	1·0	13·5	56·5	3
β-Ionone	983	—	—	0·5	4·0	—	4·5	—	1·5	1·5	7·0	—	4·5	8
Total		3·0	9·5	22·5	12·0	27·0	22·5	2·5	1·5	16·0	8·0	13·5	61·0	
Hydrocarbons														
Octane[c]	994	104·0	58·0	38·5	75·0	48·0	67·0	53·5	49·5	43·5	22·5	67·5	12·0	
Decane[c]	969	9·5	11·5	11·5	10·5	14·5	6·5	10·5	9·5	7·0	10·0	6·5	3·5	
Total		113·5	69·5	48·0	89·5	62·5	73·5	64·0	55·0	50·5	37·5	74·0	15·5	
Monoterpenes hydrocarbons														
Ocimene	970	33·0	43·5	21·0	20·0	59·0	9·0	7·5	22·0	8·5	8·5	14·0	11·0	8
β-Pinene	964	47·0	50·5	31·0	24·0	50·0	20·5	25·5	35·5	16·0	12·0	14·5	12·0	4
Total		80·0	93·0	52·0	44·0	105·0	29·5	33·0	57·5	24·5	25·5	28·5	23·0	
Benzenoid hydrocarbons														
Styrene	995	12·0	18·0	7·5	18·0	15·0	4·0	8·0	12·0	4·5	7·0	2·0	17·5	3
Total		12·0	18·0	7·5	18·0	1·14	4·0	8·0	12·0	4·5	7·0	2·0	17·5	
Furans														
2-Ethyl-3-methylfuran[c]	980	4·0	9·0	—	—	9·0	—	—	4·5	5·5	3·0	—	—	
Total		4·0	9·0	—	—	9·0	—	—	4·5	5·5	3·0	—	—	
Acids														
Nonadecanoic acid[c]	907	0·5	2·5	3·5	2·0	3·5	2·0	1·5	2·5	1·5	1·5	11·0	7·0	
Phenylbutyric acid[c]	930	107·5	164·0	127·0	—	168·0	—	—	96·5	—	—	—	112·5	
Total		108·0	166·5	126·5	2·0	171·5	2·0	1·5	99·0	1·5	1·5	11·0	119·5	

[a] Fit, Fit score from MS library; a, Unroasted nib; b, 110°C, 35 min; c, 119°C, 14 min; d, 119°C, 56 min; e, 140°C, 5 min; f, 140°C, 35 min; g, 140°C, 65 min; h, 161°C, 14 min; i, 161°C, 56 min; j, 170°C, 35 min; k, Ghana bean (140°C, 35 min); l, whole bean (140°C, 35 min).

[b] 1, Holm (1991); 2, Shibamoto *et al.* (1979); 3, Baltes and Mevissen (1988); 4, Van der Val (1971); 5, Silwar (1988); 6, Ziegleder and Biehl (1988); 7, Van Praag *et al.* (1968); 8, Flament (1991).

[c] Identified for the first time in roasted nib.

56 min (Table 3). At higher temperature (160–170°C) with longer time (35–56 min), 2,5-dimethylpyrazine was produced at relatively high unit area. The unit area of pyrazines in Malaysian cocoa nib, Malaysian and Ghanian whole beans are also shown in Table 3 (treatments f, k and l, respectively). These samples were roasted using the same conditions (140°C for 35 min). The results indicated that the unit area of pyrazines for roasted Malaysian nib was 1456 unit, while those of Ghanian and Malaysian whole beans were 1890 and 1161, respectively. Zeigleder and Biehl (1988) reported that Ghanian beans produced two to three times of pyrazines compared to Sanchez beans.

Pyrazines were formed in cocoa beans at the lower roasting temperature (110°C); however, temperatures of 130°C and higher and time more than 25 min were needed before the pyrazines could be detected in relatively high unit area (Fig 1). In cocoa industry, the nib are often roasted at temperature above 125°C, which should result in the production of relatively high concentrations of these compounds.

The increase in the unit area of pyrazines was also detected after increasing the roasting time from 5 to 65 min at 170°C. The unit area also increased steadily when the roasting temperature was at 130–170°C and roasting time more than 35 min. According to Reineccius *et al* (1972), the pyrazines of Ghanian beans were generated quite rapidly and linearly during the first 30 min of roasting at 150°C.

Esters

Esters, which is correlated with 'fruity' flavour represent the second important group of volatiles after pyrazines

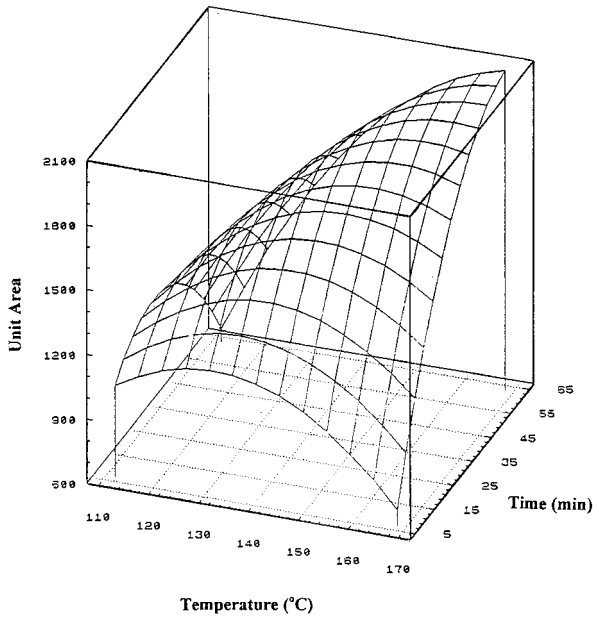

Fig 1. Response surface plotting on the effect of temperature and time on the unit area of pyrazines during nib roasting of cocoa beans.

in roasted nib. The study found that 20 ester compounds were present in the roasted nib from a total of 53 volatile substances (Table 3). Keeney (1972) found 54 ester compounds. Ethyl, methyl esters and acetates dominated. The study has found five esters which have not been reported before, present in cocoa volatiles (Table 3).

Figure 2 shows the effect of temperature and time on the unit area of esters during nib roasting. The unit area increased at all roasting time even at the lowest temperature (110°C). This indicate that the amount of esters present in nib is very much affected by roasting temperature more than time.

About 700–1000 units of the total unit area of esters were present during early roasting time (5–15 min). This area gradually increased to 1700–1800 unit when the roasting time was increased to 65 min (at 110–120°C). There was also a slow increase of esters, to 1700 unit, when the roasting temperature was increased from 110 to 170°C (at 5–10 min).

The highest unit area of esters was obtained in nib which was roasted at higher temperatures (160–170°C) but at shorter time (5–15 min). This area is significantly higher than that is obtained in nib which was heated at lower temperature (110–120°C) for longer time (45–65 min). However, the unit area sharply decreased with increasing temperature from 140 to 170°C (at 40–65 min). Higher temperatures (150–170°C) with longer roasting time (45–65 min) may cause destruction of esters (Keeney 1972).

Carbonyls

Aldehydes derived from Strecker degradation of free amino acids during roasting is essential in the development of cocoa aroma (Silwar 1988). In this study, 2-phenylacetaldehyde and benzaldehyde were found to be the most abundant (Table 3). 2-phenylacetaldehyde which is formed by Strecker degradation of phenylalanine is present, in much higher concentrations after roasting (Silwar 1988).

Figure 3 shows the effect of temperature and time on the unit area of carbonyls during nib roasting. The unit area linearly decreased with increasing roasting temperature at shorter time (5–25 min). However, there was a gradual increase after 25 min of roasting at all temperature levels.

Carbonyls were present in the highest unit area at a lower temperature (110–120°C) with a longer roasting time (55–65 min). At lower temperature (110–120°C), the unit area exceeded that at higher temperature (150–170°C) with a longer roasting time (55–65 min). It increased to the highest of 500 unit when nib were roasted at 110°C for 65 min.

The decrement of carbonyls at shorter (5–35 min) and longer time (35–65 min) at roasting temperature of 110–170°C may be due to the development of 2-phenylbut-

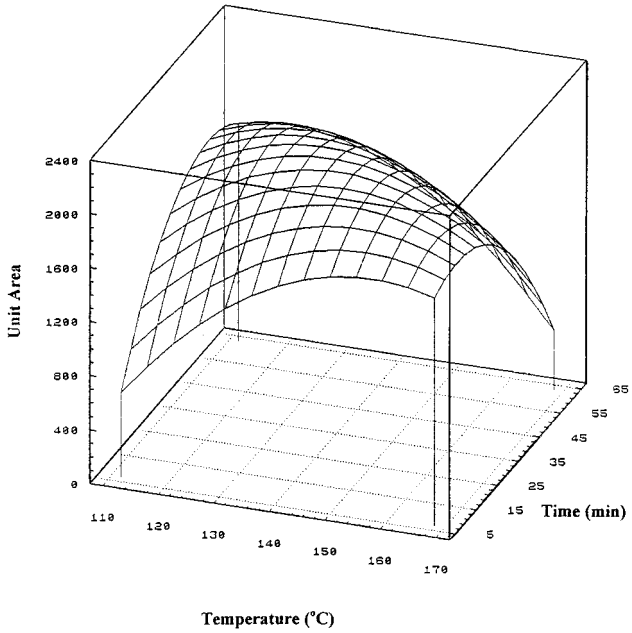

Fig 2. Response surface plotting on the effect of temperature and time on the unit area of esters during nib roasting of cocoa beans.

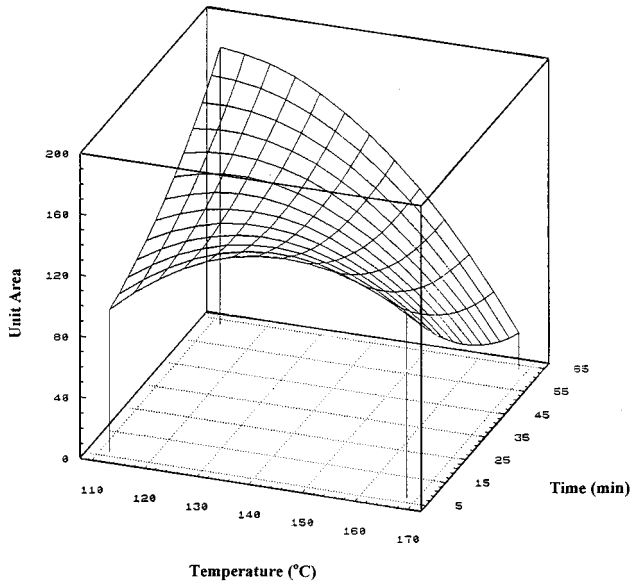

Fig 4. Response surface plotting on the effect of temperature and time on the unit area of phenols during nib roasting of cocoa beans.

enal. 2-phenylbut-2-enal is an aldol condensation product from 2-phenylacetaldehyde with acetaldehyde (Silwar 1988). The 2-phenylbut-2-enal increased at 1400C for 35 and 65 min, and at 110 and 170°C for 35 min (Table 3).

Phenols

Figure 4 shows the response surface plotting of unit area of phenols during nib roasting. The unit area was significantly reduced at the highest roasting temperature (160–170°C) with longest roasting time (45–65 min) (by 100–30 unit). It increased when nib were roasted at 110–140°C for 5–30 min. However, the highest area was detected at 162 unit in under-roasted nib (140°C; 5 min) (Table 3). High unit area of phenols probably results from the wood fire smoke during drying (Ziegleder and Biehl 1988). Smoke from wood or charcoal fires can also contaminate cocoa drying (Lehrian *et al* 1978).

The unit area of phenols slowly fell to 128 then 93 units after the nib temperatures were increased to 140°C and 170°C (at 35 min) (Table 3). Normally, phenols are not present in significant amount in cocoa (Flament 1991) and cocoa of good quality should be mostly free of them (Ziegleder and Biehl 1988).

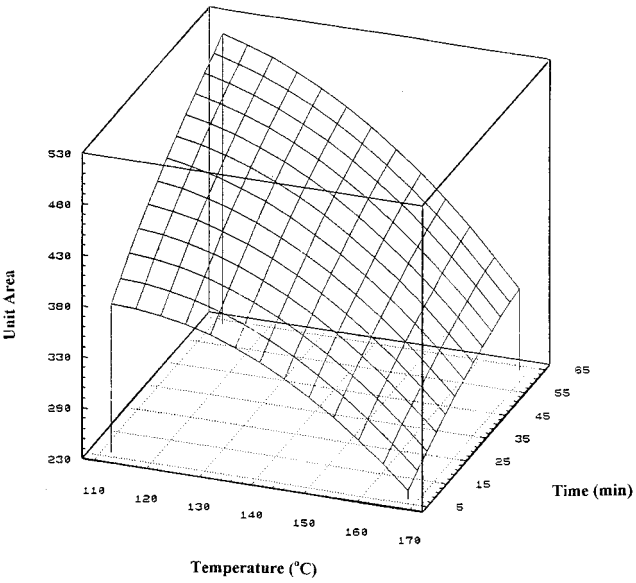

Fig 3. Response surface plotting on the effect of temperature and time on the unit area of carbonyls during nib roasting of cocoa beans.

Alcohols

Figure 5 shows the response surface plotting of unit area of alcohols during nib roasting. Alcohols are presumed to exist from microbial activity during fermentation of beans (Silwar 1988). This postulation may agree with the plot in Fig 5 which shows the existence of alcohols before roasting (269 of unit area).

The unit area of alcohols slightly decreased as roasting time and temperature were increased. With increasing roasting time at lower temperature (110–120°C), the unit area slightly fell (170–200). However, it was reduced after roasting time was extended up to 65 min at higher temperature (150–170°C). This decrement may be due to either the volatilisation or destruction of alcohols during roasting. The unit area of alcohols was found to be higher at lower temperature (110–120°C) at all times. The response surface plotting also shows that the highest unit area of alcohols was present in nib

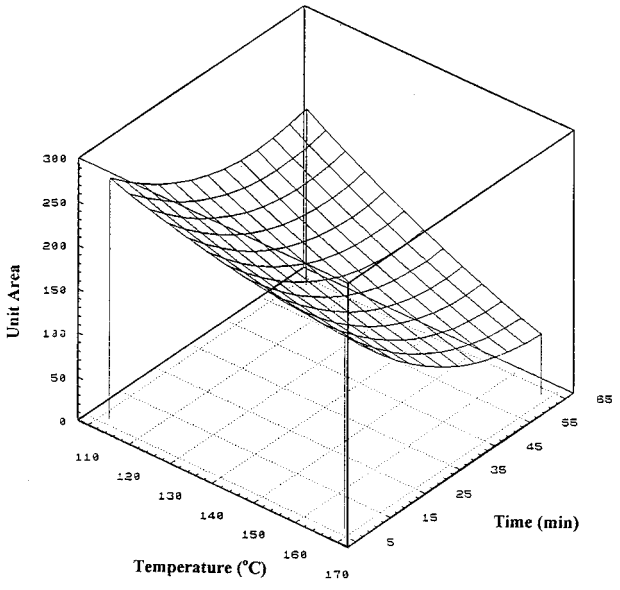

Fig 5. Response surface plotting on the effect of temperature and time on the unit area of alcohols during nib roasting of cocoa beans.

which were roasted at temperature range of 110–140°C and time of 5–14 min. At this level, the unit area of alcohols were in the range of 240–280.

The alcohols are responsible for the fruity and floral odour of the products (Flament 1991). Linalol and 2-phenyl ethanol were the two major alcohols present in the roasted nib (Table 3). Both of them are widely found in cocoa (Silwar 1988). Linalol is a derivative of the monoterpenes series that occur most abundantly in nature (Flament 1991). 2-Heptanol is associated with 'fruity', 'herbaceous flowery' and 'spicy' aroma (Flament 1991) and was present in nib at all variables time at 140°C (Table 3). The unit area increased from 2 to 18 with increasing roasting time from 5 to 65 min.

CONCLUSION

Temperature and time are shown to be an important variables which affected the development of cocoa flavour. Fifty-three volatile compounds had been detected in roasted nib. Among them, pyrazines and esters were two major groups which presented in cocoa volatiles. Higher temperatures than 130°C with times longer than 25 min were desirable for the formation of pyrazines. However, the highest unit area of esters were present at higher temperature (160–170°C) for shorter time (5–15 min) and they decreased during longer roasting time (45–65 min). Alcohols were also present in higher unit area during lower roasting temperature (110–140°C) for all roasting times but was decreased at higher temperatures (160–170°C) and longer roasting time (45–65 min). Contrary to alcohols, lower temperatures (110–120°C) with longer time (55–65 min) were required in order to produce higher unit area of carbonyls.

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