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THE EFFECTS OF ROASTING CONDITIONS ON COCOA NIB AND COCOA LIQUOR PROPERTIES

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Major professor

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THE EFFECTS OF ROASTING CONDITIONS ON COCOA NIB AND COCOA LIQUOR PROPERTIES

By

Harry Thomas Zechman, III

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ABSTRACT

THE EFFECTS OF ROASTING CONDITIONS ON COCOA NIB AND COCOA LIQUOR PROPERTIES

By

Harry Thomas Zechman, III

Color and pH are two important quality traits of cocoa liquor; color influences consumer acceptability of the finished product, while pH affects palatability as well as functionality. The purpose of this study was to assess the effects of moisture content and temperature on the pH and color of the resulting liquor during batch roasting of cocoa nibs.

A computer software package developed by the ECHIP™ Company was used to design an experiment which was conducted on a pilot scale Barth roaster. A wide range of initial bulk moisture contents and final bulk temperatures were used. Particle size distribution was determined before and after batch roasting to assess the effect of processing conditions.

The raw cocoa beans used as starting material were found to be underfermented, with a higher than typical pH. Redness and darkness were found to be sensitive to moisture content and temperature; however, pH and particle size distribution were relatively insensitive. The darkest liquor was obtained at an initial bulk moisture content of 20% and a final bulk temperature of 130°C. Redness was maximized by raising the initial bulk moisture content above 10% and roasting to a final bulk temperature of 110°C.

DEDICATION

To Kathleen and the children.

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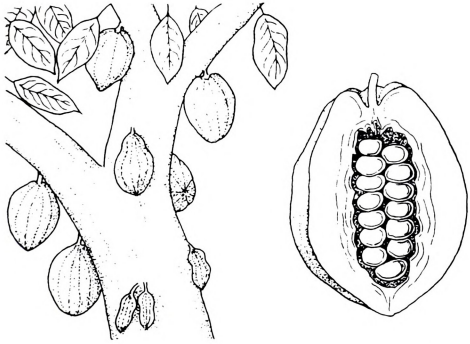
1.0 INTRODUCTION

The processed cocoa bean forms the critical raw material for chocolate. The bean starts out as a seed found in the pod of the tropical tree *Theobroma cacao* (Figure 1). The name *theobroma* is Greek for "food of the gods." The trees grow to about 8 meters in height and only within 20 degrees latitude north and south of the equator. The pods are about 20 cm long and 9 cm in diameter.

The history of this bean is fascinating. The tree originated 4,000 years ago in and around the valleys of the Amazon and Orinoco Rivers in South America (Young, 1984). There is evidence that cacao has been cultivated for more than 3,000 years. Cocoa seeds were carried north into Mexico by the Mayas before the 7th century A.D. (McGee, 1984). The first Europeans to encounter cocoa were the crew members of Columbus' fourth voyage in 1502. It was not until 1519, however, that the use of cocoa was understood. The Spanish explorer, Hernán Cortés, found that the Aztecs valued the cocoa bean highly. The seed contains a large amount of fat as well as starch and protein. Eaten in large amounts, it was an important food and was valued enough to be used as a form of currency.



(a) (b)

Figure 1. (a) Cocoa tree with pods. Note how the pods grow on both the main trunk and branches. (b) Cocoa pod cross section, showing the organization of seeds inside the pulp.

Source: McGee (1984)

Human consumption of cocoa was typically in the form of a beverage, known as xocolatl, an early form of the word chocolate (Young, 1984). The seeds were collected, fermented, sun dried and roasted in earthen pots. The shells of the roasted cocoa beans were then removed. The remaining kernel, called a nib, was ground into a paste called cocoa liquor, either alone or with herbs and spices. The liquor was then cooled, which allowed it to solidify. Small pieces of the solid were consumed directly or dissolved in water and beaten to a foamy consistency. The beans contain two related alkaloids – caffeine and theobromine. Caffeine, which has the strongest effect on humans, caused the bean to be identified early as medicine.

Spain held the secrets to cocoa for about 150 years. By the late 1600's, however, the secrets had escaped Spanish control and "drinking chocolate," a mixture of cocoa liquor and cane sugar (another New World commodity), was popular throughout continental Europe and the United Kingdom. In 1828, while searching for a way to decrease the high fat content of drinking chocolate, Dutchman Coenraad Johannes van Houten developed a mechanical method using a screw press to separate the cocoa liquor into a fat fraction, called cocoa butter, and a partially defatted fraction, called cocoa cake or powder. van Houten also invented another process, aptly called "dutching". Dutching is the process of treating cocoa nibs, cocoa liquor, or cocoa cake with an alkaline solution to darken its color, make its flavor milder and improve its

solubility in water (McGee, 1984).

In 1847, the English company Fry and Sons found that, by adding cocoa butter to a mixture of cocoa liquor and sugar, a product easy to handle could be created. This product was referred to as "eating chocolate" (McGee, 1984). Chocolate is solid at room temperature and melts at a temperature just below that of the human body. Due to its melting characteristics, it releases its flavor in an optimal fashion which results in a pleasant eating experience for the consumer.

World demand for cocoa beans has steadily increased over recent decades (Figure 2) as a direct result of the popularity of chocolate and cocoa powder-based products (Anon, 1994). In the United States, 1992 annual per capita consumption of chocolate was approximately 10.6 pounds (Anon, 1994).

All cocoa beans are first manufactured into cocoa liquor via roasting and grinding processes. The grinding process is simply a method of breaking the cells within the roasted cocoa nib to release the cocoa butter and hence liquefy the cocoa material. Cocoa roasting, however, takes on many forms and is the subject of significant research. It is one of the most critical processing steps as it yields both the flavor and color that is characteristic of cocoa products (McGee, 1984). As new markets for cocoa-based products develop and as new countries begin growing and producing cocoa, the understanding of the effects that this critical process has upon cocoa is increasingly important.

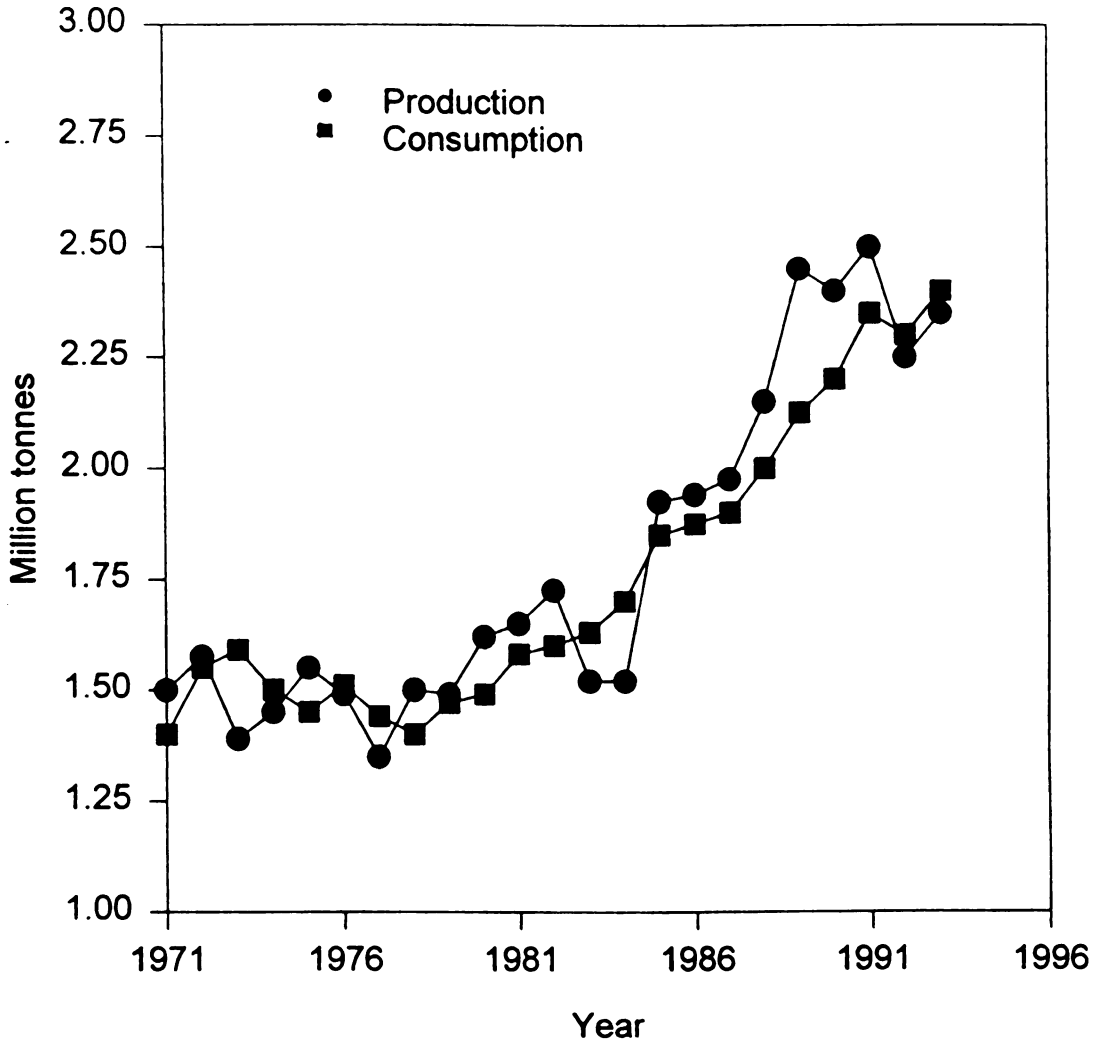


Figure 2. World cocoa production and consumption, 1971-1993.

Note: 1 tonne = 1,000 kg. Source: Anon (1994)

2.0 PROBLEM STATEMENT

There are differences in the acidic characteristics of dried cocoa beans produced in different countries. For example, cocoa from Brazil and the Far East has been known to be excessively acidic in comparison to West African cocoa. Highly acidic cocoa can only be used in limited amounts in product formulations. Researchers have attributed possible variations in the acidic characteristics to the fermentation and drying techniques used in the country of origin, as well as the degree of fermentation.

Additionally, cocoa beans exist in the commercial market which are partially fermented or are simply harvested and dried in the sun. Their pH is higher than that of normal West African cocoa; they also lack the normal concentrations of typical chocolate color and flavor precursors which are formed as a result of proper fermentation and drying. This underfermented condition results in a higher than normal percentage of grey, slatey color which is undesirable when compared to the chocolate brown color of normal cocoa. Since underfermented cocoa beans are a relatively inexpensive commodity, there is an opportunity to modify their pH and color through processing to allow for their extensive use in cocoa product formulations.

Typically, the confectionery manufacturer has no control over the preharvest and postharvest processing methods used for preparing fresh cocoa seeds for the commercial market.

Requests for the use of abnormal preharvest and/or postharvest processing techniques are either ignored by the farmer or result in less than economical prices. Hence, the finished material, if available, is not economically viable for the manufacturer. Therefore, the challenge becomes: how can the undesirable properties of underfermented cocoa be altered during processing of the dried bean after it has been purchased?

Batch roasting of cocoa nibs has become popular over the past 15 years. There are a number of process advantages to batch roasting over continuous roasting. These include the ability to: 1) produce specialized lots of roasted cocoa through recipe manipulation and the addition of a variety of ingredients during roasting, and 2) manufacture small discrete batches.

The purpose of this study was to assess the effects of moisture and temperature during batch nib roasting on pH and color of the resultant cocoa liquor. Color and pH are two important quality traits of cocoa liquor. The color of cocoa liquor will influence the consumer's acceptability of the finished product. The pH of the liquor will affect palatability as well as functionality of the finished product. Changes in cocoa nib particle size distribution during the batch roasting process as well as moisture profiles during roasting was also studied. Flavor, which tends to be subjective and difficult to quantify, was not explored in this study.

3.0 LITERATURE REVIEW

3.1 Preharvest Practices

There are three main types of *Theobroma cacao:* Forastero, Criollo and Trinitario. The Forastero has pale to deep purple cotyledons or seeds, and the Criollo has white, ivory or very pale purple cotyledons. The purple color results from anthocyanins, a group of natural colorants found in red and blue flowers. The anthocyanin pigments form a subgroup of phenolic compounds. The tannins are also part of this subgroup. In Criollo cocoa, the colored anthocyanins are replaced by colorless proanthocyanins (Beckett, 1988). The Trinitarios apparently originated by hybridization of Criollo and Forastero (Wood, 1987). The seeds yielded by Trinitarios are variable in color, although white beans rarely occur. The beans are irregular since the characteristics of the parents are so different. The name Trinitario results from the fact that the hybrid was planted extensively on the island of Trinidad during the eighteenth century.

The Forasteros are the type most frequently used to make chocolate. Processing of their seeds results in the deep brown color reminiscent of chocolate. The Criollo types usually yield a red-brown chocolate which is much lighter than that of Forastero. The color of Trinitario chocolate is lighter than that of a Forastero but darker than that of a Criollo.

Pod ripeness of these varieties is judged by the external

color of the pod wall or husk. When mature, pods change from an unripe green or dark red-purple color to bright yellow, orange or red depending on the variety.

3.2 Postharvest Practices - Overview

During harvest, ripe pods are manually removed from the trunk and limbs of the tree using machetes. The pods are then broken open, and the wet seeds are removed. The seed is actually composed of the cotyledon which is enclosed by a seed coat or testa. They are surrounded by a sugary, mucilaginous pulp which is greater than 80% water (Table 1). The moisture content of the seed and pulp mixture is approximately 60%.

The seeds are typically prepared for transport and storage by a two-step process called curing (Figure 3). First, the seeds are fermented, a process which breaks down the sugars and mucilages in the pulp so that the pulp drains away. Swain (1957) states that during fermentation, it is only the surrounding pulp that is actually fermented and not the bean itself. Important changes are, however, also brought about in the bean. Apart from the removal of the pulp, the main purpose of pulp fermentation is to provide a suitable environment for the enzymatic curing of the cotyledons (Hunter, 1958). During fermentation, the major changes inside the seed are its death followed by the numerous chemical changes that eventually contribute to chocolate flavor and color. The second step is drying. The drying is necessary to remove the moisture present in and around the fermented seeds.

Table 1. Components of ripe cocoa pods

PULP	%
Water	82 - 87
Sugars	10 - 13
Pentosans	2 - 3
Citric Acid	1 - 2
Salts	8 - 10

COTYLEDON	%
Water	32 - 39
Cellulose	2 - 3
Starch	4 - 6
Pentosans	4 - 6
Sucrose	2 - 3
Fat	30 - 32
Protein	8 - 10
Theobromine	2 - 3
Caffeine	1
Polyphenols	5 - 6
Acids	1
Salts	2 - 3

TESTA: mucilage cells, vascular bundles, epidermis cells

Source: Lopez (1987)

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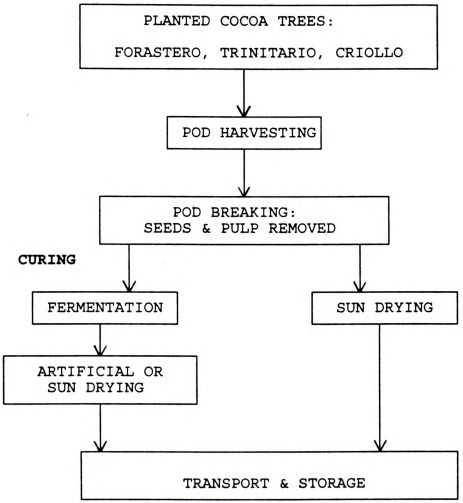

Figure 3. Schematic of preharvest and postharvest practices

3.2.1 Fermentation Methods

Methods of fermentation vary throughout the cocoa growing regions. The two most common methods are the box and heap.

The box method involves the use of strong wooden boxes with small openings in the bottom and sides for draining of fermenting pulp, or sweatings, as well as for access to air for the fermenting mass. During box fermentation, the mass is typically covered with banana leaves to maintain heat. The contents are turned every day or every other day to introduce air into the mass and ensure a more homogeneous fermentation. The entire process typically lasts 4 to 8 days for Forastero varieties and 1 to 3 days for Criollos.

In the heap method, beans are placed on a bed of banana or plantain leaves and heaped together into a conical shape. The heap is then covered with additional leaves which are held in place by rocks or wooden staves. Heaps are fermented for 3 to 5 days and are turned once or not at all.

3.2.2 Fermentation

Many different techniques of cocoa fermentation have been studied in the past (Tomlins et al, 1993; Abdul Samah et al, 1992; Abeygunasekera and Jansz 1989; Biehl et al, 1989; Kirchoff et al, 1989; Biehl et al, 1985; and Adomako et al, 1981). Proper fermentation is an important processing step because it produces the chemical precursors for the characteristic color and flavor of chocolate.

When removed from the pods, the fresh seeds are covered

with pulp which is initially sterile. The external surface of the seeds appears pink-white and the seeds have a faint sweet smell. The presence of sugars and citric acid contribute to a pulp pH of 3.5. In the living seed, the testa is impermeable to the citric acid present in the pulp. The pulp composition provides an ideal medium for growth of microorganisms. These microorganisms are introduced to the pulp primarily by the workers' hands, fruit flies and from the box and/or banana leaves.

Initially, the fermentation is anaerobic. The low pulp pH favors yeasts and discourages fungi and bacterial growth. The yeasts metabolize most of the sugars in the pulp to ethanol. This conversion also produces a large amount of carbon dioxide.

Through enzymatic changes and mechanical pressure of the fermenting mass, the pulp cells break down. As the cells break down, the pulp liquefies and runs off as sweatings. The sweatings amount to 12 to 15% of the weight of the wet beans. Within the first 36 hours of fermentation, the majority of the sweatings are lost. After the sweatings have run off, the remaining pulp is dull white and gradually darkens to a red-brown color.

As the sweatings flow away from the fermenting seeds, the citric acid diminishes significantly. The subsequent rise in pulp pH favors growth of lactic acid bacteria (*Lactobacilli*). During the second day, *Lactobacilli* predominate but eventually diminish as the temperature rises

and conditions become more aerobic through physically turning the mass. These conditions favor bacteria which convert alcohol to acetic acid, and can metabolize the strongly dissociated acids (citric, malic, and lactic) to acetic acid which is relatively weakly dissociated. With the loss of the citric acid and its replacement by the lactic and acetic acids, the pH of the pulp rises from the initial level of 3.5 to 5.0 or higher if the fermentation is prolonged (Figure 4) (Dougan, 1979 and Holden, 1961).

On the second day, the seeds die due to the high temperature (above 40°C) and an increase in acidity. The pH of the seeds falls from approximately 6.5 to 5.0 (Dougan, 1979). This increased acidity is due to acetic acid formed in the pulp passing through the testa into the cotyledons. The build-up of acetic acid in the cotyledons is slow at first, but accelerates after the third day, rising to 15 mg per bean by the fifth day, after which it may decline (Dougan, 1979). Lactic acid builds up slowly and steadily during fermentation but at much lower levels than acetic acid, final amounts being 1 to 2 mg per bean (Dougan, 1979). At this time, the relative impermeability of the cell walls within the cotyledons is destroyed, and all of the previously segregated materials are free to intermingle and react (Cook and Meursing, 1982). Cells disruption and other complex structural changes occur, allowing various enzymes and their substrates to come together.

As the fermentation of the pulp proceeds, an acidic smell

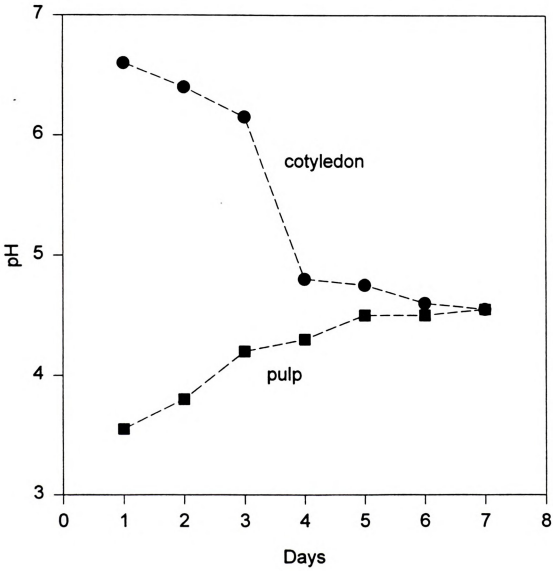

Figure 4. pH changes in pulp and cotyledon during fermentation. The two will achieve the same pH if fermentation proceeds over a long enough period.

Source: Wood (1987), Dougan (1979)

develops and is retained during the normal fermentation period. At the end of a six or seven day box fermentation, the beans in the corners of the box have darkened further, becoming nearly black, and such beans will have an unpleasant ammonia-like smell. This marks the onset of over-fermentation. When this smell arises, the fermentation should be brought to an end and drying started immediately.

3.2.3 Drying

The main objective of drying is to reduce the moisture content of the beans to a level (approximately 7%) which is safe for storage and shipment. The drying process is a continuation of the oxidative stage of fermentation. This plays an important role in reducing bitter and astringent flavors and developing the brown color of well fermented beans. Some fermentation activity takes place during drying before moisture content is significantly reduced (Wood, 1987). Unless drying is very rapid, deficiencies in the fermentation are remedied to some extent during the first few days of drying.

The rate of drying of raw cocoa has an important bearing on the quality of the dried beans. If the drying is too slow, molds can develop and penetrate the testa which may cause undesirable flavors in the finished product. Rapid drying may prevent the oxidative changes from being completed and may result in excessive acidity. Acidity is due to the presence of volatile and non-volatile acids in the seeds, and drying

will not influence the non-volatile acids, of which lactic acid is the most important. Therefore, excess acidity due to lactic acid will not be changed by the drying process, but acidity due to the volatile acetic acid will be influenced by drying and drying rate.

Beans dried in the sun are less acidic than beans dried artificially. Artificial drying of cocoa is an operation comprising a rotating cylinder or a perforated surface for the placement of the fermented beans. Warm or hot air is forced over or through the beans to reduce their moisture content. The beans may be agitated continuously, periodically, or not at all. For many years, there has been a general belief that sun drying is preferable and produces a bean of better quality. Recent trials showed that increasing the drying temperature increased astringency and acidity, and it was therefore concluded that drying with ambient air for 72 hours followed by drying for 15 hours at a maximum air temperature of 60°C is the optimum time-temperature history to minimize the acidity of artificially dried beans (Selamat et al, 1991b; Duncan et al, 1989). Comparing artificially dried samples with sun dried samples showed that artificial drying increases the volatile acidity and lowers the pH of the dried beans (Jacquet, et al. 1980).

During artificial drying, it may be that there is some point in the drying process when the testa becomes less permeable to acetic acid so that it becomes trapped inside the bean (Wood, 1987). To counteract the effects of artificial

drying, researchers have addressed techniques of lowering the amount of sugars in the pulp. This reduction is thought to reduce the chemical precursors necessary for acid production. However, Biehl et al (1989) suggested that reduction of pulp sugars through pod storage resulted in residual amounts of sugars that would be sufficient to produce enough acetic acid to lower nib pH to less than 4.5 during fermentation. Abeygunasekera and Jansz (1989) have shown that the process of "maturation," holding fermented cocoa beans in thin layers at ambient temperatures during which little or no drying took place, resulted in the pH of the cocoa rising from 4.8 to 5.2, thereby lowering the acidity of the cocoa. During maturation, acetic acid was converted to carbon dioxide through oxidation via the Krebs cycle.

3.2.4 Summary of Color and Acidity Changes

In the freshly removed seeds, a small number of intensely colored cells are dispersed among colorless cells. The colored cells contain most, if not all, of the polyphenolic compounds which play a significant role in the internal chemical changes. Initially, conditions inside the seed are anaerobic, and at this stage hydrolytic reactions take place. One specific reaction involves the breakdown of the anthocyanins which give color to all Forastero types. This change leads to a bleaching of the cotyledons during fermentation. Polyphenols are oxidized by polyphenol oxidase which is found in the cells not containing polyphenols.

Oxidation occurs during later stages of fermentation and during drying, and causes the internal color to darken.

The internal appearance of the beans is a useful indicator the progress of fermentation. Initially, Forastero beans will be bright violet with a white germ. The bright violet in the fresh unfermented beans is due to anthocyanins. These are esters of anthocyanidins and sugars. Procyanidins are present in cocoa as mono-, di- and trimers of epicatechin. They are also found in the form of sugar ester derivatives. After the death of the seed, the surface cracks within the bean become filled with an exudate of a similar violet color and this, together with the cotyledons and the germ, turns brown rapidly when the bean is cut open.

At a later stage, the exudate becomes a reddish brown and the cotyledons become paler in the center with a brownish ring around the outside. Such beans have been adequately fermented and are ready for drying. The difficulty in assessing the end-point in fermentation is that the beans are not uniformly changed into a homogeneous mass. The development of this symptomatic change to a brown color, at least in the periphery of a cut bean, indicates that the beans are ready for drying (Wood, 1987; Cook and Meursing, 1982; Quesnel, 1958). As oxidation is involved, the reaction takes place during the second oxidative stage of fermentation and sun drying of the beans. The result of this oxidation is a brown pigment, which is stable and insoluble in water.

The color changes in the bean through fermentation are

dramatic. The typical deep purple of the Forastero becomes progressively less intense and finally red-brown. The Criollo beans, which are initially white, turn yellow-tan or cinnamon-brown. All dried cocoa beans are acidic to a certain degree and contain a number of volatile and non-volatile acids, the most important of which are acetic, citric and lactic acids (Table 2).

The presence of acetic acid is obvious from the pungent smell of the dried bean. Due to its volatility, most of the acetic acid is dispelled during full factory processing of chocolate, after which little or no acid flavor remains. On the other hand, lactic acid is non-volatile and is not driven off during manufacturing. The presence of these acids lowers the pH of the dried bean and, as acid beans often lack chocolate flavor, it is possible that low pH (below 5.0) interferes with reactions which create chocolate flavor precursors.

3.3 Measurements of Cured Cocoa Quality

The overall quality of a parcel of cocoa will affect its value and acceptability with relation to other cocoa beans. One of the most popular methods to measure the quality of cocoa curing is through the use of the cut test. The cut test involves cutting lengthwise 300 beans taken from a random sample of the cocoa whose quality is to be assessed.

The color of the raw beans is a determinant of the level of fermentation that the bean has been subjected to. While

Table 2. Volatile fatty acids in cocoa

ACID	CARBONS	MW	BP (°C)	THRESHOLD (ppm)	ODOR
Acetic	2	60	118	54	sharp, vinegary
Propionic	3	74	141	20	pungent, cheesy
Butyric	4	38	163	7	fecal, rancid
Isobutyric	4	88	154	8	pungent, wet sock
Isovaleric	5	102	176	1	acrid, rancid cheese

Source: Hoskin and Dimick (1979)

the pigments contained in fresh unfermented cocoa may not be directly involved in the formation of chocolate flavor precursors, the changes that these pigmented substances undergo are at least concomitant with the formation of the precursors. Their condition is therefore a reliable indicator of the extent to which chocolate flavor precursors are present. Beans which are dried without undergoing a fermentation step have a characteristic slatey color. If fresh Forastero seeds are carefully cleaned of pulp and dried without any fermentation of the surrounding pulp, the dried cotyledons within the bean will not be the brown or purple-brown color of fermented cocoa beans but an unattractive dark slatey grey (Beckett, 1988). Criollo beans similarly treated are whitish-grey or yellow-grey (Cook and Meursing, 1982). These seeds have been killed by drying instead of by the heat and acid arising during fermentation. None of the changes which take place as a result of the breakdown of the internal cell structure has occurred. With normal fermentation (heap or box) there should be no slatey beans present.

Beans which are underfermented can also have a bright purple color which is due to the presence of unchanged anthocyanin. The anthocyanin is normally hydrolyzed during fermentation and changed to a colorless proanthocyanin. This indicates that the seeds were dried, after death, before enzymatic action had the opportunity to cause the chemical changes that result in the change from purple to red-brown (Cook and Meursing, 1982).

The color of cut beans is usually brighter and more purple soon after drying is completed than when samples are cut and analyzed months later. There is a gradual change in color with storage. Wickens (1954) has shown that in samples containing 50 to 70% purple beans initially, this proportion was frequently reduced by half after six months of storage. This change has been associated with a decreased anthocyanin content.

The colors of a normal sample of cut beans cover a range from the chocolate brown or red-brown of fully fermented beans to the full purple of beans that have been inadequately fermented. Overfermentation can be revealed by a dull dark appearance of the beans when cut. In this case the beans begin to rot and the pH rises sharply as proteins in the bean break down. During this process, dark pigments are produced. They are probably combination products of flavanoids and amino acids.

Acidity level is another quality concern. Less acidic West African beans have a pH of 5.5, while strongly acidic beans have a pH of less than 5.0. A high degree of acidity is usually associated with a pH of 5.0 or less in dried beans (Musa and Said, 1988).

3.4 Factory Processing of Cocoa - Overview of Roasting

Roasting is a thermal process applied to many foodstuffs as a means of developing flavor. It is probably the oldest culinary technique and is applied to meats, legumes, and nuts

to prepare them for consumption. Roasting will cause flavor and color development through browning reactions and will alter texture via starch gelatinization.

Cocoa beans are roasted to develop further the true chocolate flavor, which should already exist in the form of precursors arising from proper fermentation and drying of the original fresh seeds. During roasting and drying of fermented and dried whole beans, the following changes occur: (1) the bean loses moisture, (2) the shell (dried testa) is loosened, (3) the nib becomes more friable and generally darkens in color, (4) there is some degradation of the amino acids (Rohan and Stewart, 1966) and (5) there is a loss of volatile acids and other substances that contribute to overall flavor. In addition, Abo-Bakr and Shekib (1987) and Hoskin et al (1979) note that dry roasting of cocoa causes the cotyledon to become porous and brittle, and the cellular contents become thermally coagulated.

The degree of change is related to the time/temperature history of the roasting process and the rate of moisture loss. Lopez (1987) notes that the best flavor is produced at an internal bean temperature of between 120 and 140°C. Roasting conditions vary, depending on the equipment and the desired attributes of the final product.

The two most popular types of roasting are whole bean roasting and nib roasting.

3.4.1 Whole Bean Roasting

The traditional whole bean process (Figure 5) involves cleaning, roasting and winnowing to remove the shells. Whole bean roasting was the conventional process from the earliest industrial development until comparatively recent years (Urbanski, 1989). In the early days of cocoa roasting, all roasting was done on whole beans in simple pans, and later in revolving drums or spheres. All roasting was done on a batch basis and heat transfer was accomplished mainly by conduction. A significant amount of artistry was used by those who were responsible for the roasting processes. Changes in color, odor, and texture were used to predict end points in the process.

Conduction and convection were combined into the equipment subsequently developed. The surfaces of the roasting drum were heated and hot combustion gases were passed through the mass of beans. Since the temperatures on the drum surfaces were required to be very high for adequate conduction, the risk of over-roasting was high. This problem resulted in the development of pure convection roasting machines. The use of convection to heat whole beans lends itself to the development of continuous roasting machines. Vertical roasters where beans flow from top to bottom and warm air flows countercurrently are one example of continuous convection roasters. Another example is a horizontal continuous fluidized bean roaster where combustion gases of different temperature are blown down from different zones onto

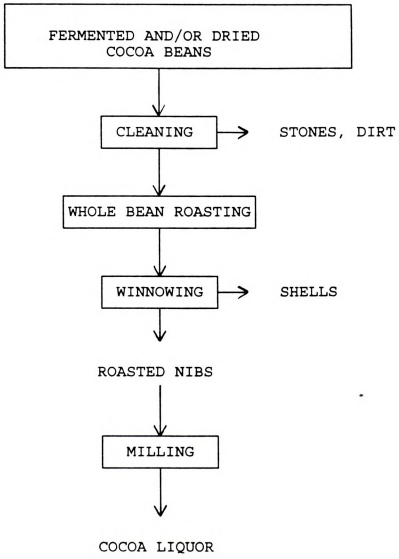

Figure 5. Schematic of the whole bean roasting process

a passing stream of fluidized beans.

There are a number of disadvantages to whole bean roasting by forced convection. Typical flavor of roasted cocoa depends on the development of the flavor and aroma compounds contained in the nib. Some of the volatile compounds play no part in aroma development. Others are detrimental to it, and these compounds must be removed from the nib. This removal is typically accomplished by steam distillation using naturally occurring water in the nibs or by addition of water. In whole bean roasting, the shell is a barrier to the required heat and mass transfer.

During forced convection, the evaporating moisture will be removed at a faster rate from the surface of the bean than the rate at which capillary action can bring "new" moisture to the surface (Mayer-Potschak, 1983). This causes the shell to shrink around the nib and impede heat and mass transfer. Since drying rate is slowed in this circumstance, the temperature of the nib rises and roasting takes place on the external regions of the nib. Temperature differences across the layers of the nib cause uneven roasting to occur. Eilers (1965) has reported that after 10-20 minutes of roasting at an air temperature of 180°C, the temperature difference between the inner and outer part of the nib was as high as 9°C. In addition, since cocoa beans naturally show a variability in size, whole bean roasting results in the over-roasting of small beans and the under-roasting of larger beans.

3.4.2 Nib Roasting

Due to the disadvantages of whole bean roasting outlined above, nib roasting was developed and has become popular in the past ten years. The process steps involved in nib roasting are whole bean cleaning, thermal treatment of the whole beans designed to loosen the shells without roasting the nib, winnowing the whole, unroasted beans to remove the shells, followed by wet or dry roasting of the nibs (Figure 6).

The most widely used thermal pretreatment technique is micronizing. During micronizing, the raw beans are subjected to infra-red radiation for 30 to 120 seconds. They pass as a thin layer on a vibrating conveyor under high temperature heating elements powered by gas or electricity. The motion of the vibrating conveyor causes the beans to turn over as they are conveyed and this results in even treatment to all external surfaces.

The shells of the bean are rapidly heated, causing them to dry, expand, crack and detach themselves from the nibs. The internal temperature of the nibs typically does not exceed 100°C; however, the slight thermal expansion of the nibs as well as the limited amount of escaping vapor assists with the loosening of the shells. Ideally, the moisture content of the nib is 4 to 6% at the discharge of the micronizer. Since the nib is less friable and remains tough, less breakage occurs. This assists with higher yields during subsequent winnowing. The infrared energy is concentrated on the surface of the bean

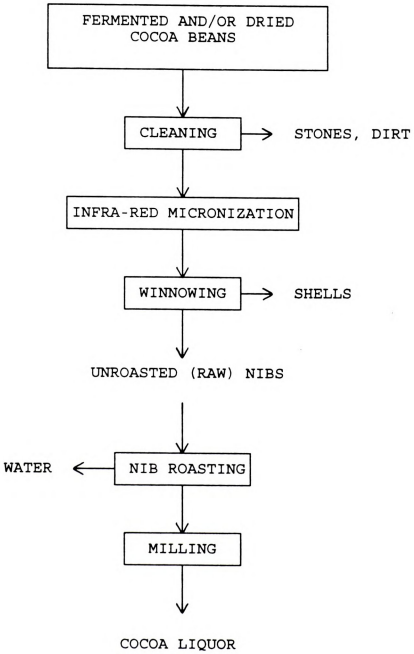

Figure 6. Schematic of the nib roasting process

and thus dust particles, pulp remains, rodent hair and insect fragments are incinerated. The loss of fat through the transfer of cocoa butter from the nib to the shell is also minimal versus some roasting processes such as whole bean roasting where this loss can be very significant (Minifie, 1989).

Winnowing is the process where roasted or thermally pre-treated whole cocoa beans have their shells removed. The valuable part of the cocoa bean is the nib, and the outer shell is waste material of little value. The whole beans are normally mechanically broken while they are still hot. The shell and the germ are then separated from the nibs. Because of the high cost of raw cocoa, nib yield is very important. The principle of winnowing is to remove the shell by exploiting the density difference between the shell and the nib.

Typical modern machines use a multilayer vibrating sieve frame with meshes of different sizes, one above the other, with the largest mesh at the top. The shell pieces are removed by air aspiration from above as the nib and shell stream flows down through the machine. The shell content of a cocoa bean is normally 12%. The sieves are kept free from blockage by means of the vibratory movement and by mechanical rakes which move across the sieves. The stream of finished material produced may contain a maximum of 1.75% shell by weight (CFR, 1990).

As previously mentioned, a recurring problem with dry

whole bean roasting is size distribution, and this is also the main disadvantage of dry roasting of nibs. Nib sizes usually vary from 0.8mm to 8mm, a size ratio of 1:10. In normal convection roasters, small nibs are roasted much faster than large nibs. If roasting time is calculated according to a nib size of 4mm, overroasting and underroasting is unavoidable (Mayer-Potschak, 1983).

According to Mohr (1971), optimum nib roasting involves a preliminary drying phase which reduces moisture content to about 2.3%. This should be followed by a rapid rise in heat level to the exact roasting temperature required to achieve maximum aroma development. Mohr's experiments were conducted with cocoa nibs of homogeneous size. Manufacturing of nibs of one size, however, is not practical, and Mohr's results cannot be reproduced under factory conditions.

Recently a humid atmosphere nib roasting system (Figure 7) was developed to negate all of the disadvantages of whole bean roasting and convection nib roasting. Many of the principles found in Mohr's results were used to design this process. This system will dry the nibs at a temperature below 100°C until the moisture content is reduced to approximately 2.5%. This condition is essential for an optimal roast based on flavor development. In the second phase, the nibs are rapidly heated to the exact roasting temperature and can be maintained at the temperature until the desired roast level is achieved.

The transfer of thermal energy is effected mainly through

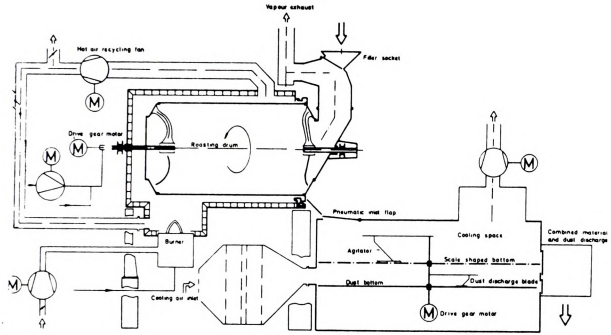

Figure 7. Schematic of TORNADO 2600RS nib roasting system

Source: Anon (1980)

conduction and natural convection. The nib material and surrounding air receive their heat from the inner surface of an externally heated, rotating horizontal roasting drum. A natural gas or propane burner produces heat which circulates around the outside of the drum. Since forced convection is not employed, a humid atmosphere develops inside the drum as a result of the vaporization of the nibs' internal moisture.

The nib moisture content of 4 to 6% after micronizing forms the medium for steam distillation of volatile compounds which are detrimental to aroma and flavor. In the drum, there is always equilibrium between nib moisture and the moisture content of the surrounding air. The nib drying occurs along the saturation curve. Mayer-Potschak (1983) claims that the surface evaporation never moves into an unsaturated phase, and transport of water by capillary action is not interrupted. Moreover, with forced air roasting, the surface of the nibs dries rapidly which results in case hardening and retards drying of the internal parts of the nib (Minifie, 1989). Nib roasting allows temperature and moisture in the nib to remain uniform throughout. The moisture can therefore evaporate through the vapor exhaust without resistance until the end of the roasting process, providing maximum removal of volatile acids. Over-heating of the nibs and resultant over-roasting cannot take place (Mayer-Potschak, 1983). The batch is discharged into a an agitated circular cooler to lower the product temperature and stop the roasting process.

3.4.3 Effects of Roasting on Color and pH

Much has been written about flavor development with respect to the roasting process. Limited information has been published, however, on the effects of roasting on pH and color. Selamat and Dimick (1991a) reported that dry roasting of whole beans for 30 minutes to an internal temperature of 148°C caused an increase in pH from 5.12 to 5.32. This was accomplished with a laboratory scale oven with an air temperature of 150°C. They have reported that this pH increase was accompanied by a loss of 22% and 10% of the volatile and non-volatile acids, respectively. Bonar et al (1967), however, reported a change in pH from 5.63 to 5.32 during roasting. Bonar found these changes to be difficult to interpret as he also measured an accompanying decrease in both volatile and non-volatile free acidity.

Minifie (1989) claims that low roasting temperatures give reddish colors, whereas high roasting gives dark-brown colors. In addition, Urbanski (1989) suggests that the color of a finished product can be affected by the use of cocoas which are known to promote one color cast or another. He adds that Java cocoa, for example, delivers a characteristic light color. This is due in great part to the fact that Java cocoa is predominantly of Criollo parentage.

3.4.4 Water Treatment and Alkalization

If cocoa liquor or cocoa cake are subjected to the action of water, this produces slightly more red shades than would

normally be the case, and the pH does not change (Minifie, 1989).

Alkalization is a treatment of cocoa nibs, liquor or powder with aqueous solutions of alkali such as carbonates and hydroxides to change the color of the starting material. The chemical reactions occurring during alkalization have not been published and may not be precisely known. Polyphenolic substances are modified as shown by color variations in the finished products. Wiant et al (1991) have reported in their patent that alkalization is an alkali-induced oxidation reaction, and that aeration is a critical component for producing deeply colored alkalized cocoa powder. That is, ample supplies of oxygen are needed in order to maximize color development.

The process can raise the pH of cocoa powder or cocoa liquor to as high as 8.5, but a typical range is 6.8 to 7.5 (Minifie, 1989). Welch (1981) notes that high pH cocoa powder is a potential problem since it accelerates lipase action and with lauric fat on high moisture fondant centers such as nougats and caramels in confectionery products, can represent a severe risk to the product.

A variety of alkalization process methods are used to produce a wide array of colors (Table 3). Since the level of color precursors varies with the type of bean used and the type of fermentation and drying regimes used, finished materials are typically blended to maintain consistent colors.

Table 3. Effect of quantity and concentration of potassium carbonate on the color and pH of cocoa powder

K_2CO_3 (lb per 100 lb nib)	Water (lb per 100 lb nib)	Concentration of K_2CO_3 (%)	pH of Cocoa	Color
1.7	20	8.5	7.3	Dull brown
1.7	30	5.6	7.1	Darker brown
1.7	50	3.4	7.2	Reddish brown
2.5	20	12.5	7.6	Rich brown
2.5	30	8.3	7.7	Deep red brown
2.5	50	5.0	7.6	Deep red

Source: Minifie (1989)

4.0 MATERIALS AND METHODS

4.1 Experimental Design

A computer software package developed by the ECHIP™ Company (Hockessin, DE) was used to generate the experimental design (Table 4) and analyze the experimental data. Multidimensional response surfaces were used by the package to produce a process picture by which the effect of moisture content and final temperature on pH and color can be assessed. The results show how pH and color continuously change across the range of the process variables.

It is worth noting that since the actual product temperature could not be measured during the process, the bulk temperature, measured as explained later in this section, was used in lieu of product temperature. Secondly, the initial bulk moisture content was calculated by a mass balance of batch materials and the quantity of water injected during the process. It is not the true moisture content of the nibs, since there is obviously insufficient time for all of the added water to completely diffuse into the nibs.

4.2 Raw Material Analysis

Eight bags of commercially available cocoa beans, each approximately 60 kg, were blended together to form a homogeneous starting material.

From the starting material, a sample of 5 kg was removed. Three hundred beans were cut lengthwise to determine the raw

Table 4. ECHIP™ experimental design

ECHIP trial #	Indigenous moisture content (%)	Target initial moisture content of batch (%)	H2O to add (kgs)	Target final product temperature (C)	NOTES
1	3.2	20	2.1	110	
5	3.6	3	0	130	
8	3.6	3	0	116.7	
9	3.6	8.7	0.559	130	*
11	3.3	14.3	1.28	116.7	
2	3.7	11.5	0.88	110	
7	3.5	3	0	123.3	
2	2.8	11.5	0.98	110	R
1	3	20	2.13	110	R
6	3.5	3	0	110	
4	3.6	20	2.05	130	*
3	3.4	20	2.075	120	
5	3.7	3	0	130	R*
3	3.3	20	2.088	120	R
10	3.4	14.3	1.27	130	
5	3.6	3	0	130	R

NOTES:

Batch size – 10 kilograms.
Burner temperature – 250C.
Internal vacuum – 2.5mm water.

R – trial is a replicate.
* – trial designated for drying curve and PSD analysis.

Drying curve analysis: batch moisture content measured every 15 minutes
PSD analysis: Split sample of raw nib starting material and finished material after cooling analyzed using sieve shaker.

bean color composition. Raw bean samples were ground in a Braun coffee mill and then passed through a 40 mesh screen. Ten grams of the ground material which passed through the screen were pulverized in 90 mL boiling distilled water using a Professional blender (Waring, New Hartford, CT). The slurry was centrifuged at 1000 RPM for 5 minutes in a GS-6 centrifuge (Beckman, Palo Alto, CA). 50 mL of the supernatant was then pipetted into a 150 mL beaker and cooled to 25°C. The pH was then measured using a model 125 pH meter (Corning, Corning, NY). The mixture was continuously stirred during measurement.

250 g were roasted in a convection oven (Farberware, Bronx, NY) for 15 minutes at an air temperature of 150°C. Shells were removed by hand and a moisture loss from benchtop roasting was determined.

4 - 3 Processing Operations and Analysis

The remaining 475 kg of raw beans were micronized to loosen the shells using a MR-2 micronizer (Micronizing UK, Framlingham Suffolk, England). The feed rate to the micronizer was 2.3 kg per minute, and the residence time on the vibrating bed was 50 s. The micronized beans were then run through a BR61 winnowing machine (Bauermeister, Memphis, TN) where the shells were removed and the micronized nibs were recovered.

For certain trials, particle size distribution (PSD) was measured before and after roasting. For these trials, the starting material for the roaster and the roasted product were

screened using a Portable Sieve Shaker Model RX-24 (CM Tyler, Mentor, OH) with progressively smaller screens with the following openings: 9.5mm, 6.4mm, 3.4mm, 2.8mm, 1.5mm, 0.9mm. Since each roasting trial involved 10 kg of nibs, the sample to be analyzed for PSD was obtained by splitting the 10 kg down to 500 g with a Model H-3085 sample splitter (Humboldt, Chicago, IL).

Each trial began with ten kg of micronized nibs. The moisture content of these nibs was determined with an LP 16 Infrared Dryer (Mettler, Hightstown, NJ) at 160°C. A RS50 pilot batch roasting machine (Barth, Freiberg/Neckar, Germany) similar to that of the full scale version pictured in Figure 7 was used to roast the nibs. This roaster is a horizontal drum which rotates about a central shaft. Fixed baffles on the interior are angled so as to gently turn the product over for uniform heat transfer during the roasting cycle. A slight vacuum of 2.5mm water was maintained on the interior of the drum during the entire cycle to remove vapors. Heat is transferred through the outside of the drum by two electric burners which heat room air blown past the burners and across the exterior of the drum by a separate fan. Distilled water was sprayed into the batch with an injection system which had an atomizing nozzle mounted to the interior of the front door of the drum. When the batch reached its final temperature, it was discharged into an agitated cooler which was fed with air at 15°C to cool the nibs and terminate the roasting process.

The roasting procedure involved preheating the roaster so

that the circulating air through the annulus on the outside of the drum was maintained at 250°C. The 10 kg charge of nibs was then introduced into the roaster. When the charge was completely loaded into the roaster, water was injected into the batch, if required by the trial conditions. The bulk temperature of the batch was measured using a thermocouple which was immersed in the nibs during the entire roasting process. When the final bulk temperature was reached, the entire contents of the batch were discharged and cooled. Cocoa liquor was prepared from each trial by starting with a representative sample of the batch and grinding it in a single pass stone mill (Probat, Memphis, TN).

4 - 4 Finished Product Analysis

The pH of the liquor was measured by melting the liquor sample and weighing 5 g into a 250 mL beaker. 25 mL of neutralized ethyl alcohol and 25 mL of distilled water were then added. The beaker was covered and the mixture was stirred and heated on a standard hot plate to a rolling boil. The boiling was maintained for 30 s. Following boiling, the mixture was centrifuged in the same manner as described above. 25 mL of the filtrate was then transferred to a 150 mL beaker. 25 mL of distilled water was added, and the mixture was continuously stirred during pH measurement.

The color was measured with an XL-20 tristimulus colorimeter (Gardner Instruments, Bethesda, MD). The basis for tristimulus colorimetry is that any color can be

reproduced from a combination of three other colors. The scale used for measuring the liquor colors has three values which are termed R_d, a, and b. R_d is defined as 100 times the amount of light reflected by a sample divided by the amount of light reflected by a perfectly diffusing sample when the light is incident upon the sample at an angle of 45°. The measuring device records the light diffused perpendicularly from the sample. A completely absorbing specimen would have an R_d value of zero, and a perfectly diffusing white specimen would have a value of 100. A positive value of a indicates redness, and a negative value indicates greenness. A positive value of b indicates yellowness, and a negative value indicates blueness. Before each measurement, the meter was calibrated with a known standard (R_d=90.0, a=-1.2, b=2.7). The liquor was heated to 100°F and then a portion was placed onto a clean glass slide. The slide was then placed onto the colorimeter lens and the color coordinates were obtained.

5.0 THEORETICAL DEVELOPMENT

5.1 Mass Transfer Analysis

The methods described by Singh and Heldman (1984), Geankoplis (1983) and Heldman and Singh (1981) were used to analyze the loss of moisture from the cocoa nibs during roasting. Expressions were used for the two drying rate regimes which typically occur during the dehydration of foods.

The constant rate drying period, which occurs during the removal of free moisture, may be modeled by

$$R_c = \frac{dw}{dt} = \frac{W_0 - W_c}{t_c} \qquad (1)$$

where R_c is the constant drying rate, w is the moisture content, t is the time, w_c is the critical moisture content or the point where the drying rate changes from constant to falling rate, and t_c is the duration of the constant rate drying period.

During falling rate drying,

$$-\frac{dw}{dt} = \frac{R_c}{w_c} w \qquad (2)$$

from which,

$$-\frac{w_c}{R_c}\int_{w}^{w_c}\frac{dw}{w} = \int_{t}^{t_c} dt \qquad (3)$$

where w is the moisture content at any time t. Integration yields,

$$t - t_c = \frac{w_c}{R_c} \ln\left(\frac{w_c}{w}\right) \quad (4)$$

The quantity on the left hand side is the duration of the falling rate drying period, t_F:

$$t_F = \frac{w_c}{R_c} \ln\left(\frac{w_c}{w}\right) \quad (5)$$

The sum of the two time periods gives the total drying time:

$$t = \frac{w_0 - w_c}{R_c} + \frac{w_c}{R_c} \ln\left(\frac{w_c}{w}\right) \quad (6)$$

The drying times predicted by the above equation were compared to the experimental drying times for trials 4, 5, and 9.

5.2 Heat Transfer Analysis

The experimental data from trial 5 was used to estimate the convective heat transfer coefficient. This trial was conducted with no additional moisture being added to the nibs. Therefore the sample was not subject to significant changes in nib heat capacity or density during processing.

To determine the appropriate method to analyze the heat transfer to the nibs during the drying and roasting process,

the Biot number was first estimated. Estimates of the thermal conductivity and the heat transfer coefficient were obtained from Geankoplis (1983) and Perry (1984) as k = 0.35 W/mK and h = 5.68 W/m^{2}K, respectively. Over 70% of the particles before and after roasting were found to be larger than 3.4mm. For all of the theoretical analysis, the cocoa nibs were assumed to be spherical with an estimated diameter of 4mm.

The characteristic length of a sphere is r/3. Therefore, the expression for the Biot number becomes

$$Bi = \frac{h(\frac{r}{3})}{k} \tag{7}$$

and for the relevant parameters of this study,

$$Bi = \frac{(5.68)(\frac{0.002}{3})}{0.35} = 0.011 \tag{8}$$

Since the Biot number for this case is less then 0.1, internal temperature gradients can be assumed to be negligible. Therefore, the *lumped capacity method* of analysis can be used (Geankoplis, 1983).

An energy balance on the nib gives

$$\rho V C_p \frac{dT}{dt} = hA(T_b - T) \tag{9}$$

where T_b is the roaster burner temperature. Separating the variables, one obtains

$$\frac{dT}{(T_b-T)} = \frac{hAdt}{\rho C_p V} \tag{10}$$

which can be integrated as

$$\int_{T_i}^{T} \frac{dT}{(T_b-T)} = \frac{hA}{\rho C_p V}\int_{0}^{t} dt \tag{11}$$

After applying the limits of integration, one gets

$$-\ln\left(\frac{T_b-T}{T_b-T_i}\right) = \frac{hAt}{\rho C_p V} \tag{12}$$

which can be simplified to

$$h = \left(\frac{\rho C_p V}{At}\right)\left(-\ln\left(\frac{T_b-T}{T_b-T_i}\right)\right) \tag{13}$$

The density was found by averaging the weight of 20 roasted nibs from the 3.4mm screen. Assuming that the volume change was negligible during processing, the weight of a single cocoa nib at a moisture content of 1.0% (roasted) and 3.5% (unroasted) were calculated and averaged. The average weight was then divided by the volume of a 4mm sphere to compute the average density of a nib.

An average nib heat capacity was also computed at 1.0 and 3 - 5% moisture content. The heat capacity was calculated with the following equation (Singh and Heldman, 1984):

$$C_p = 1.424m_c+1.549m_p+1.675m_f+0.837m_a+4.187m_m \qquad \textbf{(14)}$$

where ***m*** is the mass fraction, and the subscripts ***c***, ***p***, ***f***, ***a*** and ***m*** stand for carbohydrate, protein, fat, ash, and moisture, respectively. The carbohydrate, protein, fat and ash composition of the nibs were obtained from Minifie (1989).

6.0 RESULTS AND DISCUSSION

6.1 Raw Material Characteristics

The starting material for the trials was analyzed for a variety of characteristics (Table 5). The shell content and bean count per 100 g were typical at 11.98% and 104, respectively. The sample showed no signs of internal mold or insect infestation. The moisture loss from benchtop convection oven roasting was quite small at 3.81%. Typical samples lose approximately 5% moisture during this type of laboratory roasting. This low moisture loss may mean that the beans were stored for a longer duration than normal and subsequently dried during storage.

The cut test revealed that the parcel of beans contained a significant amount of underfermented cocoa. This is seen by the high percentage of slatey beans present. Grade I cocoa as defined in the International Cocoa Standards (Wood, 1987) must have less than 3% slatey beans. The pH of the composite sample of raw beans was 6.10. This is high, relative to the thirty samples analyzed by Selamat and Dimick (1990) where the pH of the bean extracts ranged from 4.70 to 5.74. Holm et al (1993) found that pH values ranged from 4.6 to 5.8 after analysis of fifty-four samples from different regions of the world. The pH values associated with the individual slatey, purple and brown raw beans were 6.47, 6.18 and 5.99, respectively. This explains in large part why the composite sample, which was approximately 11% slatey, showed a higher

Table 5. Characteristics of the raw cocoa starting material

Shell content (%)	11.98
Bean count per 100 grams	104
Moisture loss on laboratory roasting (%)	3.81
Mold (%)	0
Insect infestation (%)	0

Raw color	Count per 300 beans	%
Slate	32	11
Purple	10	3
Purple-brown	121	40
Brown	137	46

Sample component	pH
Composite	6.10
Slate	6.47
Purple	6.18
Brown	5.99

than normal pH.

Normal pH values of raw cocoa are in the range of 5.0 to 5.5. The low pH is due primarily to the infiltration of acetic acid into the bean during fermentation. Since this acetic acid initiates the process which eventually causes the raw cocoa to become brown, it is evident that the slate and purple beans have not been part of a fermentation process and therefore probably contain less acetic acid than fully fermented beans. Bopaiah and Shantaram (1991), Adomako et al (1981) and Dougan (1979) have shown that the pH of the fresh cocoa cotyledons starts at approximately 6.5 on day one of the fermentation process and drops to less than approximately 5.0 if the mass of beans is fermented for seven days. Lopez (1987) showed that after only 2 days of fermentation, the percentage of slatey beans dropped from 98 to less than 5. The high pH values found in this study are in agreement with the pH results from underfermented samples analyzed by Selamat (1990).

6 - 2 pH of Cocoa Liquors

The pH values of the cocoa liquors from each trial were all similar, ranging from 5.34 to 5.60, regardless of initial batch moisture content and final product temperature (Table 6). Moreover, statistical analysis of the pH data by the ECHIP package showed that the smallest measurable pH difference, or resolution, of this experimental design was larger than the measured pH effect across all of the trials.

Table 6. pH of cocoa liquors processed under several conditions

Trial	Initial moisture content (%)	Final temperature (°C)	pH
1	20	110	5.49
1R	20	110	5.45
2	11.5	110	5.50
2R	11.5	110	5.48
3	20	120	5.50
3R	20	120	5.50
4	20	130	5.60
5	3.5	130	5.47
5R	3.5	130	5.48
5R*	3.5	130	5.54
6	3.5	110	5.47
7	3.5	123.3	5.45
8	3.5	116.7	5.49
9	8.7	130	5.34
10	14.3	130	5.54
11	14.3	116.7	5.48

R denotes a replicate trial.

* denotes a second replicate run to obtain drying curve data.

The pH values of the liquor were lower than the pH of the composite raw bean sample as well as the individual color groups. This is a clear indication that the processing resulted in cocoa liquor which was more acidic than the raw nibs. Other researchers have shown that high pH raw cocoa does become more acidic upon roasting. The mechanism for this, however, has not been discussed in the technical literature. It may be that the roasting process releases compounds held within the unbroken cells of the unfermented beans which react with one another to form a conglomerate of finished products which are more acidic than the starting material.

The relative insensitivity of pH to a wide range of process conditions can be seen graphically in Figure 8. It is clear that altering initial batch moisture content and final product temperature does not significantly change the pH of the cocoa liquor. This provides increased flexibility in product development situations where liquors of various levels of color are used. Selamat (1988) studied 38 raw bean samples from 13 different cocoa producing countries. Of the 38 samples, six had a pH value greater than 5.50. Each of the samples was subjected to two roasting conditions – long roast (air temperature of 150°C for 30 min) and a short roast (air temperature of 150°C for 20 min). The beans from 12 trials were measured for pH, and 11 were found to have a lower pH than the starting material, in agreement with the results obtained in this study.

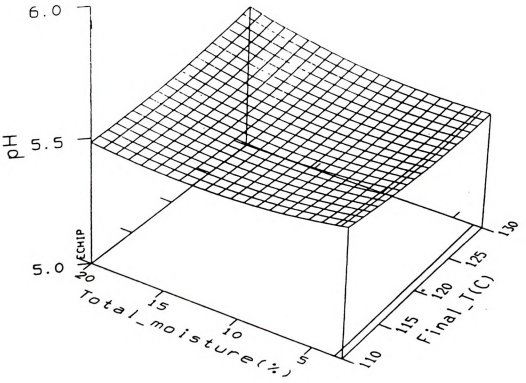

Figure 8. Response surface diagram for liquor pH

6.3 Color of Cocoa Liquors

In comparison to pH the data for the two important components of cocoa liquor color – darkness (R_d) and redness (a) – show a much greater sensitivity to the process variables (Figures 9, 10). The ECHIP® package fits a given experimental data, for example darkness, to an equation of the form

$$R_d = a+bx+cy+dxy+ex^2+fy^2 \qquad (15)$$

and selects the coefficients a through f by a process of multiple linear regression. A typical statistical summary of results is shown in Table 7. The effects tables for darkness and redness summarize the importance of each of the six terms in the equations for the two response variables and their interaction term, using an asterisk as an indication of rank or relative importance. For example, the summary in Table 7 shows that the process variables "Final_T(C)" and "Total_moisture(%)" are ranked highest and are the only main effects for darkness. Similarly, the two process variables as well as their interaction term are all important in determining redness.

The three-dimensional representation in Figure 9 shows that the darkest liquor is obtained at an initial batch moisture content of 20% and a final product temperature of 130°C. Experimentally, trials 4 and 10 resulted in the darkest liquors with an R_d value of 1.3 (Table 8). These trials were run from initial batch moisture contents of 20%

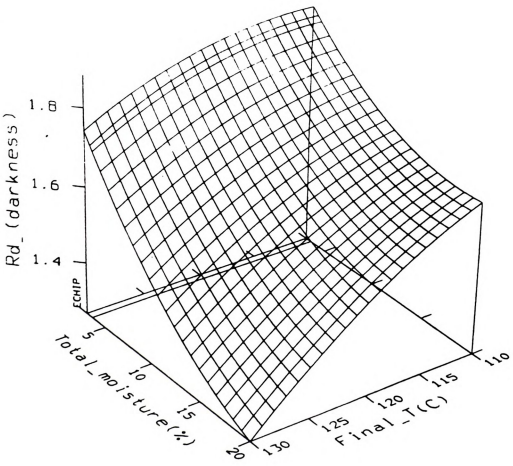

Figure 9. Response surface diagram for darkness (R_d)

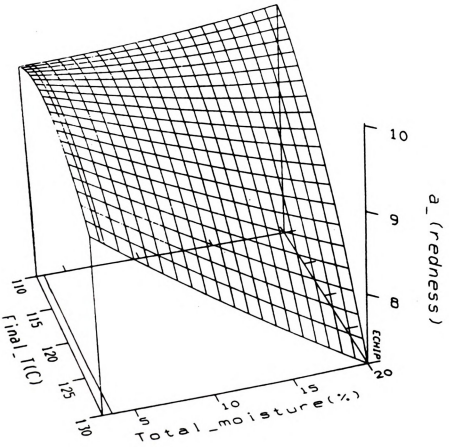

Figure 10. Response surface diagram for redness (a)

Table 7. Summary of typical statistical results from ECHIP*

```
pH
.   Rd_(darkness)
.    .  a_(redness)
.    .   .   b_(yellowness)
-----------------------------
.  *** *** ***     1 Final_T(C)
.  ***  **  **     2 Total_moisture(%)
.    .  **   *     3 Final_T(C)*Total_moisture(%)
.    .   .   .     4 Final_T(C)^2
.    .   .   .     5 Total_moisture(%)^2
```

Table 8. Color of resultant cocoa liquors

Trial	Initial moisture content(%)	Final temperature(°C)	Rd	a
1	20	110	1.6	10.0
1R	20	110	1.7	9.8
2	11.5	110	1.7	10.2
2R	11.5	110	1.7	9.9
3	20	120	1.6	9.5
3R	20	120	1.4	8.4
4	20	130	1.3	7.6
5	3.5	130	1.7	9.3
5R	3.5	130	1.7	9.2
5R*	3.5	130	1.8	9.3
6	3.5	110	1.9	9.6
7	3.5	123.3	1.8	9.9
8	3.5	116.7	1.8	9.7
9	8.7	130	1.5	8.5
10	14.3	130	1.3	7.1
11	14.3	116.7	1.7	9.8

R denotes a replicate trial.

* denotes a second replicate used to obtain drying curve data.

and 14.3%, respectively, to a final product temperature of 130°C. The lightest color (R_d = 1.9) was produced from trial 6 which was run using the indigenous moisture content of the micronized cocoa nibs (3.5%) at the lowest final product temperature (110°C).

Following a constant minimum initial moisture content (approximately 3.5%) contour on Figure 9, the liquor became darker as the final product temperature increased. Similar rates of change in darkness were observed along a constant final product temperature of 130°C as the initial batch moisture content increased from 3.5% to 20%, and as the final product temperature increased from 110°C to 130°C.

The redness of the liquor followed similar trends (Figure 10). The maximum redness was found at a final product temperature of 110°C and a batch moisture content of 20%. The highest redness values were found along all batch moisture values at a constant final product temperature of 110°C. The minimum redness was found at a batch moisture content of 20% and a final product temperature of 130°C.

It is apparent from these results that the darkest, least red liquors are obtained by raising the bulk moisture content and roasting the batch to the maximum temperature. High temperature roasting has been shown to cause the development of black pigments during the Maillard reaction (Fennema, 1985).

The color, therefore, can be changed significantly through alteration of the initial batch moisture content and

final product temperature. The Maillard browning reaction is the most probable cause of the darker, less red liquor produced at higher temperatures. The role of added water, though, is not clear. Perhaps the color compounds, such as the anthocyanins, are chemically interacting with the water. The water may be transporting them from within the intact cell structures and causing them to come into contact with other compounds which cause color changes.

The overall results have several implications for process engineering. For example, the confectionery manufacturer can simply add water to the batch to change the redness and darkness of liquor to predictable levels. This will enhance product perception by the consumer without causing any significant change to the pH of the liquor. In addition, new formulations containing this color-enhanced liquor may be possible. Flexibility in the roasting process with respect to color will also allow liquors produced on distinctly different cocoa processing systems to be color-matched on a Barth system through the manipulation of moisture content and final product temperature.

Applying the results obtained in this study to a full scale roasting system may require additional development. As the capacity of the roasting drum increases from the pilot to the production scale, the ratio of the surface area for heating to the internal volume of the drum will decrease. This will make the heat transfer less efficient in the production roaster than in the pilot scale roaster. The bulk

temperatures, bulk moisture contents and resulting processing times used in this pilot study may be different than those required to produce liquors of similar pH and color on a production-scale system.

6.4 - Cocoa Nib Particle Size Distribution

For trials 4, 5, and 9, the overall particle size distribution (PSD) before and after roasting was measured (Figures 11, 12, 13). The initial particle size distribution of the micronized nibs was measured after the product had been run through the winnowing machine. The particle size distributions of the three trials were all approximately the same before roasting, with over 70% of the nibs larger than 3.4mm.

In general, a slight shift from the mass percent retained on the 6.4mm opening sieve toward that retained on the smallest sieve (0.9mm) was observed. However, the overall profile, or shape, of the particle size distributions did not change significantly. The roasting machine used in this study did not change the physical integrity of the product during processing. The cocoa nibs were agitated only to promote uniform roasting, without inducing physical damage. The initial batch moisture content and subsequent total process times associated with these trials were all very different. The final product temperature for all of the trials was 130°C.

The fact that no size changes occurred during processing means that the observed changes in pH and color were

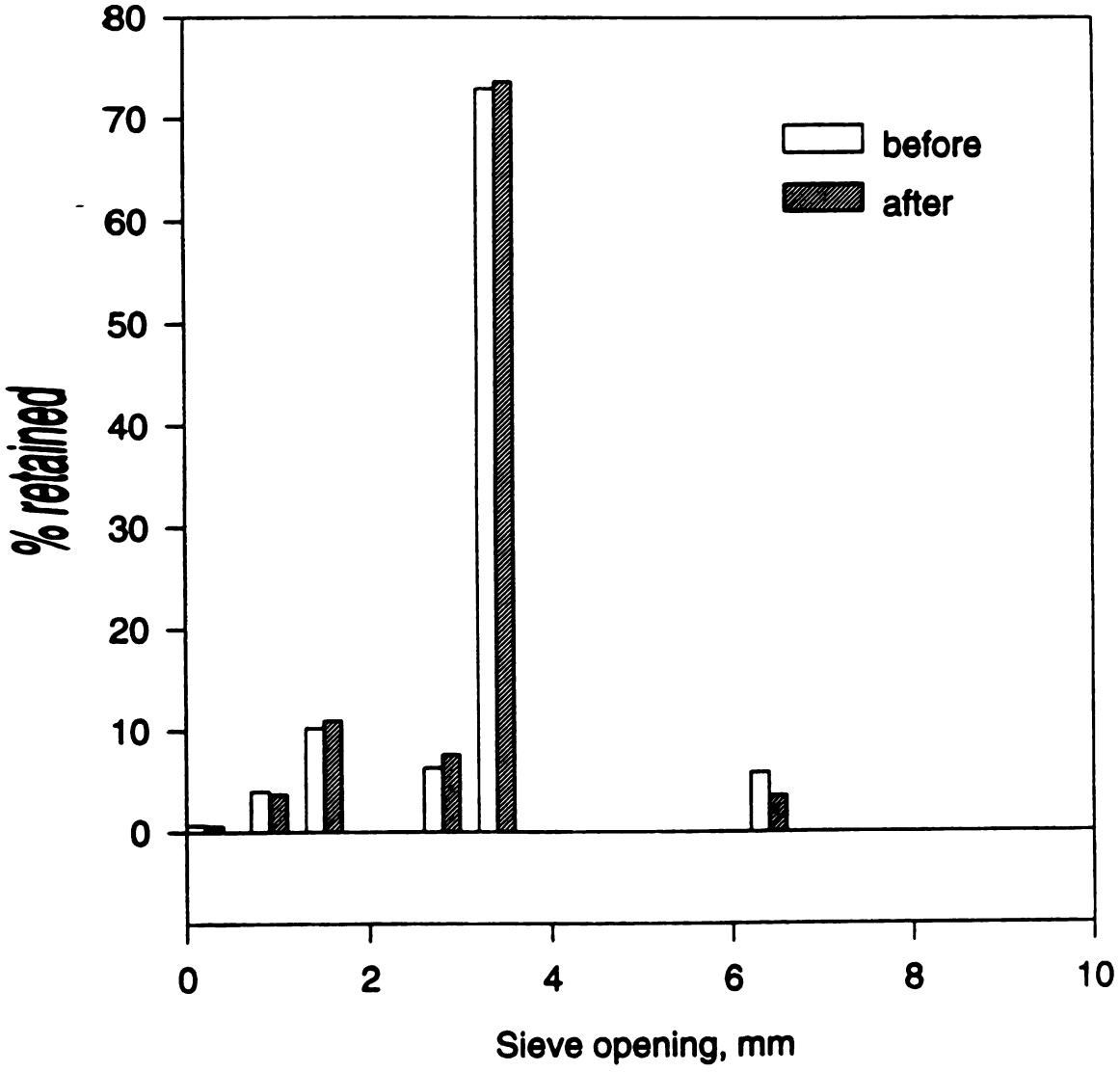

Figure 11. Particle size distribution before and after roasting (trial 4: initial batch moisture content - 20%; final product temperature - 130°C)

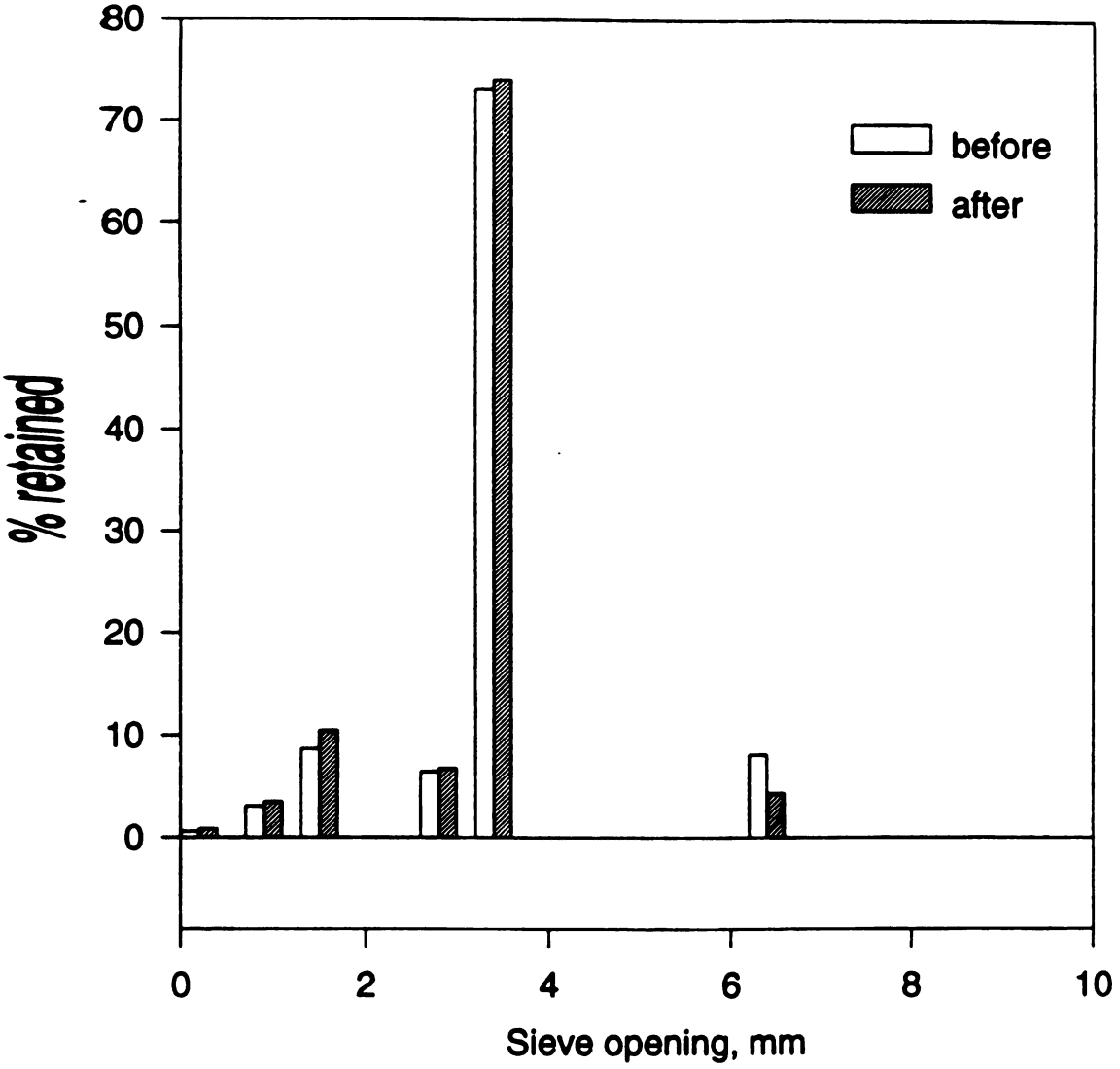

Figure 12. Particle size distribution before and after roasting (trial 5: initial batch moisture content - 3.7%; final product temperature - 130°C)

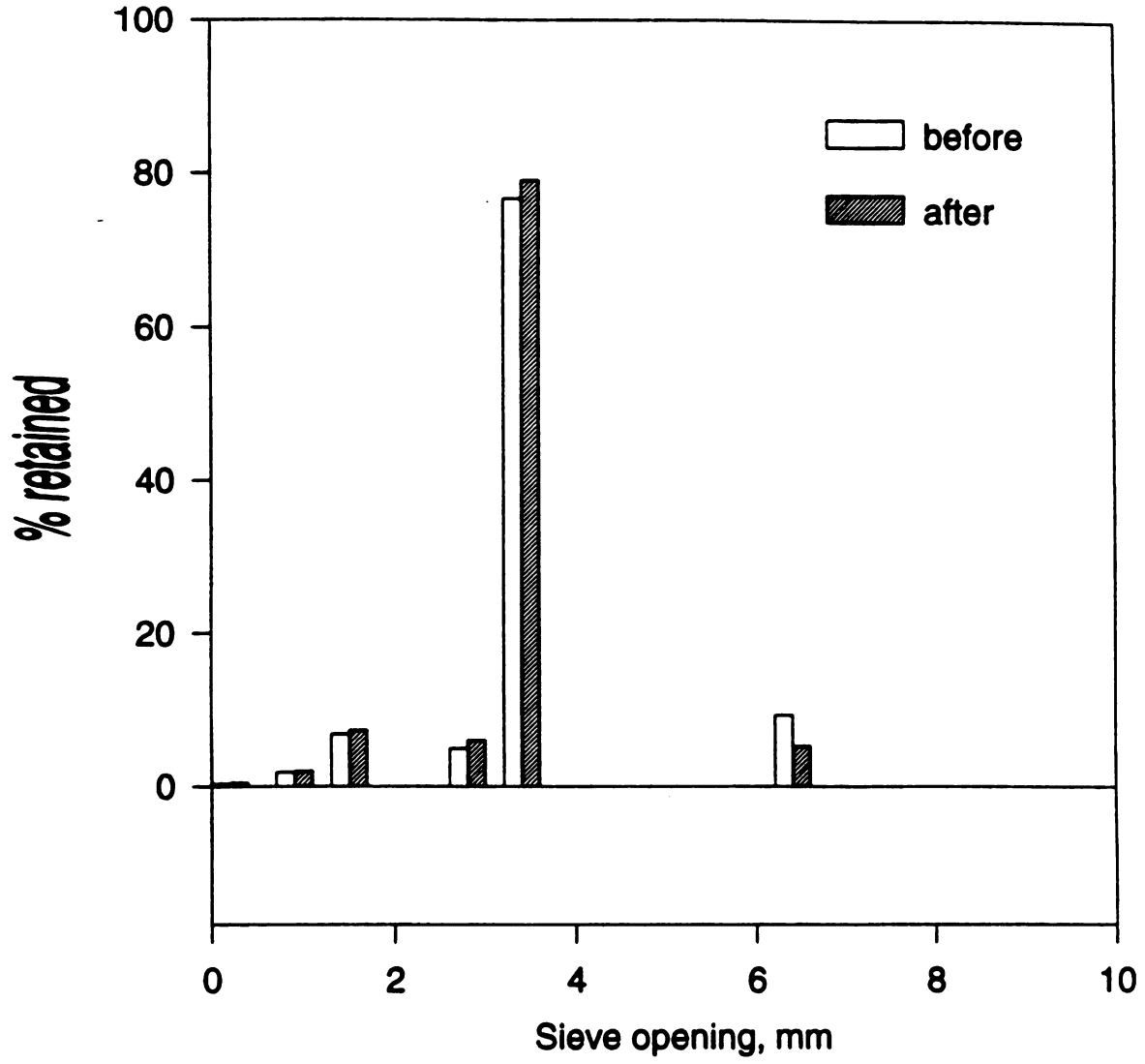

Figure 13. Particle size distribution before and after roasting (trial 9: initial batch moisture content - 8.7%; final product temperature - 130°C)

independent of particle size distribution.

6.5 Cocoa Nib Drying Curves

The bulk moisture content of the batch was measured approximately every 15 minutes during trials 4, 5 and 9. The slope of the drying profile for trial 4 (20% initial bulk moisture content) indicates that this trial had the highest initial drying rate (Figure 14). This was probably due to the large amount of free and surface moisture which was easily removed during the first portion of processing.

The estimated critical moisture contents between constant rate drying and falling rate drying were similar for all three trials, ranging from 3.7% to 2.9% (Figures 14, 15, 16). The rate of drying is much faster during the constant rate drying period as the evaporation of water from the saturated surfaces takes place very rapidly. It is reasonable to expect that, since the water is free for removal, the burner temperature may be raised to higher temperatures until the nib moisture content reaches approximately 3.9% without risk of burning the product. This will decrease the process time and effectively increase roasting capacity.

The predicted total drying times were similar to the experimentally measured values (Table 9).

6.6 Estimation of the Convective Heat Transfer Coefficient

Figure 17 shows three key points on a typical time/temperature history for all of the trials. Point A is

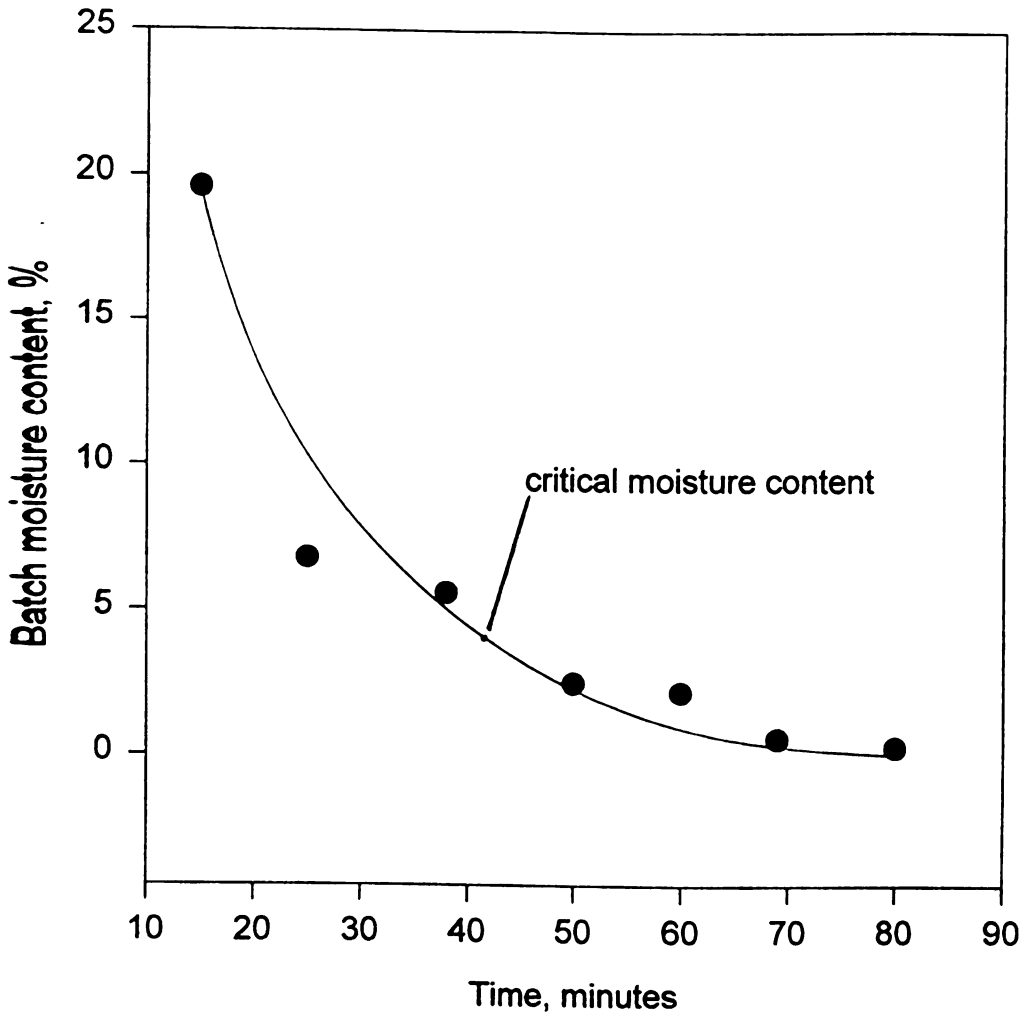

Figure 14. Drying curve - trial 4: initial batch moisture content - 20%; final product temperature - 130°C

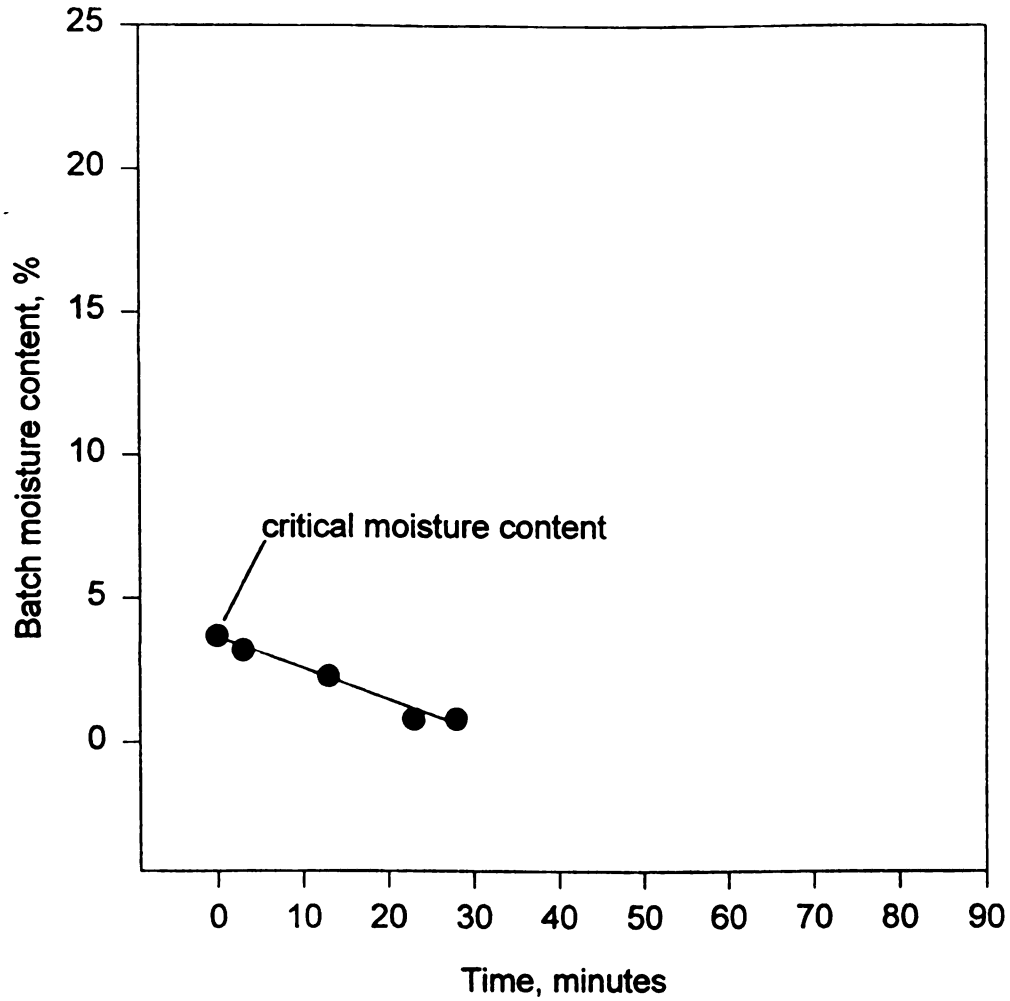

Figure 15. Drying curve - trial 5: initial batch moisture content - 3.7%; final product temperature - 130°C

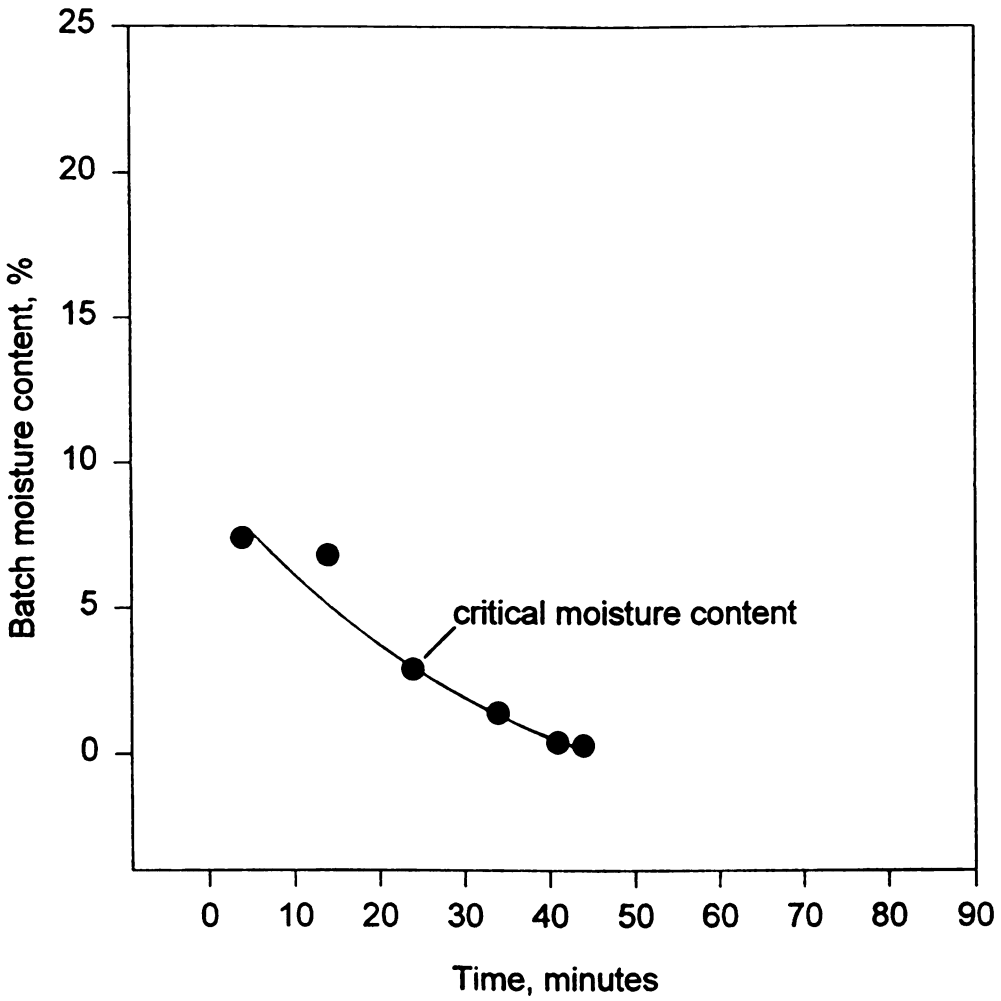

Figure 16. Drying curve - trial 9: initial batch moisture content - 8.7%; final product temperature - 130°C

Table 9. Experimental and predicted drying times for trials 4, 5 and 9

Trial #	Initial bulk moisture content (%)	Final bulk temperature (°C)	Actual time (minutes)	Predicted time (minutes)
4	20	130	69	52.65
5	3.7	130	23	16.32
9	8.7	130	41	52.78

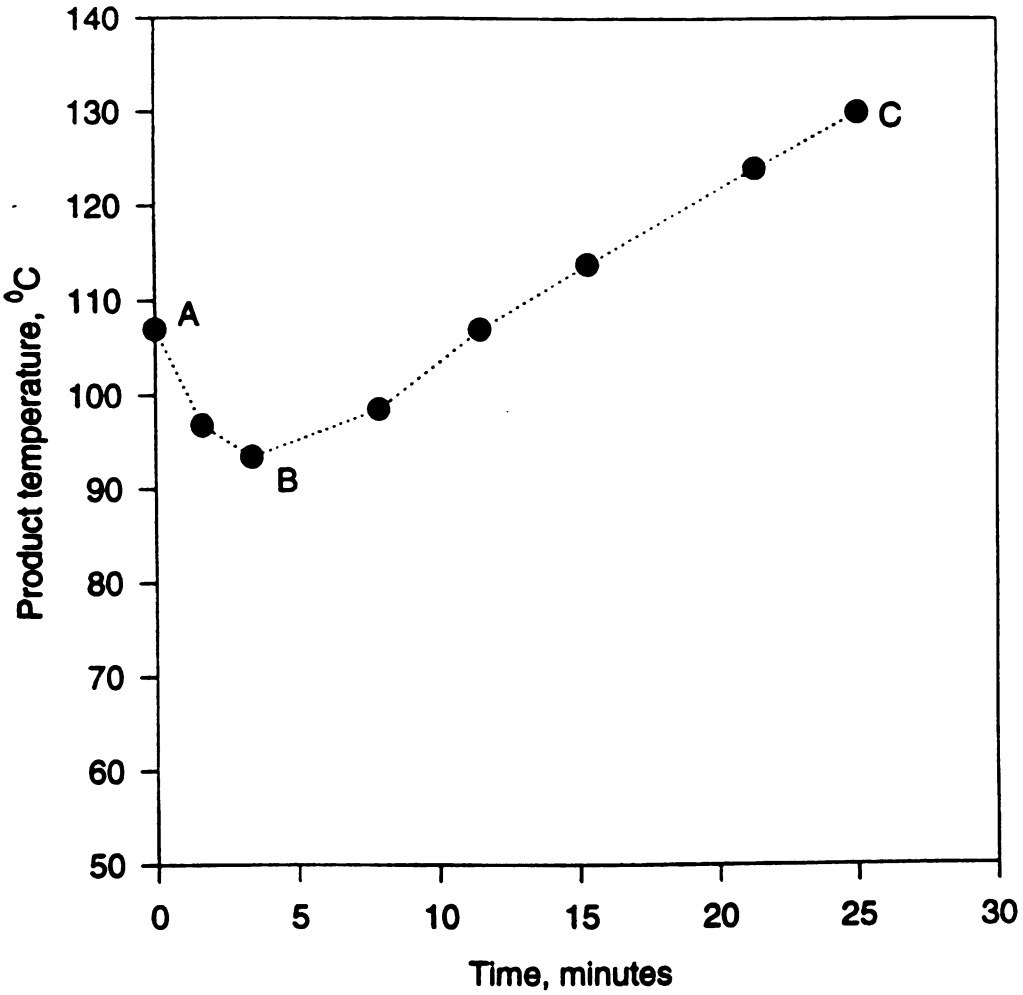

Figure 17. Typical time-temperature history of cocoa nibs during roasting (trial 5: initial batch moisture content - 3.7%; final product temperature - 130°C)

the point where the batch was introduced into the roaster. The introduction of a cold mass into the roaster reduced the temperature rapidly. Point B is where the minimum bulk temperature occurred, and the batch began to heat up. Point C is the point at which the product reached the target bulk temperature. Using the portion of the curve in Figure 17 where the temperature was rising monotonically, the convective heat transfer coefficient was estimated using Equ. 13.

An effective heat transfer coefficient was estimated at 0.0526 W/m^2K, and appears to be quite low for this natural convection roasting process. The only value in the literature for a similar process was the coefficient of 5-10 W/m^2K predicted by Hayes (1987) for naturally circulating air, a value that is two orders of magnitude higher than the coefficient estimated in this study.

Several factors may account for this large difference in values. The primary factor is that the temperatures used in estimating h were the bulk mass temperatures rather than the actual nib temperatures which could not be measured. Thus, there is no way of accounting for latent heat effects in the process, including the energy for inducing phase changes in cocoa butter, and the possibility that the reaction that causes color changes in the nibs is endothermic.

7.0 CONCLUSIONS

The pH of cocoa liquor appears to be unaffected by changes in the key process variables of initial batch moisture content and final bulk temperature.

An initial bulk moisture content of 20% and a final bulk temperature of 130°C produced the darkest and least red cocoa liquor. Conversely, the least dark liquors were produced by adding no water to the batch and roasting to a final bulk temperature of 110°C.

Redness of a liquor can be maximized by raising the initial bulk moisture content above 10% and roasting to a final bulk temperature of 110°C.

Moisture content was a key factor in the alteration of the color of the cocoa liquor.

The pilot scale Barth processing system used in this study did not significantly alter the particle size distribution of the cocoa nibs.

8.0 SUGGESTIONS FOR FUTURE RESEARCH

This study found that the color of cocoa liquor could be altered through manipulation of key roasting process parameters – moisture content and final batch temperature, without altering the pH. It will be necessary to use these liquors to produce chocolates for color and sensory analysis to determine their potential value. For example, producing cocoa powder for use in drink mixes and baked products from these liquors may reveal that similar color changes are also possible. The basics of color changes in cocoa during processing are not well understood. Since color is so important to the perception of product quality, a comprehensive study of color alteration during processing will be valuable.

Although the particle size distributions of the trials in this study did not vary after processing, the nib microstructure may have been altered by water addition and high temperature. This may be most important when unfermented beans are used. Electron microscopy techniques and diffraction techniques can be used to understand any changes during processing. With an understanding of these microstructural changes possible during roasting, there is potential for the process engineer to carefully manipulate cell components to provide colors and flavors not currently available.

APPENDICES

APPENDIX A - Time-Temperature Data

Table 10. Time-temperature data for trial 4

Time (minutes)	Temperature (°C)
0	88.3
0.71	73
2.59	62.8
4.26	58.13
10.7	81.5
20.4	78.1
28.93	77.2
35.53	81.5
42.2	90
47.5	98.5
54.15	107
65.1	117.2
77.99	130

Table 11. Time-temperature data for trial 5

Time (minutes)	Temperature (°C)
0	107
1.65	96.8
3.41	93.4
7.94	98.5
11.55	107
15.4	113.8
21.38	124
25.06	130

Table 12. Time-temperature data for trial 9

Time (minutes)	Temperature (°C)
0	130.8
0.9	107
2.4	98.5
3.32	91.7
5.66	88.3
14.49	93.4
20.45	100.2
24.83	107
29.33	113.8
31.7	117.2
36.76	124
42.95	130

APPENDIX B - Particle Size Distributions

Table 13. Particle size distribution data for trial 4

sieve size (mm)	% retained, before	% retained, after
9.5	0	0
6.4	5.84	3.54
3.4	72.92	73.63
2.8	6.32	7.63
1.5	10.24	10.98
0.9	3.98	3.67
0.2	0.64	0.55

Table 14. Particle size distribution data for trial 5

sieve size (mm)	% retained, before	% retained, after
9.5	0	0
6.4	8.1	4.35
3.4	73.14	74.12
2.8	6.44	6.75
1.5	8.68	10.45
0.9	3.08	3.5
0.2	0.56	0.83

Table 15. Particle size distribution data for trial 9

sieve size (mm)	% retained, before	% retained, after
9.5	0	0
6.4	9.34	5.25
3.4	76.65	79
2.8	4.97	6.04
1.5	6.83	7.32
0.9	1.85	1.95
0.2	0.32	0.44

APPENDIX C - Moisture Content Profiles

Table 16. Moisture content data for trial 4

Time (minutes)	Moisture content (%)
0	3.6
15	19.6
25	6.8
38	5.6
50	2.5
60	2.2
69	0.6
80	0.3

Table 17. Moisture content data for trial 5

Time (minutes)	Moisture content (%)
0	3.7
3	3.2
13	2.3
23	0.8
28	0.8

Table 18. Moisture content data for trial 9

Time (minutes)	Moisture content (%)
0	3.6
4	7.4
14	6.8
24	2.9
34	1.4
41	0.4
44	0.3

«xxxxxxxxxxxxx» Effects for response 'pH'

LACK-OF-FIT

EFFECTS	RESLTN	SIG	TERM
5.4515			0 CONSTANT
0.0241	0.1001		1 Final_T(C)
0.0364	0.1129		2 Total_moisture(%)
0.0680	0.1687		3 Final_T(C)*Total_moisture(%)
0.0209	0.0947		4 Final_T(C)^2
0.0395	0.1184		5 Total_moisture(%)^2

Residual SD = 0.054683
Replicate SD = 0.027809

N terms = 6
N unique trials = 11
N replicates = 5
N total trials = 16

«xxxxxxxxxxxxx» Effects for response 'Rd_(darkness)'

EFFECTS	RESLTN	SIG	TERM
1.6134			0 CONSTANT
-0.2718		***	1 Final_T(C)
-0.3412		***	2 Total_moisture(%)
-0.1264	0.2578		3 Final_T(C)*Total_moisture(%)
-0.0448	0.1411		4 Final_T(C)^2
0.0711	0.1740		5 Total_moisture(%)^2

Residual SD = 0.071326
Replicate SD = 0.079582

N terms = 6
N unique trials = 11
N replicates = 5
N total trials = 16

«xxxxxxxxxxxxx» Effects for response 'a_(redness)'

EFFECTS	RESLTN	SIG	TERM
9.414			0 CONSTANT
-1.685		***	1 Final_T(C)
-0.908		**	2 Total_moisture(%)
-1.207		**	3 Final_T(C)*Total_moisture(%)
-0.422	0.977		4 Final_T(C)^2
0.057	0.651		5 Total_moisture(%)^2

Residual SD = 0.411238
Replicate SD = 0.367877

N terms = 6
N unique trials = 11
N replicates = 5
N total trials = 16

«xxxxxxxxxxxxx» ANOVA Table for response 'pH'

LACK-OF-FIT

Mean Squares	DF	P	
0.00143461	2	0.6325	Final_T(C)
0.00386312	2	0.3169	Total_moisture(%)
0.00675808	1	0.1637	Final_T(C)*Total_moisture(%)
0.00299019	10		ERROR
0.000773334	5		REPLICATE ERROR

«xxxxxxxxxxxxx» ANOVA Table for response 'Rd_(darkness)'

Mean Squares	DF	P	
0.100314	2	0.0003	Final_T(C)
0.149719	2	0.0001	Total_moisture(%)
0.0233492	1	0.0578	Final_T(C)*Total_moisture(%)
0.00508742	10		ERROR
0.00633333	5		REPLICATE ERROR

«xxxxxxxxxxxxx» ANOVA Table for response 'a_(redness)'

Mean Squares	DF	P	
4.039	2	0.0002	Final_T(C)
1.04538	2	0.0179	Total_moisture(%)
2.13023	1	0.0053	Final_T(C)*Total_moisture(%)
0.169117	10		ERROR
0.135333	5		REPLICATE ERROR

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