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Effect of Roasting Process on the Concentration of Acrylamide and Pyrazines in Roasted Cocoa Beans from Different Origins

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Abstract

Roasting is an important process that contributes to the formation of flavour compounds in cocoa beans. Pyrazines, by-products of Maillard reaction are the character impact compounds that contribute to its unique cocoa flavour. Unfortunately during roasting, carcinogenic acrylamide is also produced through the same Maillard reaction. This study was carried out to determine the concentration of acrylamide and pyrazines in different origin of cocoa beans roasted at 116°C and time of 23 min. Papua New Guinea cocoa beans contained significantly (p<0.05) the highest concentration of acrylamide (0.32 mg/100g) and the lowest was cocoa beans from Cameroon(0.11mg/100g). In this study, superior quality Ivory Coast cocoa beans can be produced with this roasting conditions; high pyrazines (2-methylpyrazine, 2,5-dimethylpyrazine, 2,3,5-trimethylpyrazine and 2,3,5,6-tetrapyrazine) with low acrylamide concentration (0.23 mg/100g).

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1. Introduction

The discovery of acrylamide in heated carbohydrate-rich food by the Sweedish Food Administration and the University of Stockholm cause concern over the safety of food \cite{1}.

International Agency on Research on Cancer has been classified acrylamide as “probably carcinogenic to human” \cite{2} and exposure to high levels was found to cause damage to the nervous system.

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This concern also because food of contain acrylamide is widely consumed; and the amount of acrylamide in food are higher than many other food borne carcinogens [3]. Acrylamide was detected in cocoa products at levels up to 909 μg/kg [4], and there are only a few researches [5] [6] on acrylamide content in roasted cocoa bean and cocoa product.

The most important precursor is the free amino acid asparagine which in Maillard reaction that also contribute to the colour and flavour in food, where it is very important for flavour development in cocoa.

Roasting of cocoa is an essential step and a technology operation to further develop chocolate aroma from the aroma processor developed during fermentation and drying.

The formation of characteristic of brown colour, mild aroma and texture of roasted beans will depend on roasting condition.

A large number of pyrazines have been identified in cocoa and it being considered extremely important in cocoa flavour.

A number of researches have reported the thermal formation of pyrazines by the Maillard reaction, involving amino acids and reducing sugar [7] [8].

Through Mailliard reaction, all of flavor compound interact each other to produce cocoa flavour compound such as alcohols, ethers, furans, thiazoles, pyrones, acids, esters, aldehyde, imines, amines and pyrazines [9].

2. Materials and Methods

2.1. Cocoa Beans

Cocoa beans from different origin (Malaysia, Papua New Guinea, Ivory Coast and Cameroon) were obtained from Malaysia Cocoa Board and Indonesia cocoa beans (fermented and unfermented) from Post Harvest Laboratory of Indonesian Coffee and Cocoa Research Institute (ICCRI).

Cocoa beans were de-shelled and samples were kept sealed in plastic and store at room temperature for further analysis.

2.2. Roasting Condition

Cocoa beans were roasted in a roaster (Mitsubishi Probat – Magnetic Contractor S-N20, (Pascall Engineering Co. Ltd., England).

Roasting was carried out at temperature of 116°C and time of 23 min [10].

2.3. Pyrazine Analysis

Pyrazines (2-methylpyrazine, 2,5-dimethylpyrazine, 2,3,5-trimethylpyrazine and 2,3,5,6-tetrapryazine) analysis was conducted using 5g of cocoa liquor.

Internal standard of 4-Picoline was applied to the cocoa liquor. SPME fiber–Polydimethylsyloxane-Divinylbenzene (PDMS-DVB) polymer was used for extraction.

The extraction was held for 30 min at a temperature of 60°C [11].

The flavour compounds in the extract were analysed using GC-FID equipped with Rtx-5(dimethylpolisiloxane crossbone) capillary column, helium with 30 ml/min constant flow as carrier gas and injector SPL-1 operating in splitless mode.

The injector temperature was maintained at 260°C and the GC temperature were programmed from 60°C (3 min) to 180°C at 5°C/min for 3 min, following the method described by [11].
Identification of the component of the standard was carried out by comparing the retention time with the standards.

2.4. Acrylamide Analysis

Ground roasted cocoa beans were defatted using hydraulic press.
The residue was extracted using Solid Phase Extraction (SPE).
Five gram of the defatted cocoa powder was added with 10 mL 0.1% formic acid solution and was shaken for 20 min.
The supernatant was filtered through 0.45 μm nylon syringe filter.
SPE C18 was conditioned with 2 mL acetone and 2 mL 0.1% formic acid. Extracted cocoa powder solution was allowed to pass through the tube by gravity flow and the SPE tube was washed with 1.0 mL water.
Excess water was vacuum dried from the tube and 2 mL acetone was used for elution. Sample (1.0 μL) was injected and held for 0.5 min in the GC-FID equipped with Rtx-5 (dimethylpolisiloxane crossbone) capillary column using helium as carrier gas with constant flow of 1.2 ml/min.
The injector temperature was maintained at 260°C and the GC temperature programme was from 100°C (0.5 min) to 200°C at 15°C/min.

2.5. Sensory Analysis

Sensory analysis of the samples was carried out by using 12 trained panellists.
A maximum of 4 samples (cocoa liquor) were served to panellist at one time.
Cocoa liquor flavour was classified as strong, moderate and weak.
The panellists were required to taste the samples, and then indicated it using 1 to 14 scales.

3. Results and Discussion

Fermented Indonesia cocoa beans were used as a model to evaluate the effect of roasting temperature and time on acrylamide formation. (Fig 1).
As roasting time and temperature increased, acrylamide concentration increased up to a certain level and started to reduce after that as shown in Fig 1.
Acrylamide is not a stable compound, will be destroyed with heating at extreme conditions. Acrylamide were formed at the beginning of roasting step and declined at the end of roasting cycle due to higher rates of elimination [12].

![Fig. 1. (a) Concentration of acrylamide with changes in temperature at constant time ,25 min; (b) and time at constant temperature ,130°C (b).](image)
Cocoa beans from different origins were roasted and analysed for acrylamide, pyrazines and pH. The results obtained are shown in Table 1. Cocoa beans from Ivory Coast contain significantly (p<0.05) the highest concentration of pyrazines with low acidity (pH 6.49).

In terms of overall acceptability, cocoa beans from Ivory Coast is the most preferred with score 11.82 and [7] also stated it as good quality cocoa beans. Indonesian fermented cocoa beans contain higher concentration of pyrazines when compared with the unfermented beans.

This is because mainly all aroma precursors will develop during fermentation and roasting process [8].

As comparing the overall acceptability Indonesian fermented cocoa beans 10.75 also is acceptable than unfermented beans with score of 10.75 and 1.56.

pH also play important role for the formation of flavour compounds and acrylamide.

Acidic beans contain lower pyrazines concentration. This is due to low pH limit the Maillard reaction, which will result in decreased browning and aroma formation.

Generally, acrylamide formation was lower in the more acidic beans and it was supported by [1] [12] [13] where formation acrylamide decreased linearly with the addition of acids to baked corn chips; presence of acids made hydrolysis of carboxamide group leading to aspartic acids at lower pH.

Table 1. Pyrazines and acrylamide concentration in different origin of cocoa beans.

<table>
<thead>
<tr>
<th>Origin</th>
<th>Mean ± SD (mg/100g)</th>
<th>pH</th>
<th>Overall Acceptability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 MP</td>
<td>2,5-DMP</td>
<td>2,3,5-TMP</td>
</tr>
<tr>
<td>Indonesia Fermented</td>
<td>0.02±0.00d</td>
<td>0.13±0.01c</td>
<td>0.14±0.00c,d</td>
</tr>
<tr>
<td>Indonesia Unfermented</td>
<td>0.08±0.02c</td>
<td>0.02±0.00c</td>
<td>0.017±0.01c</td>
</tr>
<tr>
<td>Malaysia</td>
<td>0.05±0.01ed</td>
<td>0.07±0.01c</td>
<td>0.08±0.01d,e</td>
</tr>
<tr>
<td>Papua NG</td>
<td>0.11±0.01e</td>
<td>0.39±0.01b</td>
<td>0.18±0.01c</td>
</tr>
<tr>
<td>Cameroon</td>
<td>0.65±0.02b</td>
<td>0.43±0.001b</td>
<td>0.72±0.01b</td>
</tr>
<tr>
<td>Ivory Coast</td>
<td>0.71±0.08a</td>
<td>0.92±0.05a</td>
<td>0.81±0.09a</td>
</tr>
</tbody>
</table>

Mean values within the same column with different alphabets are significantly (p<0.05) different according to SPSS.

The concentration of acrylamide obtained was in the range of 0.11 to 0.32 mg/100g. These results were agreeable with acrylamide level that be found in cocoa based products, with a minimum level of 0.2 mg and higher level of 0.83 mg [4].

Cocoa beans from Papua NG have the highest concentration of acrylamide (0.32 mg/100g).

Consumption of cocoa products with high concentration of acrylamide is hazardous to human health because cocoa product widely consumed by people.

Average intake for the general population was estimated to be in the range of 0.3-0.8 mg of acrylamide intake/kilogram of body weight/day [4].

There is no limit of acrylamide in food, but Centre for Science in the Public Interest [15], said that the limit of acrylamide in fries should be set as 0.0077 mg as an temporary acceptable level, which is much lower than the amount of acrylamide detected in the roasted cocoa bean analyzed in this study.

4. Conclusion

Superior quality Ivory Coast cocoa beans can be obtained after roasting at 116°C and time of 23 min. These beans contain high concentration of pyrazines with low acrylamide formation.
Acknowledgements

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References