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Optimization of Dark Chocolate Conching Time with Response Surface Methodology

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ABSTRACT

Chocolate conching is a batch process with a batch time lasting from 5 to 12 h. This is quite a long time for an industrial process and should be optimized for the most acceptable product in terms of flavor. For this purpose, the variation in the concentration of volatiles consisting of acids, aldehydes, pyrazines, alcohols, ketones, hydrocarbons, and esters was monitored for 30 min intervals during the span of conching using Gas Chromatograph Mass Spectrometer Solid Phase Micro extraction (GC/MS/SPME). Results showed that the quantity of the volatilized functional groups is a maximum at 270 min except esters, which increased continuously. The optimum conching time was determined to be the one corresponding to the concentration of the most desirable volatiles contributing to the sample with most acceptable flavor. The mentioned concentrations were determined to be 5890, 6085, 3685, 1573, 3391, 602, 1632 and 43667 ppb for acids, aldehydes, pyrazines, ketones, hydrocarbons, alcohols, esters and total volatiles at the end of conching.

Key words: Conching time, Optimization, Flavor change and dark chocolate GC/MS, SPME.

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INTRODUCTION

Conching is one of the most important processing steps for the development of the characteristic chocolate flavor. It takes at least 6 h with continuous heating and agitation in a tank called a conch where both flavor and texture developments occur simultaneously. Roasting and fermentation generate volatiles consisting of chemical compounds with desired and undesired flavors. Acids for example are responsible for imparting a sour and bitter taste to the chocolate. In the conching process, these volatiles causing bad flavour and taste are removed and a mellow chocolate is thus produced (Stephen, 2006). Solid particles such as sugar and cocoa powder are covered with cocoa butter and rounded by friction causing a smooth texture at the end of the process. In addition, water which causes agglomeration of sugar evaporates during conching (Guinard and Mazzucchelli, 1999). Complex biochemical modification takes place during conching as a result of heating and agitation.The mechanism of flavour development, however, is not clear. For instance, short chain volatile fatty acids remove during conching; since their boiling points (>118°C) are above the conching temperature, their removal or volatilization are considered something not to be explained easily (Stephen, 2006). The situation, however, can easily be explained in terms of mass transfer which requires only a concentration gradient over the surface of chocolate at any temperature. Coutnet et al. (2002) studied flavor change of dark chocolate before and after conching while Misnawi (2011) and Ducki et al. (2008) carried out aroma analysis of cocoa liquor and cocoa product with GC/O. Another interesting study about this issue was made by Owusu et al. (2011) who studied the effect of fermentation methods, roasting and conching conditions on the aroma volatiles of dark chocolate. There was no detailed study, however, reporting conching kinetics. In other words, no concise study, disclosing the variation of the concentrations of the chocolate volatiles with time during conching was encountered. This study was therefore carried out to examine the change in the concentration of

Table 1. Formulations of dark chocolate, all figures are in percentage.

Ingredients	Dark Chocolate
Cocoa mass	45.07
Sugar	39.14
Added cocoa butter during conching	15.45
Lecithin	0.34

volatiles with time and to optimize the conching time regarding the concentration of the most desirable volatiles causing an increase in the quality of the overall chocolate flavor.

MATERIALS AND METHODS

Conching Process

Refined chocolate mix, containing 39.14% sugar, 45.07% cocoa mass, lecithin and cocoa butter were supplied from a local plant. A 5 kg-capacity, laboratory-scale conching machine (ELK'olino single-shaft conche, Bühler, AG, Switzerland) with temperature and speed control was utilized for the conching process, which was made up of three phases; dry phase: 2 h at 50°C, pasty phase: 4 h at 80°C and final phase: 1 h with linear decrease in temperature from 80°C to 45°C. The rotation speed of the conching machine was in the range of 600 to 1500 rpm. The formulations of dark chocolates used in this study with and without additives are shown in Table 1.

SPME Extraction

Volatiles from samples were extracted by using 75 µm divinylbenzene/carboxen on polydimethylsiloxane on a Stable /Flex fiber (CAR/PDMS). Extractions were carried out in the vials. A 2g-sample together with 1µL toluene, as internal standard, was placed in a 20-ml vial. After tightly plugging its lid and inserting the SPME fiber, it was equilibrated for 60 min at 60 °C. The desorption time was 5 min and the temperature in the GC liner was 250°C

GC/MS

The volatiles adsorbed on fibers were thermally desorped and introduced in the capillary column (EQUITYTM-5 FUSED SILICA Capillary Column 30 m × 0.32 mm × 0.25 µm film thickness Supelco). The GC (Perkin Elmer Clarus 500)-MS (Clarus 500 MS Perkinelmer) was set up with constant flow of 2 ml/min (helium), the oven temperature was programmed starting at 80°C (5 min)-(10°C/min) 150°C-150°C(10min) -(10°C/min) 200°C-200°C(5min). The injector temperature was maintained as 250°C. The analysis was carried out by using gas chromatography coupled with mass spectrometry. The ionization voltage was 70eV, mass range m/z 40 to 300.

Odour Identification by Olfactometer

Two trained panelists sniffed the outflowing gas from the olfactometer's detection port. The sniffing was carried out simultaneously during GC analysis. Panelists described their perception of the sniffed odour.

RESULTS AND DISCUSSION

Chocolate has a specific flavour depending on genotype and processing steps such as roasting, fermentation and conching which is the last and most important step contributing to the flavor development.

Although the major development in flavor takes place in this step the mechanism of its formation is still not too clear. As known, conching is a batch or time-dependent process. Generally conching time varies within a range of 6 to 12 h depending on the type of process.

This is quite a long time for an industrial process and therefore in addition to the aroma development, structural changes affecting the chocolate texture are naturally expected.

In the present study, dark chocolate sampling was carried out at 30-min intervals to see the variation of both quality and quantity of the volatile compounds within the conching time and chromatogram are shown in Figure 1.

A combination of GC/MS/SPME was used for this purpose. Toluene was used as internal standard for the quantitative analysis. Design expert version 6.01.0 (Stat-Ease, Inc Minneapolis, MN) was utilized to evaluate the experimental data which were fitted to a second order polynomial statistically. The significance of terms in the model was found by analysis of variance (ANOVA) for each response. Significance was judged by determining the probability level.

The results showed that the quantity of acids, aldehydes, pyrazines, ketones, hydrocarbons, alcohols, and their sum is polynomially affected by time. The influence of time was found to be highly significant ($p<0.05$). The significance of each polynomial coefficient was statistically determined. Large F values and small p-values are thought to be significant. The coefficients given in Table 2 are significant at 95% level.

As shown Figure 2, the quantities of all volatile compounds representing different functional groups increased till 270 min from the start of conching.

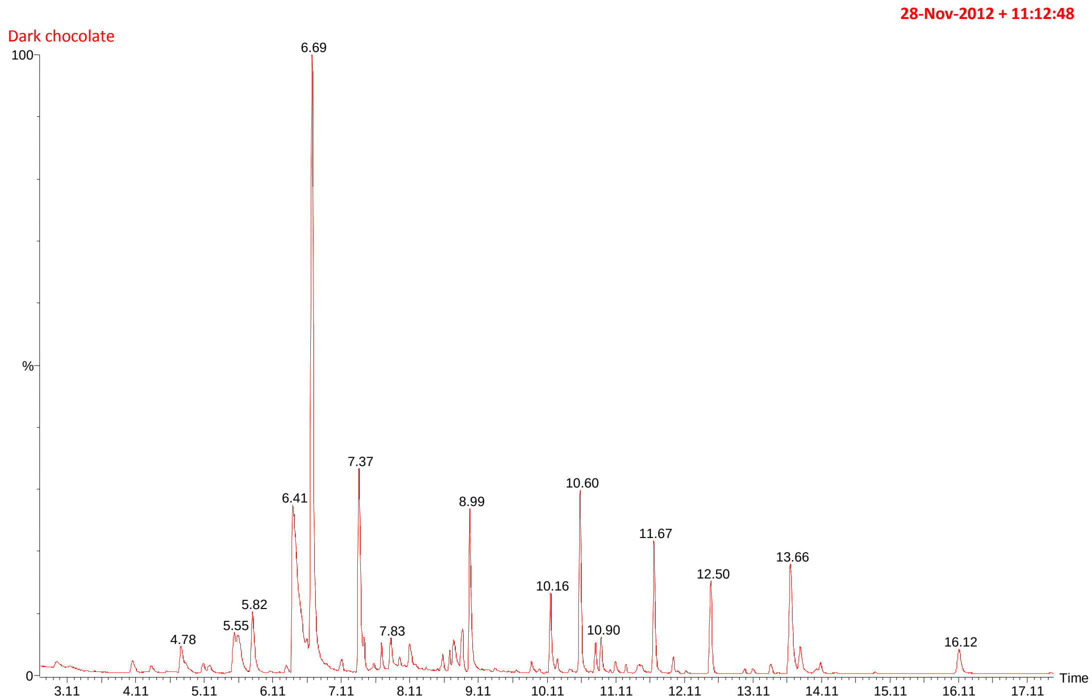

Figure 1. Chromatograms of dark chocolate.

Table 2. Statistical values of responses.

Response	F value	P value	R value
Acids	26.62	0.0002	0.9089
Aldehydes	24.95	0.0002	0.9034
Pyrazines	52.81	0.0001	0.9519
Ketones	63.55	0.0001	0.8640
Hydrocarbons	21.39	0.0004	0.8891
Alcohols	26.65	0.0002	0.8551
Esters	246.83	0.0001	0.9611
Sum of volatiles	19.58	0.0005	0.8131

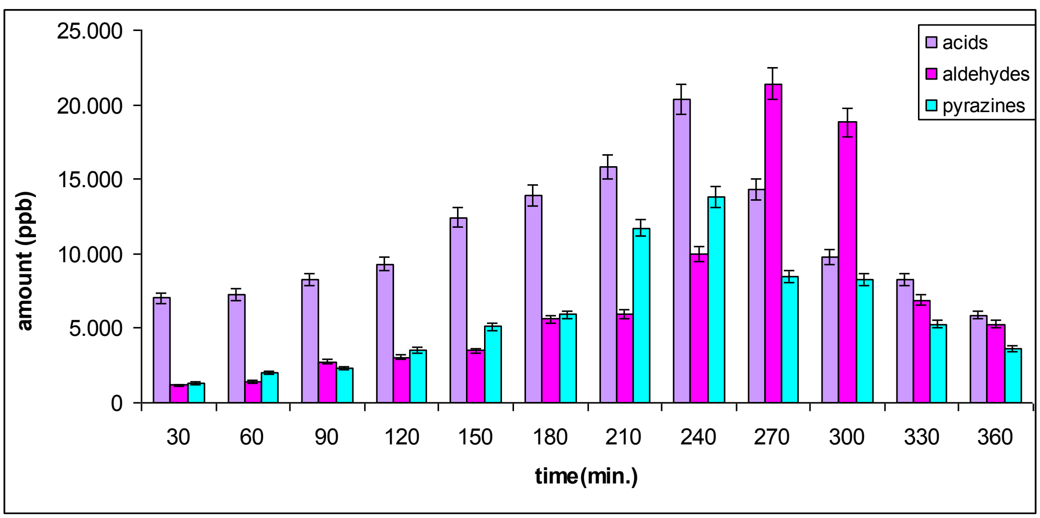

Figure 2. Variation in the quantity of acids, aldehydes and pyrazines with time during conching.

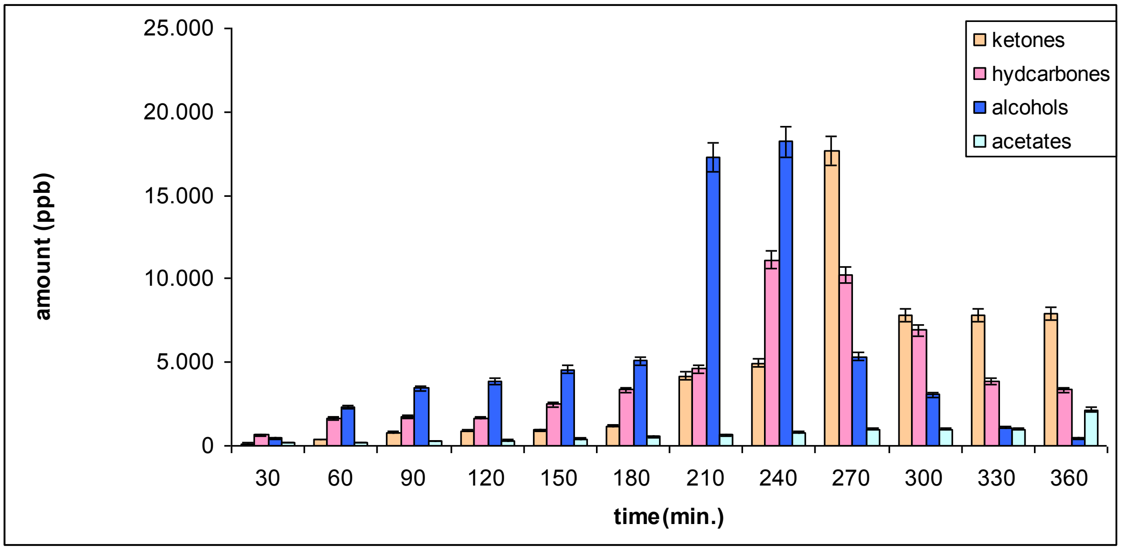

Figure 3. Variation in the amount of ketones, hydrocarbons, alcohols and esters with time during conching.

From then on, a significant decrease in their quantities was observed. This increasing-decreasing trend is seen to be quantitatively predominant for the acids whose quantity reached a value higher than 20.000 ppb for a conching time of 270 min. Acids are known to cause sourness in dark chocolate. The conching process is again seen to be effective in further reducing their quantity after the roasting process (Lopez, 1986; Jinap et al., 1995). The total amount of acids was observed to fall below 5000 ppb after a conching time of 300 min. Rodriguez et al. (2011) studied the effect of fermentation time and drying temperature on the volatile compounds in cocoa liqueur. They found that total concentration of aldehydes and pyrazines increased with increasing fermentation time. They declared that the total quantity of aldehydes was 11 mg/kg after fermentation. Owusu et al. (2011) studied the effect of fermentation, roasting and conching on the aroma volatiles of dark chocolate. They stated that fermentation, roasting and conching were the main processes affecting aroma production of dark chocolate. They found that high roasting and conching temperatures, long fermentation and conching times produce more volatiles. They did not report any variation of the mentioned volatiles with time.

The amount of pyrazines was about 2000 ppb at the beginning of conching and it reached a top value of 20.000 ppb after 270 min. Owusu et al. (2011) stated a-6 h conching at 80°C to be effective in reducing the quantity of pyrazines and aldehydes formed as a result of high roasting temperature, but they did not mention the history of their removal. The maximum quantities of ketones, hydrocarbons, and alcohols were observed to correspond to 270, 240, and 210 min, respectively from the beginning of conching as seen in Figure 3. The sum of their quantities was above 18.000 ppb. However after 270 min amount of them reduce gradually. Frauendorfer et al. (2008) reported the high alcohol content to be the cause the flowery and candy flavor. Portillo et al. (2009) claimed that sun drying decreased the amount of alcohols. In the present work, the amount alcohols, ketones and hydrocarbons were reduced to values below 2000, 8000 and 4000 ppb, respectively at the end of conching (360 min). In contrast to ketones, hydrocarbons and alcohols, the total concentration of esters (acetates in this case) increased continually during conching and they reached to 4000 pbb. In general, it is known that esters contribute a fruity flavor to the dark chocolate (Jinap et al., 1998). As seen in Figure 4, the total quantity dark chocolate volatiles increased slightly up to 180 min of conching. This step was followed by a sharp increase up to 270 min at which time total amount volatiles reached 100,000 ppb. However at the end of conching this value was reduced back to below 50,000 ppb. Dark chocolate had a mellow flavor at the end of conching, because the amount of acids, alcohols and other functional groups, causing unpleasant odor and taste decreased whereas groups, like pyrazines and esters, causing pleasant odors increased. Frauendorfer et al. (2008) investigated change in key aroma compounds of Criollo cocoa beans dring roasting. They found that roasting increased total volatiles of cocoa compared to unroasted one. Counet et al. (2002) studied odorant change before and after conching. They found that no key odorant was synthesized and while the concentration of some compounds increased that of some other compounds decreased during conching. Again no indication as the history of change was made.

Optimization of Conching Time

General factorial desing was used to determine the optimum time for flavor development during conching of

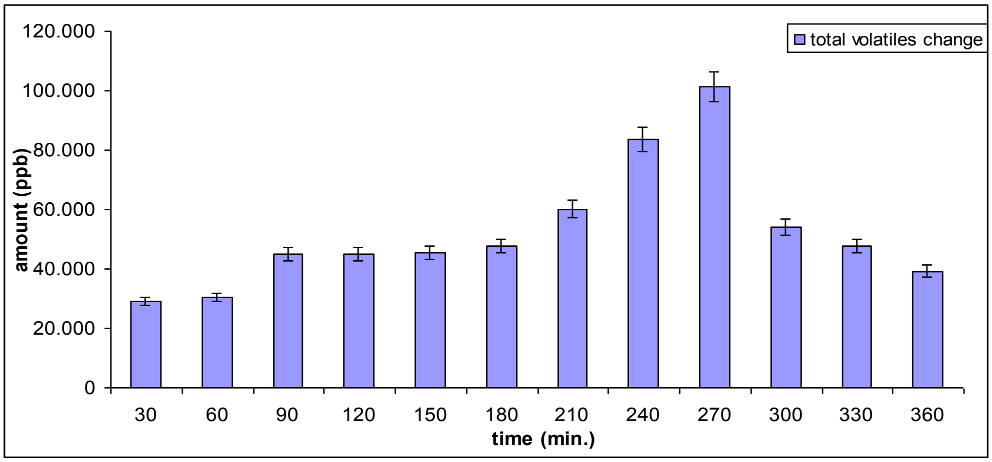

Figure 4. Variation in the total quantities of dark chocolate volatiles with time during conching.

Table 3. Optimization range of process parameter and response.

Parameter and Response	Goal	Lower Limit	Upper Limit
Acids (ppb)	minimize	5890	20,364
Aldehydes (ppb)	maximize	1160	21,411
Pyrazines (ppb)	maximize	1323	13,813
Ketones (ppb)	maximize	142	17,666
Hydrocarbons (ppb)	minimize	658	11,140
Alcohols (ppb)	minimize	441	18,217
Esters (ppb)	maximize	171	2,166
Total volatiles (ppb)	maximize	29186	10,1217

Table 4. Dark chocolate aroma profile at the optimum conching time.

Retention time (min)	Compound	Odour Description	Amount (ppb)
0.09	Acetic acid	Rancid	5353
1.58	2-methyl-heptadecane	Chocolate	5747
1.75	3-Hexene	Green	682
2.39	Benzaldehyde	Nutty	123
2.57	Hexanoic acid	Sour	124
2.86	1,1-difluoro-dodecane	Camphor	1806
3.20	2-propanol	Pungent	131
3.35	Cyclohexene	Sweet	141
3.41	2-methylene-1,3-diphenyl-1,3-propanediol	No smell	21
3.56	Benzeneacetaldehyde	Almond	149
3.92	1-methyl-2-phenylethanol	Rose	3524
4.21	Tetramethyl-pyrazine	Bean like	80
4.39	Octadecane	Honey	669
4.45	Nonanal	Coffee	394
4.66	Benzenethanol	Floral	1648
5.10	2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran4-one	Caramel	35
5.51	Hexanoic acid	Sour	298
5.58	2-decen-1-ol	Fruity	69
5.79	3,4-dimethylpentanol	No smell	10
5.86	1,5-hexenyl-1-methyl-hyrazine	Meaty	54
5.91	2-methyl-heptadecane	Chocolate	33
6.01	Nonanal	Coffe	48
6.24	2-hexanone	No smell	67
6.80	2-phenylethylester-acetic acid	Rancid	44

Table 4: Contd.

6.95	9-octadecenoic acid	Sour	104
8.07	Propanoic acid	Rancid	429
9.70	Benzocyclobuten	Sweet	3524
12.78	2-cyclobutene	No smell	705
22.28	Octane	No smell	134
22.79	1,2-Benzenedicarboxylic acid	Sweet	38
23.45	4-methyl-hexanal	Chocolate	373

dark chocolate that yield minimum quantities of acids, alcohols, and maximum quantities of pyrazines, aldehydes and ketones. In this study, time was selected in range (Table 3).

A solution was obtained by using this experimental design. According to this, the optimum time for dark chocolate conching at 80°C, in the range of 600 to 1500 rpm, is 354 min. Under these conditions, the quantities of acids, aldehydes, pyrazines, ketones, hydrocarbons, alcohols, esters and total volatiles were determined to be 5890, 6085, 3685, 1573, 3391, 602, 1632 and 43667 ppb, respectively at the end of conching. Aroma profile for the conching is given in Table 4.

CONCLUSION

The concentration of all volatiles, except esters, was observed to pass through a maximum corresponding to 270 min from the beginning of conching. The ester concentration, on the other hand increased continuously till the end of conching. As expected, dark chocolate's acidic flavor before conching changed to an acceptable, representative mellow flavor after 354 min (considered to be the optimum conching time) from the beginning of conching.

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