EFFECT OF SUPERHEATED STEAM ROASTING ON QUALITY CHARACTERISTICS OF COCOA BEANS (*Theobroma cacao* L.)

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By

WAHIDU ZZAMAN

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

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DEDICATED

TO

MY BELOVED PARENTS

MY BELOVED WIFE

LOVELY SON (JESNAUZZAMAN SHUVO)

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Wahidu Zzaman

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS/ABBREVIATION

Symblos/Abbreviation	Caption
AABA	α-amino butyric acid
AML	African Amelonado
AOAC	Association of Official Analytical Chemists
AOCS	American Oil Chemists' Society
ANOVA	Analysis of Variance
AnV	p-anisidine value
BF_3	Borontrifluoride
BI	Browning index
Cc	Cubic centimeters
CCD	Central Composite Design
CH_3OH	Methanol
Con	Conventional
CR	Cyclization reaction
CB	Cocoa butter
DPPH	1,1-diphenyl-2-picrylhydrazyl
DOE	Design of experiment
DSC	Differential scanning calorimeter
EEQ	Epicatechin equivalent
FFA	Free fatty acid
FA	Fatty acid
FAME	Fatty acid methyl esters
$Fecl_3$	Ferric chloride

FeSO4	Ferrous sulfate
FID	Flame ionization detector
FRAP	Ferric reducing antioxidant power
GAE	Gallic acid Equivalent
GC	Gas Chromatogrhapy
GC-MS	Gas chromatography-Mass spectrophotometry
ha	hectare
HCl	Hydrogen Chloride
He	Helium
HMDS	Hexamethyldisilazane
H_2O	Water
HPLC	High Performance Liquid Chromatography
IMC67	Iquitos Mixed Calabacillo 67
m/s	metre per second
MUFA	Monounsaturated fatty acid
NA33	Nanay 33
OD	Optical density
PA7	Parinari 7
PITC	Phenylisothiocyanate
POO	Palmitic-oleic-oleic
POP	Palmitic-oleic-palmitic
POS	Palmitic-oleic-stearic
PT	Proton transfer
PTC	Phenylthiocarbanyl
PUFA	Polyunsaturated fatty acid
PV	Peroxide value

R	methyl
R^2	coefficient of determination
SCA12	Scavina clones Amazon 12
SD	Strecker degradation
S.D	Standard deviation
SEM	Scanning electron microscopy
SHS	Superheated steam
SFA	Saturated fatty acid
SFI	Solid fat index
SMC	Standard Malaysian Cocoa
SOA	Stearic-oleic-arachidic
SOO	Stearic-oleic-oleic
SOS	Stearic-stearic-oleic
SPSS	Statistical Package for the Social Sciences
TAG	Triacylglycerol
TPC	Total phenolic content
TFC	Total flavonoid content
TPTZ	2,4,6-Tris (1-pyridyl)-5-triazine
UFA	Unsaturated fatty acid
UIT1	Unidentified Trinatario

KESAN PEMANGGANGAN STIM PANAS LAMPAU KE ATAS CIRI CIRI KUALITI BIJI KOKO (*Theobroma cacao* L.)

ABSTRAK

Pemanggangan adalah suatu proses pemanasan kering yang dilakukan untuk merubah karakteristik seperti warna, rasa dan menambahkan keenakanan biji koko**.** Biji koko merupakan bahan utama yang digunakan dalam proses pembuatan coklat atau produk berasaskan coklat. Dalam kajian ini, biji koko dipanggang pada suhu 150, 200 dan 250 ^{0}C dalam masa 0, 10, 30 hingga 50 minit dengan menggunakan cara stim panas lampau dan konvensional. Tujuan penyelidikan ini adalah untuk menganalisa perubahan seperti kelembapan, warna (L*, a*, b* dan BI), tekstur (kekerasan dan keretakan), komponen antioksida dan sebatian aktif rasa biji koko. Stim panas lampau pada suhu 200 ^{0}C selama 10 minit menunjukkan perubahan warna yang lebih baik manakala pada suhu 150 ^{0}C selama 10 minit menunjukkan kandungan fenol yang paling tinggi (47.46 mg GAE/g). Dengan menggunakan cara pemanggangan stim panas lampau, kandungan sebatian aktif rasa dalam biji koko panggang terutamanya pyrazine (52.78 %) memberikan nilai signifikan paling tinggi pada suhu 200 ^{0}C selama 10 minit.

Kaedah respon permukaan (response surface methodology, RSM) telah digunakan untuk mengoptimumkan keadaan pemanggangan dengan menggunakan stim panas lampau berdasarkan perubahan warna, rasa dan antioksida. Pengoptimuman berangka (numerical optimization) dan plot kontur menindih (superimposed contour plots) menunjukkan bahawa pemanggangan biji koko yang optimum dicapai pada suhu pemanggangan 180 ^{0}C selama 16 minit.

Kesan daripada kaedah pemanggangan atas sifat fizikokimia (peratus asid lemak bebas, nilai peroksida, nilai anisidin, komposisi asid lemak dan trigliserida dan sifat termal) dan mikrostruktur mentega koko yang diekstrak daripada biji koko mentah dan biji koko panggang telah dikaji. Keputusan menunjukkan nilai signifikan asid lemak bebas (2.80 % asid oleic), nilai peroksida (1.85 $MeqO_2$/kg) dan nilai anisidin (0.66) dalam sampel pemanggangan konvensional adalah paling tinggi. Cara pemanggangan konvensional telah merendahkan kandungan asid lemak dan komposisi trigliserida dengan ketara jika dibandingkan dengan cara pemanggangan stim panas lampau. Sampel stim panas lampau menghasilkan kristal yang lebih halus dan jelas.

Hasil kajian menunjukkan bahawa stim panas lampau merupakan cara pemanggangan biji koko yang berinovatif untuk menghasilkan produk koko yang berkualiti tinggi. Oleh itu, pengenalan kaedah ini dijangka akan memberi manfaat kepada pengguna dan industri dalam proses pemanggangan biji koko.

EFFECT OF SUPERHEATED STEAM ROASTING ON QUALITY CHARACTERISTICS OF COCOA BEANS (*Theobroma cacao* L.)

ABSTRACT

Roasting is one of the most important heat treatment that is usually undertaken to develop the characteristic color, flavour, as well as the palatability of cocoa beans. Cocoa beans are the primary raw material used for manufacturing chocolate and chocolate-based products. In this study, superheated steam and convectional methods were used to roast cocoa beans at 150, 200 and 250 ^{0}C for 0, 10, 30 and 50 min. The changes occurred in the moisture content, colors (L^*, a^*, b^* and BI), textural properties (hardness and fracturability), antioxidant compound and their activities, and flavor active compounds of the cocoa beans were investigated. Superheated steam at 200 ^{0}C for 10 min. showed desirable color whereas at 150 ^{0}C for 10 min. maintained high total phenol content (47.46 mg GAE/g) among treatments. The roasted flavor active compound especially pyrazines (52.78 %) was significantly higher at 200 ^{0}C for 10 min. using superheated steam roasting.

Response surface methodology (RSM) was used to optimize the roasting conditions using superheated steam based on the color, flavor and antioxidant properties. Numerical optimization and superimposed contour plots suggested the optimal roasting conditions to be 180 ^{0}C for temperature with 16 min. of roasting time.

The results exhibited significantly higher free fatty acid (2.80 % oleic acid), peroxide (1.85 MeqO_2/kg) and p-Anisidine value (0.66) levels in conventionally roasted samples. The conventional roasting method degraded the fatty acids and

important triglycerides significantly compared to the superheated-steam roasting. Superheated-steam-roasted samples exhibited finer crystals than did conventionally roasted and raw beans.

Based on the results obtained from this study, it is concluded that superheated steam can be used as an innovative method to roast cocoa beans to produce high quality cocoa products. Therefore, the introduction of this novel method is expected to bring interest for roasting process of cocoa beans that may be beneficial to consumers as well as to industries.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Background information

Cocoa is the beans obtained from *Theobroma cacao* L. tree, regardless of species and variety, it is a virtual prima donna in its requirements for healthy growth. Seldom it is found more than 20 degree north or south of the equator, with by far the greatest portion of the crop within 10 degree. Of the approximately 20 species of Theobroma presently known, *Theobroma cacao* is the commercially most important. Of more interest to the commercial grinding of cocoa beans are the many subspecies or, more correctly, varieties that have resulted from the natural and man-caused cross-breeding and seed selections that have transpired over the thousands of years. Cocoa is rich in history as it is in flavor. 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” is given (Reineccius and Henry, 2006; Minifie, 1990). Cocoa beans are rich in polyphenols. Unfermented cocoa beans contain polyphenolic compounds of 120–180 g kg^{-1} (Kim and Keeney, 1984). According to Wollgast and Anklam (2000) three groups of polyphenol can be distinguished in cocoa beans i.e. catechins or flavan-3-ols ca. 37%, anthocyanins ca. 4% and proanthocyanidins ca. 58%. Polyphenols in cocoa products are mainly responsible for the formation of astringent taste; they also contribute to bitter taste along with alkaloids, some amino acids, peptides and pyrazines (Bonvehi and Coll, 2000). During fermentation, cocoa bean undergoes a series of complex structural and biochemical changes which reduces polyphenol content and produces flavor precursors namely amino acids, peptides and reducing sugars. At initial stage of fermentation, the amounts of gaseous and dissolved oxygen diffusing into cotyledon are limited; this condition causes hydrolytic enzymatic reactions to occur. Polyphenols are subjected to biochemical modification through polymerization and complex with protein, and hence decreasing their solubility and astringency effect (Misnawi and Teguh, 2010; Bonvehi and Coll, 1997). At the same time, anthocyanins are hydrolyzed to produce anthocyanidin, galactose and arabinose; beside dimerisation of the leucocyanidins and exudation of the flavonoids out from the bean. Subsequently, during drying, polyphenol amounts are substantially reduced by enzymatic browning (Kim and Keeney, 1984). Reducing sugars are carbonyl aroma precursors in fermented cocoa bean, which are mainly produced through hydrolysis of sucrose by the action of invertase (Misnawi and Teguh, 2010).

Generally, raw cocoa beans needs to be subjected to various complicated technological process, among which one of the main steps is roasting (Krysiak, 2011). Roasting is an important heat treatment that is usually accomplished to develop color, characteristic flavor as well as the palatability of food product. These treatments are considered to produce high quality cocoa beans and cocoa butter (Reineccius and Henry, 2006; Bonvehi and Coll, 2002; Voigt et al., 1993). Maillard reaction plays an important role in the formation of this color and flavor during roasting (Ziegleder, 1991). Free amino acids and reducing sugars are two major precursors involved in the reaction which develop during fermentation. The condensation of the carbonyl group of a reducing sugar with an amino compound involves in the first stages of the Maillard reaction, followed by the degradation of the condensation products to provide a number of different compounds (Idrus and Yang, 2013; Reineccius and Henry, 2006).

Convectional method is commonly used for roasting of cocoa beans taking into account the general impact of process parameters such as temperature and time (Krysiak, 2011; Nebesny and Rutkowski, 1998). High temperatures and low moisture contents are the ideal conditions for the Maillard reaction and these conditions can be found in suitable roasting method (Heinzler and Eichner, 1992). Roasting parameters varies from 120 to 250 ^{0}C for 10 to 120 minutes depending on the color, flavor, texture and application desired (Idrus and Yang, 2013; Reed, 2010; Ramli et al., 2006). Nib roasting takes up to 60 min and up to 120 min for whole beans roasting of cocoa beans (Reed, 2010).

A number of drawbacks have been reported on due to traditional ways of heat and energy transfer and this heat treatment process takes too long that may contribute loss of aroma, increased bitterness of beans and produce carcinogenic acrylamide compounds (Farah et al., 2012). The undesirable burned flavor and odors coming from bean is considered as quality damage (S`wiechowski, 1996).

Research works undertaken have reported that convection roasting produce smoky and burned flavor in cocoa products and more than 70% of phenolic compounds and most of the antioxidant properties of raw cocoa beans to be destroyed during prolong heating (Misnawi and Teguh, 2010; Swiechowski, 1996; Wollgast and Anklam, 2000). The temperature difference between the kernel and the husk of cocoa beans is also disadvantages of this method. Another important demerit is to transfer of cocoa butter from kernel to husk of the bean using this traditional convection roasting of cocoa. It is economically important because industries only use the kernel.

The properties of the fat of cocoa beans are also damaged that is the main component of cocoa beans using convectional roasting (Nebesny and Rutkowski, 1998). Recently, Krysiak (2011) have stated that application of conventional and microwave roasting to negatively affect cocoa beans and cocoa butter qualities (physic-chemical and thermal behaviors). The types of roasting equipment in use are many, and new developments have been made every few years for the past several decades. Each undoubtedly has its advantages, but in some instances the manufacturer is tempted to sacrifice quality and distinctiveness for real and sometime imaginary economies.

In recent years, many researches have been focused and succeeded for the application of superheated steam in food industry as a new method. It is obtained by reheating saturation steam exceeding the boiling temperature of H_2O that is a colorless and transparent gas. Superheated steam has many interesting properties although it performs as a hot dry gas (Idrus and Yang, 2012; Head et al., 2011; Mujumdar, 2007). Most important characteristics of the steam are that the products are not oxidized because the air in the system is replaced by superheated steam and thus, the samples can be heated or dried under non-oxygen environments (Amatsubo et al., 2006). Research on thermal treatment such as cooking, baking, roasting, drying and sterilization has been enabled by the application of superheated steam (Idrus and Yang, 2012; Wang, 2012; Hosaka, 1999). It has been reported that the drying of sliced raw potatoes using superheated steam was better quality in term of color, flavor than hot air drying system (Prachayawarakorn et al., 2002; Iyota et al., 2001). Many reported evaluating quality of agricultural products have stated the superior quality using superheated steam than hot air drying treatments (Hamada et al., 2003). Superheated steam as drying medium is an energy efficient process compared to conventional hot air because of possibly reuse of the latent heat of evaporation (Mujumdar, 2007; Berghel and Renström, 2003). It has been claimed that this technology heats foods while retaining antioxidants, vitamins and other essential nutrients owing to the absence of oxygen (Head et al., 2011; Mujumdar, 2007; Pronyk et al., 2004).

Use of superheated steam (SHS) roasting can be an alternative method which can abolish the above mentioned demerits of conventional roasting. The application of superheated steam generates uniform heating condition in the material during thermal processing of food (Horagai et al., 2008; Methakhup et al., 2005). It is reported that superheated steams can improve the quality in term of color, textural and antioxidant properties of peanut and cocoa beans (Idrus and Yang, 2012). It is also reported that this technology can heat food faster while retaining essential nutrients and health promoting compounds (Head et al., 2011; Pronyk et al., 2004). Significant advantages of SHS over conventional hot air drying is reported (Sotome et al., 2009; Prachayawarakorn et al., 2006; Mujumdar, 1995). However, to the best of our knowledge, no reports are available on application of SHS on evaluating the quality of cocoa beans during roasting process.

Hence, the main aim of this study was to evaluate the effects of SHS roasting on the quality characteristics of cocoa beans and cocoa butter extracted from roasted cocoa beans. We expect that the information generated could provide better insight on the potential application of superheated steam technology to produce high quality cocoa-based products.

1.2 Problem statements

1. Convectional roasting brings an undesirable color and texture due to temperature difference between kernel and husk of cocoa beans.

2. Convectional roasting leads up to 70 % lose of antioxidant compound and their activities of cocoa beans.

3. Convectional roasting produces undesirable burned smell and aroma and then the product is considered as unacceptable to consumers.

4. Convectional roasting degrades the quality of the cocoa butter extracted from roasted cocoa beans.

1.3 Importance of study

1. There is no previous study and established data on cocoa beans quality which was subjected to superheated roasting process;
2. The process developed from this research could be better alternative of roasting method with possible application in cocoa-based industry;
3. This established data from this research could be relevant information aimed at the development of superheated steam roaster for industrial application.

1.4 Objectives of the study

The main objective of this study was to improve the quality of cocoa bean to produce high value cocoa products. Hence, the specific objectives of this study are as follows:

1. To measure the changes in the physical (moisture content, color and textural properties), antioxidant properties (total phenol, total flavonoids, DPPH and ferric reducing antioxidant power) and flavor active compounds (Pyrazines, alcohol, carboxylic acids, aldehyde, ester, ketone, amines, and hydrocarbons) using superheated steam and conventional roasted cocoa beans at different temperature (150, 200 and 250 ^{0}C) and time (0, 10, 30 and 50 minutes).

2. To optimize roasting condition based on color (browning index), flavor (carboxylic acids, pyrazines, aldehyde and ketone), antioxidant properties (total phenol, total flavonoids and ferric reducing antioxidant power) and sensory analysis of superheated steam roasted cocoa beans.

5. To examine the physicochemical properties (free fatty acid, peroxide and *p*-Anisidine value, fatty acid composition, thermal behavior and microstructure) of cocoa butter extracted from the roasted cocoa beans at optimum condition.

1.5 Thesis outline

In this thesis, the prospect of application of superheated steam roasting process to evaluate the quality characteristics of cocoa beans and cocoa butter extracted from cocoa beans will be discussed. This thesis consisted of eight main chapter. First and second chapter will provide general introduction of the study and literature review regarding the research. The following three chapters will discuss the quality characteristics of cocoa beans and cocoa butter including the moisture, color, textural antioxidant properties, flavor development and optimization of roasting condition and physiochemical characteristics of cocoa butter extracted from roasted cocoa beans. Overall conclusions of the research and several recommendation for further studies are stated in the last chapter. Briefly, the descriptions of each chapter are as follows:

CHAPTER 1 provides general introduction to this research, including the background information of the study as well as the current development and its challenges of roasting process. The importance of this study also described briefly, since current application of the superheated steam is still limited despite its potential.

CHAPTER 2 is aimed to provide general information of cocoa beans including its history, production, distribution and industrial usage. It is also provide the information on the potential application of superheated steam for roasting process that can be applied to improve the quality of cocoa beans.

CHAPTER 3 will discuss as the effect of roasting process on changes in the

physical (moisture content, color and textural properties), antioxidant properties (total phenol, total flavonoids, DPPH and ferric reducing antioxidant power) and flavor active compounds (Pyrazines, alcohol, carboxylic acids, aldehyde, ester, ketone, amines, and hydrocarbons) of raw and roasted cocoa beans using conventional and superheated steam methods.

CHAPTER 4 will discuss as optimization of superheated steam roasting conditions based on color, flavor and antioxidant properties of cocoa beans using response surface methodology and compared to conventional roasting method regarding flavor precursors (sugar and amino acids), microstructure and sensory evaluation of chocolate made from roasted cocoa beans.

CHAPTER 5 will discuss as the effect of roasting process on changes in the physicochemical properties including free fatty acid (FFA), peroxide value (PV) and p-Anisidine value (AnV), fatty acids, tryglycerides composition, thermal behavior and microstructure of cocoa butter extracted from raw and roasted cocoa beans.

CHAPTER 6 will provide overall conclusion of the findings in this research as well as several recommendations for further studies regarding superheated steam roasting process of cocoa beans.

CHAPTER 2

LITERATURE REVIEWS

This literature review is divided into 6 sections consist of (1) Cocoa beans, (2) Physico-chemical properties of cocoa beans, (3) General overview of cocoa beans processing, (4) Changes during roasting process of cocoa beans, (5) Sensory evaluation and (6) Superheated steam process. Section (1) is aimed to provide general information of cocoa beans including its origin, production and distribution. Subsequent sections provide the information on the physico-chemical properties of cocoa beans, primary and secondary processing of cocoa beans, and changes during roasting process of cocoa beans and sensory evaluation. Superheated steam process principle and its application in food industries are discussed in section (6).

2.1 Cocoa bean (*Theobroma cacao* L.)

2.1.1 Cocoa beans

The cocoa beans are the products derived from the seeds of the *Theobroma cacao* tree. The beans are rich in history because of its characteristics flavor. The “Aztecs” of Central America and the “Mayan” Indians considered the cocoa to be a valuable bean and believed the cocoa tree to be of divine origin, hence the name of ‘Theobroma’ meaning ‘food of the gods’ (Minifie, 1989). Cocoa (*Theobroma cacao* L.) is one among the 22 species of the genus *Theobroma* in the family of sterculiaceae. It is the most commercially important than other species because of its seed value (Bartley, 2005). The seeds are the main raw material for chocolate manufacturing, usually called as cocoa beans. The cocoa liquor, cocoa power, cocoa butter derived from cocoa beans is widely used in the food and confectionery industries. It is also used in cosmetic and pharmaceutical industry.

Cocoa products have a characteristic flavor which is related to bean genotype, growing environments, and processing features (Clapperton, 1994; Whitefield, 2005). Fermentation is one of the main primary processing steps that enable removal of the pulp and later drying. The flavor precursors development, color formation, and reduction in bitterness are occurred during this step. After those chocolate producers involved roasting, it is a cooking process that occur important changes in cocoa, including Maillard reactions with reducing sugars and amino acids and produce the characteristics flavor (Reineccius, 2006; Awua, 2002; Kealey et al., 2001; Beckett, 2000; Fowler, 1999).

After roasting, the following manufacturing routes such as winnowing, crushing, pressing and conching, directed to the final products. During the roasting step what happens exactly in the beans is very complex issue which has been under studied for many years. This step also helps to loosen the shell when whole bean is roasted. Recently several studies have been claimed that cocoa has possible benefit in human health because cocoa and its products are rich in phenolic compounds which have strong antioxidant properties (Gu et al., 2006; Miller et al., 2006; Steinburg et al., 2003; Tapiero et al., 2002; Weisburger, 2002; Wollgast & Anklam, 2000b; Erdman et al., 2000).

2.1.2 Origin, Distribution and Classification

The name "cocoa" derived from the word "cacao," but has come into common use when referring to the beans. Cacao has come to be used only in agricultural reference to the tree or husbandry. The basic words cacao and "chocolate" stem directly from the "Mayan" and "Aztec" languages. Thomas Gage wrote in his "New Survey of the West Indies", concering the origin of the word chocolate: "The name is compounded from *atte,* as some say, or as others, *attl,* which in the Maxican language signifieth 'water,' and from the sound which the water (wherein is put the chocolate) makes, as choco, choco, choco, when it is stirred in a cup by an instrument called a 'molinet' or molinillo,' until it bubble and rise unto a froath." Cortez referred to the cacao tree as "Cacap," a word derived from the Maxican "cacavaqualhitl." The Maxican called the fruit "Cacava-centli," the beans "Cacahoatl" and the beverage "Chocolatl." DeCandolle states in his "Origin of Culivated Plants," the cacao tree has been cultivated in America for 3000 or 4000 years (Tapiero et al., 2002).

The majority of cocoa tree is grown within 10^0 South and North of the equator. The suitable temperature for cocoa cultivation is generally within 18-36 ^{0}C and well rainfall across the years preferably from 1500 to 2500 mm. During cultivation high humidity is required within 90-95% at night and 70-80% during day. The density of cocoa tree usually between 600 to 1000 trees/ha. Cocoa pod in cocoa tree and cocoa beans in cocoa pod are shown in Figure 2.1 and 2.2.

Figure 2.1 Field observations of raw and ripe cocoa pods in cocoa tree at cocoa research and Development Centre at Perak, Malaysia.

Figure 2.2 Field observations of cross-sectional raw and ripe cocoa beans at cocoa research and Development Centre at Perak, Malaysia.

There are three major vatietties of cocoa beans cultivated throughtout the world namely, Criollo, Forastero and Trinitario. Criollo represents less than 3% of the world's cocoa production found in Spanish, Mexico, Nicaragua, Mexico, Columbia, Guatemala, Samoan Islands, Madagascar and Sri Lanka. These cocoa beans are high aromatic and less bitterness considered as high quality beans. Forastero found in Nigeria, Ivory Coast, Ghana, New Guinea, Central America, Brazil, Sri Lanka, Indonesia and Malaysia. It represents about 85% of the world's cocoa production. The trees give high yields and are hardy. Trinitario found mainly in the Caribbean and also in Columbia and Venezuela. It represents about 12% of the world's cocoa production (Tapiero et al., 2002). Cultivated Malaysian cocoa beans are graded before selling to market. The grading specifications are given in Table 2.1.

Table 2.1 Grade specifications of cultivated Malaysian cocoa beans

Standard Malaysian Cocoa Grades	Bean Count (100g)	Mouldy beans (% max.)	Slaty beans (% max.)	Insect damaged and germinated beans (% max)
SMC 1	<=100	<= 3	<= 3	<= 2.5
SMC 2	>100 <= 110	<= 3	<= 3	<= 2.5
SMC 3	> 110 <= 120	<= 3	<= 3	<= 2.5

-SMC denotes Standard Malaysian Cocoa.

-All percentages in the grade specifications are by count. The percentage given in the last column applies to all the mentioned therein, taken together.

Sources: http://www.koko.gov.my/lkm/index.cfm. Access date: 07 December, 2012

2.1.3 Area and Production

Cocoa and cocoa-based products are consumed in great demand worldwide due to its unique flavour and aroma that cannot be replaced by other plant products. *Theobroma cacao* L. is the only species cultivated commercially in major producing countries such as Ivory Coast, Ghana, Nigeria, Cameroon, Brazil, Ecuador, Indonesia and Malaysia is shown in Figure 2.3. Currently, Ivory Coast is the leader in cocoa production follows by Ghana and Indonesia

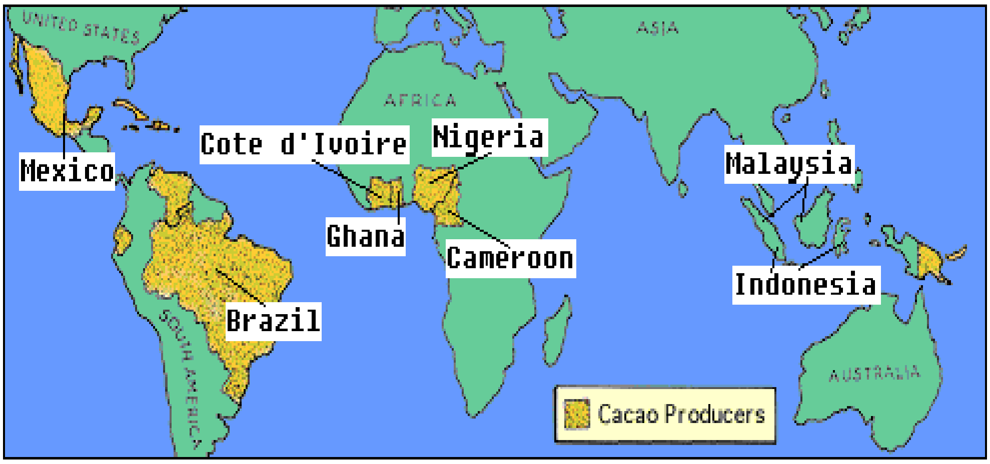


Figure 2.3 World map of cocoa production

Source: http://www.icco.org/statistics/production.aspx. Access date: 28 February 2013

Table 2.2 summarizes world-wide dry cocoa beans production. The African countries produced 69 percent and the Central and South American countries produced 12 percent of the total. The Asian countries produced the remaining 19 percent. India’s contribution is negligible (0.21 percent).

Table 2.2 Country-wise cocoa production in the world

Country	Production ('000 tons)	% of total production
African countries:		
Ivory Coast	1175	41.92
Ghana	398	14.20
Nigeria	202	7.21
Cameroon	121	4.32
Other African countries	40	1.43
Central and South American countries:		
Brazil	130	4.64
Other Central and South American countries	210	7.49
Asia and Oceania :		
Indonesia	393	14.02
Malaysia	79	2.82
Papua New Guinea	35	1.25
Other Asian countries and Oceania	20	0.71
World total	2803	100

Source: FAOSTAT (2012). Access date: 28 March 2013

Planted cocoa are in Malayisa was more than 28,000 (ha) including small-holder, production of cocoa beans was 35,180 tons in 2007 and grindings volume was 323,653 tons in 2008. The Malaysian cocoa downstream sector has expanded rapidly since 1990 contributed by the better financial returns generated through grinding and manufacturing activities. The manufacturing of chocolate and confectioneries has also shown an accelerated growth supported by the increase in consumption as a result of increasing higher income. In 2011, the consumption of chocolate and confectioneries products is estimated 10,500 tonnes in 2010. It is estimated that the total production of chocolate and confectioneries registered an average annual growth of five percnt. The Malaysian cocoa based products are exported to more than 100 countries worldwide contributing more than RM 270 million in terms of export earnings in 2010 (FAOSTAT, 2012).

2.2 Physico-chemical properties of cocoa beans

2.2.1 Cocoa beans properties

The chemical composition and characteristics of cocoa butter are greatly influenced by the variety of cocoa and the growth conditions. As a consequence there exists a lot of variation in the properties of cocoa butter, not only between the varieties but also within one variety.

2.2.2 Proximate composition of cocoa beans

The cocoa beans compose of cotyledon and a shell which consists of 10–14% of the dry weight of the entire cocoa bean, while cotyledon or kernel make up of 86–90% of the remaining weight. Cotyledon is responsible for the distinct aromas and flavours of chocolate (Osman et al., 2004) and is formed by two types of storage cells which are parenchymatous. Polyphenolic cells which make up for 14–20% of the weight of dry bean have a large vacuole filled with alkaloids and polyphenols which include theophylline, theobromine and caffeine (Osman et al., 2004). Cocoa seeds are composed of pulp and kernel. The composition and chemical components of cocoa seed are shown in Table 2.3. Fresh Forastero cotyledons has deep purple colour formed by undisturbed pigmented polyphenols. Besides, lipid–protein cells also contain cytoplasms packed with numerous small proteins, lipid vacuoles and others for example the starch granules. These components define cocoa flavour and aromas (Nazaruddin et al., 2001; Kim & Keeney, 1984). Osman et al. (2004) reported15.8 mg/g sucrose and small amounts of inositol inositol, mannitol, fructose and sorbose could be found in fresh and unfermented cocoa beans. 24.8 mg/g unfermented beans has sucrose content around 90 % of overall sugars which is 27.1 mg/g. Fructose and glucose (reducing sugars), form around 6 % (0.7 and 0.9 mg/g, respectively) and others sugars including inositol and mannitol are less than 0.50 mg/g. Distinctness is due to type of methods and duration used for harvesting, origin and type of cocoa beans. Components of tissue remain compartmentalized to separate flavour components that may have interaction with cell membrane and cause disintegration of cell wall during the subsequent fermentation. Table 2.4 showed the made up of unfermented West African (Forastero) cocoa bean. Make up of West African (Forastero) unfermented cocoa bean.

Table 2.3 Chemical components and composition of cocoa seed

Component	**Composition**
Pulp	
-Water	82-87%
-Sugar	10-13%
-Salt	8-10%
-Pentosans	2-3%
Citric acid	1-2%
Cotyledon	
-Water	32-39%
-Fat	30-32%
-Protein	8-10%
-Polyphenols	5-6%
-Starch	4-6%
-Pentosans	4-6%
-Sucrose	2-3%
-Cellulose	2-3%
-Theobromine	2-3%
-Caffeine	1%
-Acids	1%

Source: Lopez and Dimick (1995)

Table 2.4 Bean composition of West African unfermented cocoa bean

Components	Fat-free material (%)	Dried whole bean (%)
Cotyledon	89.60	-
Fat	53.05	-
Shell	9.63	-
Water	3.65	-
Germ	0.77	-
Ash	2.63	6.07
Polyphenols	7.54	17.43
Acid	0.30	0.70
Nitrogen		
-Total nitrogen	2.28	5.27
-Protein nitrogen	1.50	3.46
Theobromine	1.71	3.95
-Caffeine	0.085	0.196
Carbohydrates		
-Glucose	0.30	0.69
-Sucrose	1.58	3.86
-Starch	6.10	14.09
-Pectins	2.25	5.20
-Fibre	2.09	4.83
-Pentosans	1.27	2.93
-Mucilage and gums	0.38	0.88

Source: Afoakwa (2010)

2.2.3 Phenolic and antioxidant properties of cocoa beans

Polyphenols, otherwise known as tannin, are distinct family of secondary metabolites present in the leaf, bark, bean and fruit of higher plants. They are believed to participate in the defense of the plant by rendering the tissue unpalatable and non-nutritious thus unacceptable as food source to herbivores and omnivores. Their presence in foods is important since they are a part of human diet (Kroll and Rawel, 2001) and contributes to the formation of food flavor (Baxter et al., 1997; Lindsay, 1996; Fowler, 1995).

Kim and Keeney (1984) found that cocoa beans are rich in polyphenols and unfermented cocoa bean was found to contain 120–180 g kg^{-1} of polyphenolic compounds. The role of polyphenols in cocoa products is mainly responsible for the formation of astringent taste and contributing to bitter taste along with alkaloids, some amino acids, peptides and pyrazines (Bonvehi and Coll, 2000).

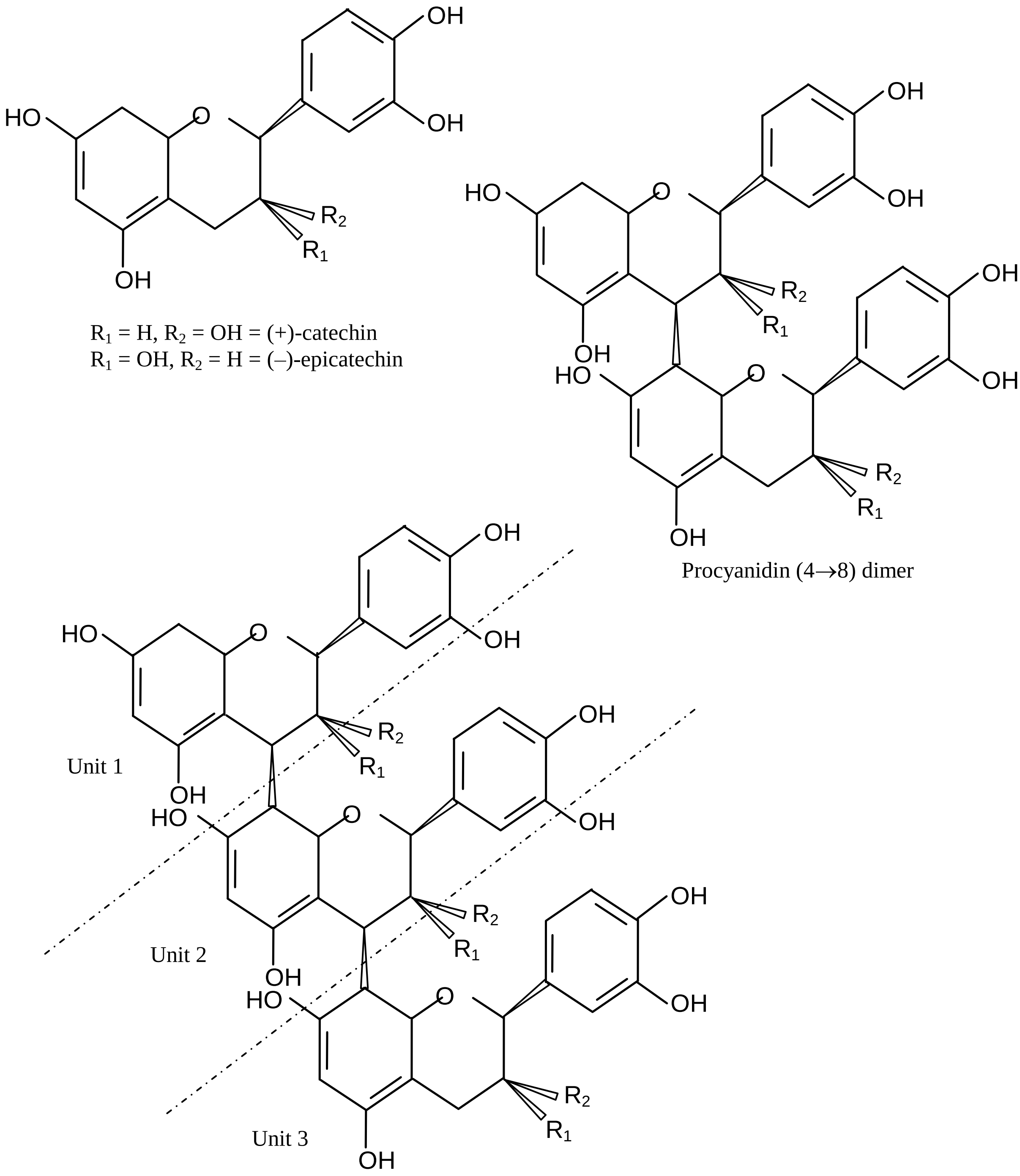
Kim and Keeney (1984) identified the major phenolic compounds in cocoa bean viz. 1) anthocyanins: cyanidin-3-arabinoside, cyanidin-3-galactoside and cyanidin hydrochloride; 2) leucocyanidin and 3) (–)-epicatechin. However, Bonvehi and Coll (2000) reported that anthocyanins were not found in Criollo cocoa bean. Based on a series of chromatographic experiments, Lee et al. (2004) identified and estimated the concentration of major polyphenols in Forastero cocoa bean as presented in Table 2.5. Eight compounds in the three main fractions viz. catechin, leucocyanin and anthocyanin were identified, however another fraction which moves very slow on the paper chromatography suggested as complex tannins.

Table 2.5 Polyphenol concentrations in Forastero cocoa bean

Polyphenols	Fractions	Percentage in Dry weight	Percentage in Total polyphenols
Catechins	(–)-Epicatechin	2.75	35
	(+)-Catechin		
	(+)-Gallocatechin	0.25	3
	(–)-Epigallocatechin		
			33–42
Leucocyanidins	Leucocyanidins 1	1.6	21
	Leucocyanidins 2, 3	0.8	10
			25–39
Anthocyanins	3-α-L-Arabinosidyl-cyanidin	0.3	2.5
	3-α-L-Arabinosidyl-cyanidin	0.3	2.5
			5
	Complex tannins	2.0	24–40

Source: Lee et al. (2004)

Wollgast and Anklam (2000a) stated that cocoa polyphenols are mainly monomers and oligomers of flavan-3-ol basic compound (Figure 2.4) and they also classified cocoa polyphenol into three groups i.e. catechins or flavan-3-ols ca. 37%, anthocyanins ca. 4% and proanthocyanidins ca. 58%.



R_1 = H, R_2 = OH = (+)-catechin
R_1 = OH, R_2 = H = (–)-epicatechin

Procyanidin (4→8) dimer

Procyanidin oligomers

Figure 2.4 Structure of polyphenol found in cocoa. Source: Wollgast et al. (2001)

The presence of polyphenols in cocoa bean is not only responsible for the formation of astringent and bitter tastes but also projecting brown color characteristic of dried fermented cocoa bean (Bonvehi and Coll, 2000). During cocoa fermentation, polyphenols are subjected to biochemical modification through oxidation and polymerization and binding with protein, hence decreasing their solubility and astringency effect (Bonvehi and Coll, 1997). At the same time, anthocyanins are hydrolyzed to produce anthocyanidins, galactose and arabinose; beside dimerisation of leucocyanidins and exudation of the flavonoids from the bean. Subsequently, during drying, amount of polyphenols are substantially reduced mainly by enzymatic browning (Kim and Keeney, 1984).

Hoskin and Dimick (1994) reported that decreases in (–)-epicatechin (a polyphenol monomer) and leucocyanidins during fermentation were due to exudation. Porter et al. (1991) found that (+)-catechin was not associated with the polymer biosynthesis during cocoa fermentation, thus it was not significantly decreased. Similar result was found by Misnawi et al. (2003), where (+)-catechin was more resistance against enzymatic oxidation compared to (–)-epicatechin.

Recently, cocoa bean polyphenols have gained much attention owing to their antioxidant activity and their possible beneficial implications in human health, such as in the treatment and prevention of cancer, cardiovascular disease and other pathologies. Experiment using *in-vitro* and animal models found that most of the cocoa bean polyphenol fractions indicate antioxidant activities and give beneficial effects to human health (Osakabe et al., 2000).