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EFFECT OF ROASTING TEMPERATURE AND TIME ON PRECURSORS, VOLATILE COMPONENTS AND FLAVOUR QUALITY OF COCOA BEANS DURING NIB ROASTING

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LIST OF ABBREVIATIONS

kg	kilogram
g	gram
mg	milligram
μg	microgram
m	metre
mm	millimetre
μm	micrometre
l	litre
μl	microlitre
ml	millilitre
cm	centimetre
sec	second
min	minute
hr	hour
M	molarity
N	normality
bp	boiling point
rpm	revolution per minute

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The effect of roasting temperature and time on precursors, volatile components and quality of cocoa beans during nib roasting was studied using response surface methodology (RSM) which consisted two independent variables of temperature (110-170° C) and time (5-65 min). 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. The pH linearly increased during roasting period at 120° C. The colour was used for 1.20-1.80 Fermentation index value. The moisture content of the nib decreased (to 1.1%) as the roasting time and temperature were increased. Fifty three volatile compounds had been detected in roasted nib. Among them, pyrazines and esters were two major groups which constituted of 34

different compounds. Tetramethylpyrazine, trimethylpyrazine, phenethyl acetate, isoamyl acetate, 3-methylbutyl acetate, 2-methylbutyl acetate, phenylacetaldehyde, and benzaldehyde were present in all treatments. The pyrazines formation increased as roasting time and temperature were increased. When roasting time was increased from 5 to 35 and 65 min at 140° C, the number of pyrazines increased from 4 to 10 and 11, respectively. The ratio value of esters increased when the roasting time was increased from 15 to 65 min (at 110-120° C). However, the ratio value of carbonyls linearly decreased with an increasing roasting temperature at shorter time (5-25min). The ratio value of phenols was enormously reduced at the highest roasting temperature (170° C) with the longest roasting time (65 min) while that of alcohols slightly decreased as roasting temperature and time were increased. With the increase in roasting temperature and time, the concentration of free amino acids, reducing and non-reducing sugars had decreased. The concentration of total free amino acids decreased by 23.0% and 73.3% in the range of 1287.34 - 76.43 mg/100 g. Sugars concentration decreased from 24.87 to 12.98 and 11.30 mg/100 g respectively as roasting temperature was increased from 110 to 140 and 170°C. The nib roasted at 140° C had higher response percent of cocoa taste, moderate response of bitter taste and low response of sour; astringent and absent of smoky. However, the nib roasted at 170°C had the lowest percent of cocoa taste but higher in bitter and high roast taste.

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KESAN SUHU DAN MASA TERHADAP PREKURSOR, KOMPONEN MERUAP DAN KUALITI BIJI KOKO SEWAKTU PEMANGGANGAN NIB KOKO

Oleh

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Kajian terhadap suhu dan masa pemanggangan bagi prekursor, komponen meruap dan kualiti biji koko semasa pemanggangan nib koko meggunakan kaedah `Response Surface Methodology' (RSM) dengan dua pembolehubah tidak bersandar (suhu: 110-170°C dan masa: 5-65 min) telah dilakukan. Kaedah pengekstrakan sulingan stim (SDE) digunakan untuk mengekstrak komponen meruap dan gas kromatografi dan spektrum jisim (GCMS) digunakan untuk mengenalpasti komponen meruap. Keputusan kajian menunjukkan pH meningkat secara linear semasa pemanggangan pada suhu 120°C. Indeks fermentasi pula adalah dalam julat 1.20-1.80 dengan perubahan warna kepada perang adalah ketara. Kandungan lembapan dalam nib koko juga menurun (kepada 1.1%) apabila suhu dan masa pemanggangan ditingkatkan. Lima puluh tiga komponen berbeza telah dikenalpasti hadir dalam nib

yang dipanggang. Daripada jumlah keseluruhan komponen meruap, sebanyak 34 komponen yang hadir adalah daripada kumpulan pyrazine dan ester. Tetramethylpyrazine, trimethylpyrazine, phenethyl acetate, isoamyl acetate, 3-methylbutyl acetate, 2-methylbutyl acetate, phenylacetaldehyde dan benzaldehyde pula hadir dalam semua rawatan. Pembentukan pyrazine meningkat dengan peningkatan suhu dan masa pemanggangan. Bilangan pyrazine juga meningkat daripada 4 kepada 10 dan 11 apabila masa ditingkatkan daripada 5 kepada 35 dan 65 min pada suhu 140°C. Nilai nisbah ester meningkat (sehingga 1700-1800) apabila masa pemanggangan ditingkatkan daripada 5 kepada 65 min (pada suhu 110-120°C). Bagaimanapun, nilai nisbah carbonyl menurun secara linear dengan peningkatan suhu pada masa singkat (5-25min). Nilai nisbah phenol pula mururun dengan banyak pada suhu tertinggi (170°C) dan masa terpanjang (65 min) manakala nilai nisbah alkohol menurun sedikit sahaja apabila masa dan suhu pemanggangan dinaikkan. Peningkatan suhu dan masa pula menyebabkan asid amino bebas dan gula penurun dan bukan penurun, terurai. · Kepekatan keseluruhan asid amino bebas menurun dalam julat 1287.34-76.43 mg/100 g manakala kepekatan gula pula menurun daripada 24.87 kepada 12.98 dan 11.30 mg/100 g pada suhu berbeza (110, 140 and 170°C). Nib koko yang dipanggang pada 140°C mempunyai peratusan rasa koko yang tinggi, sederhana rasa pahit, dan sedikit rasa masam; kelat dan tiada rasa 'smoky'. Walaubagaimanapun, nib koko yang dirawat pada suhu 170°C menunjukkan peratusan rasa koko terendah serta mempunyai rasa pahit dan hangus yang tinggi.

CHAPTER 1

GENERAL INTRODUCTION

The cocoa plant belongs to the genus Theobroma of which *Theobroma cacao* is the only species of commercial value. It is taxanomically classified under the family of Sterculiaceae under the order of Malvales. Cocoa, the product of this tree, is the essential ingredient of chocolate. Cocoa is as rich in history at it is in flavour. The Mayan Indians and the Aztecs of central America considered cocoa to be a valuable product and believed the cocoa tree to be of divine origin, hence the name Theobroma, meaning `food of the gods' (Minifie, 1989).

The cocoa plant is believed to have been introduced to Sabah as early as 1700, after having been brought in by the Spaniards from Latin America to the Philippines in 1670, and then to Indonesia subsequently. The earliest report of cocoa in Peninsular Malaysia was recorded by J. C. Koenig in 1778. In 1882, Von Donop mentioned in his report on Agricultural Prospects of North Borneo' that he had seen Cocoa of at least 20 years fruiting well in Sabah despite their neglected condition (Wood and Lass, 1985).

The primary production to-day shows that national average yield in cocoa is above 700 kg per ha p. a., while some of the more efficient plantations have recorded yields above 1,200 kg per ha p.a. The cocoa and chocolate products industry in Malaysia has also shown impressive growth and now accounts for an annual usage of 100 000 tonnes of beans, which is equivalent to 50 per cent of Malaysia's cocoa bean production. Up to now, there are 11 companies in Malaysia which are involved in cocoa grinding, some of which also manufacture chocolate, cocoa-based confectionery and beverages (MICF, 1994).

Traditionally, chocolate manufacture involved roasting , a cooking process which over centuries has been developed by chocolate manufacturers who were guided by their sensory skills. Eventually, their learned experience of how beans of differing roast behaved in the subsequent manufacturing processes such as winnowing, grinding, pressing and conching, led to the development of continuously improved roasting systems (Urbanski, 1989). Exactly what happens in the bean during the roasting process is an extremely complex issue which has been under investigation for many years.

The roasting step is important because of the chemical reactions that occur which convert precursors (present from the earlier fermentation of the cocoa bean) into flavours characteristics of chocolate. In addition, excess moisture is driven off early in this stage of processing. The heat treatment also serves to loosen the shell when whole bean roasting is employed.

There are two very general divisions in roasting technique namely whole bean and nib roasting. The traditional whole bean mode involved the cleaning, roasting and winnowing of beans in that order. Today, nib roasting, where one cleans, pretreats the beans, winnows and finally roasts the separated nibs, seems to be the preferred method. Modern nib roasting system employ one of three means of thermal pre-treatment following bean cleaning. These are: hot air treatment, infra-red treatment and saturated steam treatment. Advocates of the traditional whole bean method of roasting concept still exist in today's industry. When whole beans are roasted, there is always a range of different size beans involved. Setting the roast conditions for the average sized bean results in larger beans being undercooked with the smaller beans being over-roasted. Poorer flavour could be the result.

Beans of varying size are especially a problem when a bean blend (consisting of beans from different countries of origin) is roasted. When beans of a single variety are roasted by themselves, their size is normally fairly homogeneous. The uneven roasting detailed above is then less of a problem. Wasted energy is significant when roasting a whole bean (Minson, 1992). Thorz and Schmitt (1984) reported that 40% of the total roasting energy is utilized in penetrating the shell. Foreign material is often adhered to the bean shell (even following cleaning). Combustion gases from these materials can be especially harmful to the flavour of the cocoa mass (Kleinert, 1988). This represents another good reason to eliminate the shell prior to roasting.

An additional rationale for removal of the shell prior to the cooking of the nib comes from a microbiological perspective. The shell contains a large portion of the bacterial load of the whole cocoa bean. Other steps can further assist in reducing levels of microbial activity. If it is decided that the shell will be removed before roasting, it must then be determined whether the nib itself is roasted or if cooking is deferred until after the nibs are already ground into liquor.

A low moisture nib or bean does not readily transfer heat. This explains the difficulty in roasting a whole bean. Once this whole bean is dry (a difficult task in itself)-it is hard to cook the entire bean due to the shell preventing the escape of steam and volatiles (Schmitt, 1988).

Another modern method of roasting is liquor roasting. Liquor roasting offers advantages such as more uniform roasting, and heat and mass transfer take place faster since case hardening occurs when nibs are roasted in a hot-air stream. This means that the transfer processes are retarded. However the fat film around the liquor particles has a similar effect (Mayer-Potschak and Newton, 1987). Liquor roasting also results in the `burnt' flavour because of the large surface area and high fat content in the cocoa liquor.

Hence, nib roasting with uniform size were chosen in this study in order to overcome these problem. Since this modern technique has been introduced to chocolate industry, the proper roasting temperature and time are still not yet published. The effects of temperature and time of nib roasting on the volatile compounds and the precursors of flavour are still unknown.

Thus, the objectives of the study were:-

a) To evaluate the effects of temperature and time on the destruction of free amino acids and reducing sugars during nib roasting.

b) To determine the effect of roasting temperature and time on the volatile components profile of cocoa.

c) To determine the effect of roasting temperature and time on flavour quality of nib through sensory evaluation.

CHAPTER 2

LITERATURE REVIEW

Introduction

Cocoa beans are widely used in the cocoa and chocolate products manufacturing. A good quality cocoa is one with the inborn flavour of the type of beans concerned. The major stages that contribute to good chocolate flavour are during the harvesting, fermentation, drying as well as the roasting process. If any of these stages is mishandled, the proper mixture of the constituents in the beans may not be present to develop a good chocolate flavour.

Generally, early processing of cocoa beans involves harvesting, fermenting and drying before undergoing the secondary processing which include cleaning, roasting and winnowing. The mass or liquor is produced after grinding the roasted beans. Cocoa butter and cake are produced after pressing the mass or cocoa liquor.

Primary Processing

Harvesting

The ripe pods are removed from the tree using knives, and those out of arms reach are harvested with special long-handled tools. Harvesting is normally carried out over a period of 3 to 4 days, at intervals of three weeks (Lopez, 1986). The harvested fruits should be broken open to remove the beans immediately after harvesting but this is not always practical. A maximum delay between harvesting and splitting can be four to five days (Lopez, 1986).

Fermentation

After harvesting, cocoa beans undergo a fermentation that helps to remove mucilage from the beans. Fermentation starts after splitting the cocoa pod and the microorganisms originating from fruit flies, pod walls and the farmer's hand would react with sugars containing pulp and acid (Ostovar and Keeney, 1973). Normally, fermentation may take between 3 to 6 days with various methods and is influenced by the ripeness and length of storage period of pods, type of cocoa, variations in pulp to bean ratio, time and bean turning and climate and seasonal difference (Wood and Lass, 1985). The methods of fermentation vary from country to country and in many instances even neighboring farms differ in their processing practices. Box fermentation is the favoured method amongst large producers of cocoa which is practiced in most countries including Malaysia. The only variations are in the size of boxes, the turning regime and the duration of fermentation and the methods of exudation and aeration, (Lopez, 1986).

Fermentation is the beginning process to the formation of chocolate flavour and aroma. A proper fermentation process is required in order to produce a cocoa aroma and flavour of chocolate. Foster (1978) stated that precursors of flavour are produced by the process of fermentation from the products furnished by the breakdown of the proteins and sugars. The major precursor namely sugars, amino acids and peptides were developed after the beans has died during fermentation (Forsyth and Roberts, 1960). Details on chemical changes which occur during fermentation are discussed in the following passages.

The fresh cocoa beans have a pH of about 3.50 in the pulp and 6.50 in the cotyledon. During the course of fermentation, the sugar undergoes degradation by microorganisms and the acids produced will diffuse into the cotyledon. During the first 2 days of fermentation, anaerobic yeasts become dominant and flourish in the mass. Anaerobic yeasts together with pectinesterase activity will cause `sweat' and breakdown of the pulp (Jinap, 1994). As sweating increases, the pH of the pulp rises as citric acid is metabolized by the organism.

The aerobic condition which prevails after the collapse of the pulp cells, improves aeration and causes acetic acid producing bacteria to predominate (Dimick