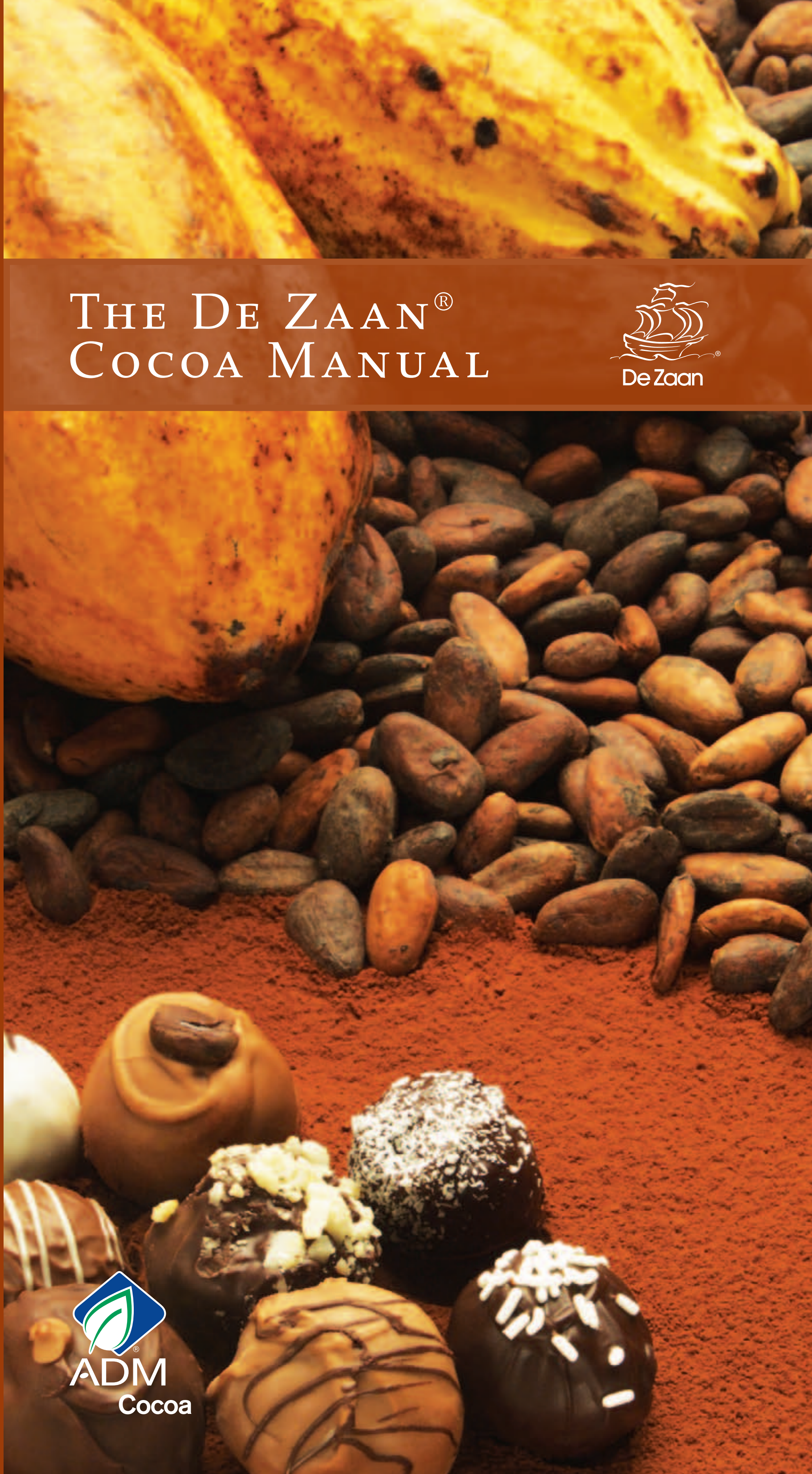

The De Zaan® Cocoa Manual

De Zaan

Cocoa

Candy & Confectionery

Baking & Cereals

Beverages

Dairy

Snack Foods

ADM Cocoa

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Table of Contents

Module 4
Flavor and Flavor Development

Module 5
Color and Color Development

Module 6
Health and Nutritional Aspects

Module 7
Cocoa Liquor

Module 8
Cocoa Butter

Module 9
Cocoa Powder

History and Supply of Cocoa 1

1. A brief history of cocoa

Introduction

Throughout history, many discoveries' future significance to man was never fully appreciated at the time. The cocoa bean is such a discovery. Now used for a wide range of foods and delicacies, the cocoa bean enriches the lives of us all.

The first time that people far from the areas of its origin were confronted with the cocoa bean was thanks to Columbus. On his fourth voyage to America, he reportedly discovered a canoe off the Yucatan Peninsula laden with fruit and cocoa beans. But it was only years later at the beginning of the 16th century that Cortez confirmed the remarkable value assigned to the cocoa beans. He found that the Aztecs valued them so much that they used them both as means of payment and as the source of a beverage drunk at court and religious ceremonies.

Little is known as to how the bean came to take on such a powerful role. One can surmise that the realization of its potential occurred in much the same way as wine. That is to say, a natural product was accidentally left in storage and subjected to the forces of nature, and a series of chance events then led to the discovery of its potential.

Although its exact origins are not known, the Cacao tree was then exclusive to the Americas. The closest estimates put the area of origin in and around the valleys of the Amazon and Orinoco Rivers. High ambient temperatures were clearly necessary for the development of the bean. Evidence suggests that the tree has been cultivated for more than 3,000 years.

Cortez

In 1519, Cortez arrived in Mexico and met Montezuma II, a most significant patron of cocoa. Because of the Aztecs' belief that Cortez was the reincarnation of their God Quetzalcoatl, he was showered with gifts and honors, including cocoa beans. The tributes requested by Montezuma from his subject people were in part taken in the form of supplies of cocoa beans. The cocoa beans were then consumed primarily in the form of a drink known as *xocolatl*, the Aztec name for the bitter stimulant. Its name would later be applied to all products, drinkable or solid, that were made from the cocoa bean. It is a word that perhaps has the remarkable distinction of being one of the first ever to be adopted from one language and then applied on a truly global scale.

Recipes for *xocolatl* were rarely recorded and probably varied by location. The beans would have first been collected, left to ferment naturally, sun dried, roasted in earthen pots, and deshelled by hand. The kernels were then ground on a slightly concave stone called a *metate* using a cylindrical grinder. At this point, spices and herbs of various kinds, including vanilla, might have been added to improve the taste. The resulting paste was then formed into cakes to cool and harden. For consumption, the cakes would be broken up, dissolved in water, and beaten to a foamy consistency.

The attraction of this bitter drink clearly lay in the physiological effects it offered the drinker, many of which are still not clearly explained. The fact that cocoa is chemically very complex and that many of its components have not been fully identified confirms the complexity of this natural bean's biochemistry. Its stimulating effects certainly offer clear reason for its traditional use in medicine. (See also: Module 6: Health and Nutritional Aspects).

Cocoa tree with ripe fruit

Spread of the cocoa tree

As the first main colonizing power, it was the Spaniards who ruled in this region of the Americas. The popularity of the bean conquered the court of Spain. As imports grew, although only under close and direct supervision of the Spanish royal court, attempts were initiated to reduce dependence on a single source of the bean. Cultivation across all of their colonized territories was encouraged, not without frustration, as the cocoa trees were strangely susceptible to disease. In 1525, for example, the Spaniards transplanted one of the main types of cocoa beans from Mexico to Trinidad, where it flourished until being completely wiped out in an epidemic.

Over time, the cocoa tree was planted throughout many islands and countries of the Caribbean and later to other continents, all areas that offered the ideal climatic and soil conditions for successful cultivation.

The popularity of the cocoa drink at the Spanish royal court was such that still in the 16th century, cocoa was declared a state secret by decree from King Charles V of Spain. Cocoa was to remain a Spanish possession. Cortez was instructed never to divulge its origin. Though it was actually known to people other than the Spanish, no one invested the effort to research it further. The secrets of cocoa took almost 140 years to filter out of Spain. Eventually, through a diplomat, the secret passed into Italy, then to Austria and France, and on to northern Europe, where the Dutch encouraged and later came to dominate cocoa trade.

By the end of the 17th century, drinking cocoa had become so popular in Europe that it was serving as a source of tax revenue for governments, a sure sign that consumption was spreading beyond the small elitist groups that initiated its success.

The Food of the Gods, or *Theobroma cacao L.*, as it is known by its scientific classification, would become one of the world's great commodities.

Main cocoa growing areas

The spread of the cocoa bean across the world was a long and frequently interrupted journey. Pests and disease frustrated many attempts to transplant the tree. Its successful cultivation required specific climatic conditions. The tree first spread out in regions close to its origins, from Brazil and Mexico in the 15th century across Central America and the Caribbean islands in the 16th. By 1560, the Spaniards had introduced it to some of the Indonesian islands. They brought the bean to the West African island of Fernando Po, where it was later transferred to the mainland. The great growth of cocoa trade in the 19th century saw its expansion across many other countries, especially in West Africa and Southeast Asia.

Early processing and trade

The Dutch were the first to actively trade the commodity and, until the 18th century, dominated the world trade in cocoa. Because of this, the Dutch also became more involved in research into cocoa processing. In the 16th and 17th centuries, most processing was in the hands of the Spanish, even though they bought most of their beans from Amsterdam or the Dutch port of Zeeland.

Cocoa processing developed during the 18th century in the Netherlands. In 1825, to reduce the fattiness of the chocolate drink, Coenraad Johannes van Houten developed a mechanical pressing process to fractionate the cocoa liquor, the result of grinding the roasted beans into a fatty fraction (cocoa butter) and a partially defatted fraction (cocoa cake or powder). Another process developed by van Houten was alkalization, or the "Dutch process," a procedure of treating cocoa with alkali. This was originally done in order to improve the solubility. It was found that at the same time, taste and color were also changed.

Some years later, cocoa butter would come into its own: Originally used as a simple household fat, it would pave the way for the creation of chocolate.

In 1847, an important discovery was made by John Fry in England. By adding cocoa butter to a mixture of liquor and sugar, chocolate was created, one of the confectionery industry's greatest discoveries. This is not only an easily handled product, but it is solid at room temperature and melts just below body temperature. Thus, it is a product that, when eaten, releases its flavors in an optimal manner.

Meanwhile, cocoa powders with different tastes and colors became widely used as flavors and color ingredients in the food industry.

Major Cocoa Bean Producing Areas (x 1,000 MT and %)	1980/1		1990/1		2000/1		2002/3		2003/4	
Africa	1,010	**59**	1,418	**57**	1,948	**68**	2,229	**70**	2,544	**72**
Central/South America	542	**32**	613	**24**	369	**13**	372	**12**	405	**11**
West Indies	47	**3**	51	**2**	54	**2**	56	**2**	57	**2**
Asia & Oceania	97	**6**	424	**17**	487	**17**	510	**16**	511	**15**
Total world production	1,696		2,506		2,858		3,167		3,517	

Source: International Cocoa Organization

2. Cocoa today

Cultivation of cocoa

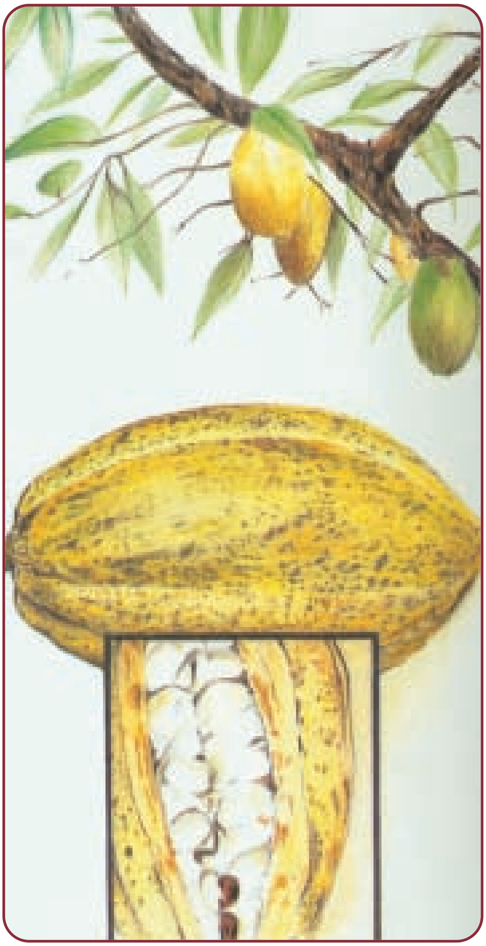
The successful cultivation of cocoa requires a special climate that is mostly found within the area bounded by the Tropics of Cancer and Capricorn. The majority of the world's crop is now grown within 10° North and South of the equator. It will grow from sea level up to a maximum of some 1,000 meters, although most of the world's crop grows at an altitude of less than 300 meters. Temperatures must generally lie within the band of 18°-30° C (65°-86° F). Rainfall must be well distributed across the year, with a minimum of 1,000 mm. The trees must be protected from strong winds (the root system is not robust); soils must be well aerated, and pests and diseases must be carefully controlled.

The original cocoa tree grew to a height of ±10 meters at maturity and preferred the shade of other larger trees. Modern breeding methods have led to the development of trees of a standard ±3 meters tall to allow for easy hand harvesting.

Certain cocoa trees become productive in three to four years, while in the past six to seven years was common. When the evergreen cocoa tree reaches its bearing age, flowers and fruits begin to appear in modest amounts. These can be found on the tree at all seasons of the year, although typically two crops are harvested each year.

The fruits grow directly from the trunk of the tree and the thicker branches. While there may be several thousand flowers on a mature tree, only a small number matures into fruits or pods. These take some six months to grow from a fertilized flower, measure 10-15 cm at the center, and are 15-25 cm long. The pod contains some 40 seeds or beans. After fermentation and drying, one pod produces some 40 g of beans, one bean typically weighing around 1 gram.

Yields per hectare have risen over time from around 350 kg to more than 1,500 kg on the most efficient farms. Today, cocoa trees are cultivated in more than 40 countries around the world, across an estimated area of 3.6 million hectares, producing an annual crop of more than 3.0 million tons of dried beans ready for processing.



A cocoa pod contains some 40 seeds.

Types of beans

Typical attributes of the bean, such as bean size, flavor, color, and chemical composition of the fat, vary considerably in beans of different origins. There are two main types of cocoa bean: Criollo and Forastero. Criollos are light colored with a mild, nutty character. Forastero cocoas are dark brown, strongly flavored, slightly bitter, and have a higher fat content. The greater part of the world's cocoa crop consists of the Forastero type, more specifically a sub-type known as Amelonado. Parts of Ecuador boast a very specific type of cocoa, Cacao Nacional or Arriba. The Criollo is known for its flavor characteristics, while the Forastero plant is known for its ability to withstand more severe climatic conditions. But it would be wrong to claim that certain natural varieties of cocoa are better than others. Each has its own specific chemical and physical characteristics that are taken into careful consideration when beans are blended.

The ultimate quality of cocoa, whatever its origin, is significantly affected by weather conditions during growing, soil status, fermentation, and drying. Storage conditions are also important in preventing deterioration of the quality.

Harvesting and fermentation

Although nearly 500 years have passed since Cortez first witnessed the making of hot cocoa by the Aztecs, the basic methodology for processing cocoa beans has remained much the same. While a vast amount of research has been undertaken to speed up the cocoa bean fermentation process, there has been little success. Clearly, the different stages of fermentation are essential in the creation of the complex organic components essential to the final taste and enjoyment of cocoa.

The pods grow directly from the trunk of the tree. Mostly they are harvested by hand using long-handled knives and broken open to reveal the beans and the white pulp surrounding them. Beans are then extracted and directly subjected to fermentation.

The traditional process in West Africa, the world's largest cocoa growing area, is simple: Farmers place the pulp-covered beans on the ground, cover them with layers of leaves (often banana), and allow the heap to remain for four to seven days, depending on the variety of the bean. It is preferable to mix the heap every two days so that the bean mix ferments evenly. The fermentation is critical for the future development of color and flavor of the cocoa, although there are still many unknowns as to the exact processes occurring. Development of aroma precursors is essential to the eventual creation of flavors.

A more industrial fermentation uses three to five stepwise-positioned boxes: the highest box is filled with pulp-covered beans, and after one to two days the content is mixed and transferred to the lower box, a process which is repeated until the lowest box is reached. In four to six days, this box fermentation can reach the result of the traditional heap process.

After the fermentation process is completed, during which the white pulp is totally degraded, the cocoa beans have to be dried. In Africa the traditional method is to spread the beans out on mats or in trays in the open air to dry in the sun. Because of the high rainfall and cloud cover in Brazil and Malaysia, other techniques are more popular. In Brazil the beans are typically laid out on broad mats on stilts above ground level to dry. In the event of rain, a roof can be slid across the mats, and hot air is used to dry them. In Malaysia widespread use is made of mechanical rotary driers. After drying, the beans are bagged and made ready for transport to buying stations and regional warehouses.

Quality and grading

Cocoa is a natural product and suffers all the risks inherent to that. The flower is very susceptible to rain and temperature conditions during its development. The pod can be attacked by a variety of molds, insects, and rodents, and the shell may be contaminated microbiologically.

The quality of beans is assessed under

Fermentation of beans under banana leaves

Drying of cocoa beans on mats

various headings:

- degree of fermentation
- number of defects
- number of broken beans
- bean count (number per 100 g)
- flavor
- color
- fat content
- fat quality
- shell content
- moisture content
- uniformity
- insect and rodent infestation

The bean cut test is used to evaluate defects and the degree of fermentation. (See also Module 4: Flavor and Flavor Development.)

A key criterion is flavor. An expert panel grades a consignment, seeking to identify off-flavors. This depends on the type of bean and its handling. Moldy off-flavors come from molds; smoky taints may come about during drying; acidic off-flavors are due to excessive acid created during fermentation or improper drying. Off-flavors can also be caused by the proximity of another strong-smelling product during storage and shipping.

The yield of a consignment of cocoa beans is the usable proportion—the cocoa nib. Bean size is important because small beans have a proportionately lower amount of nib and a higher shell content, neither conducive to a good yield. Beans should also be uniform in size because variable-sized beans are harder to break and deshell. The shell percentage is dependent on the type of bean. Asian beans typically have a higher shell content than African beans. Shells should be whole but loose. The higher the moisture content, the higher the chances of mold development. The fat content, the amount of foreign matter, broken beans, insect damage, and other such factors may negatively influence the true value of the beans for the user.

Cocoa beans vary in size, shape, color, and other features.

The cocoa butter should be low in free fatty acids and show specific melting and solidification characteristics.

Good cocoa beans should be well fermented, dry, and free from abnormal odors and adulteration. The beans should be reasonably uniform in size; reasonably free from broken beans, fragments, and pieces of shell; and free of foreign matter.

In the past, cocoa bean marketing in origin countries was mainly government controlled (purchasing from farmers, selling, and setting prices), but today free marketing systems more often prevail.

When the beans are grown on very small farms, the collection, grading, and financing of the crop can be rather complex. At the buying station, a farmer's crop is weighed, inspected, and paid the current market (or government set) price. Price discounts/premiums can be made for poor/good quality. From the buying stations, the cocoa beans are collected and finally arrive at the nearest port of embarkation or are delivered to local processing plants.

Sales are made to licensed traders and cocoa merchants or directly to cocoa processors. Cocoa brokers can be intermediaries who have expertise on crops and trade and who advise and act for both buyers and sellers.

Physical cocoa versus cocoa futures

Physical cocoa is real cocoa, bought and sold according to its actual quality, tonnage, delivery time, place, and price. Cocoa traded on the terminal or futures market is paper cocoa, traded according to a uniform description and lot tonnages, with price and delivery period as the only variables.

In West Africa cocoa is traded through government-controlled marketing boards (Ghana) as well as by local exporters and cocoa processors (Ivory Coast, Cameroon, and Nigeria), where the cocoa trade has been privatized and deregulated. The level of trade regulations and taxes levied on cocoa usually reflects the importance of cocoa for the national economy. By and large, foreign ownership of cocoa farms in

West Africa is not allowed.

In other major producing areas, such as Central and South America and Asia, cocoa is freely traded and exported. Cocoa does not play as dominant a role in these economies. Farming in some countries like Brazil and Malaysia is done on a much larger scale than in Africa or Indonesia.

With more than 3.0 million tons consumed annually (2002/2003), cocoa beans are today a major commodity. The main cocoa exchanges are London and New York. The physical traders of cocoa are located in many other cities such as Amsterdam, Geneva, Hamburg, London, Paris, Kuala Lumpur, Philadelphia, San Salvador, and Singapore.

As a commodity exposed to oversupply by bumper harvests, or to shortage caused by weather or disease, the price of cocoa naturally varies. As with other commodities, the futures market allows manufacturers to purchase for future requirements at a known price. In that way, the prices of beans and intermediate products are based on the market's perception of the current and future supply and demand. Everyone can see what is happening. Cocoa is thus traded openly.

Terminal prices, however, do not necessarily reflect the values of the specific types of beans. Each cocoa bean origin will have its own price, selling at a premium above the terminal price or at a discount below it. This is because the market recognizes that each bean origin has a particular demand due to its specific characteristics, such as flavor, color, and cocoa butter properties. These distinct characteristics can play a significant role in the pricing.

Major ports of entry are Amsterdam, Philadelphia, and Hamburg. Amsterdam receives more than 600,000 tons of cocoa beans annually, about 20% of the world crop.

Industry trends

Bulk shipment of cocoa beans has made its entrance in Europe since 1995. Instead of receiving the beans in traditional jute bags, cocoa may now be shipped to a large extent in bulk in containers or directly in vessel holds. New handling technology, as well as innovative quality control procedures, were developed and implemented both at the loading and discharging points, leading to a highly efficient bulk transportation system.

In the countries of origin, there is a sustained trend to grind a larger part of their cocoa bean output into semi-finished products like cocoa liquor, butter, and powder.

Liberalization of the cocoa trade and industry in the countries of origin, notably those in West Africa, will continue, resulting in greater transparency of the cocoa trade, while various bean grading systems control the quality of the beans shipped to the consuming countries.

Major Cocoa Processing Countries (based on bean grind) (x 1,000 MT and %)	1980/1		1990/1		2000/1		2002/3		2003/4	
Netherlands	140	**9**	268	**12**	452	**15**	450	**15**	445	**14**
USA	186	**12**	268	**12**	456	**15**	410	**13**	410	**13**
Germany	180	**12**	294	**13**	227	**7**	193	**6**	225	**7**
Ivory Coast	60	**4**	118	**5**	285	**9**	300	**10**	320	**10**
United Kingdom	80	**5**	145	**6**	151	**5**	133	**4**	130	**4**
France	48	**3**	71	**3**	145	**5**	145	**5**	150	**5**
Malaysia	7	**-**	78	**3**	125	**4**	135	**4**	200	**6**
Former USSR	114	**7**	83	**4**	102	**3**	85	**3**	85	**3**
Indonesia	13	**1**	32	**1**	87	**3**	115	**4**	120	**4**
Others	730	**47**	974	**41**	1,033	**34**	1,088	**36**	1,121	**34**
Total world grindings	1,558		2,331		3,063		3,054		3,206	

Source: International Cocoa Organization

3. World demand for cocoa

Major cocoa processing countries

The world demand for cocoa beans, supported by relatively low cocoa prices, has steadily increased over recent decades as a direct result of increased world demand for chocolate and chocolate-flavored products. On the other hand, because cocoa is an agricultural product subject to the influences of nature, the supply fluctuates from year to year.

The bean grinding quantities do not indicate what is actually made from cocoa. For example, in the Netherlands, the world's largest cocoa bean processor, almost the entire quantity of beans is processed by the cocoa press industry into intermediate cocoa products rather than directly into chocolate.

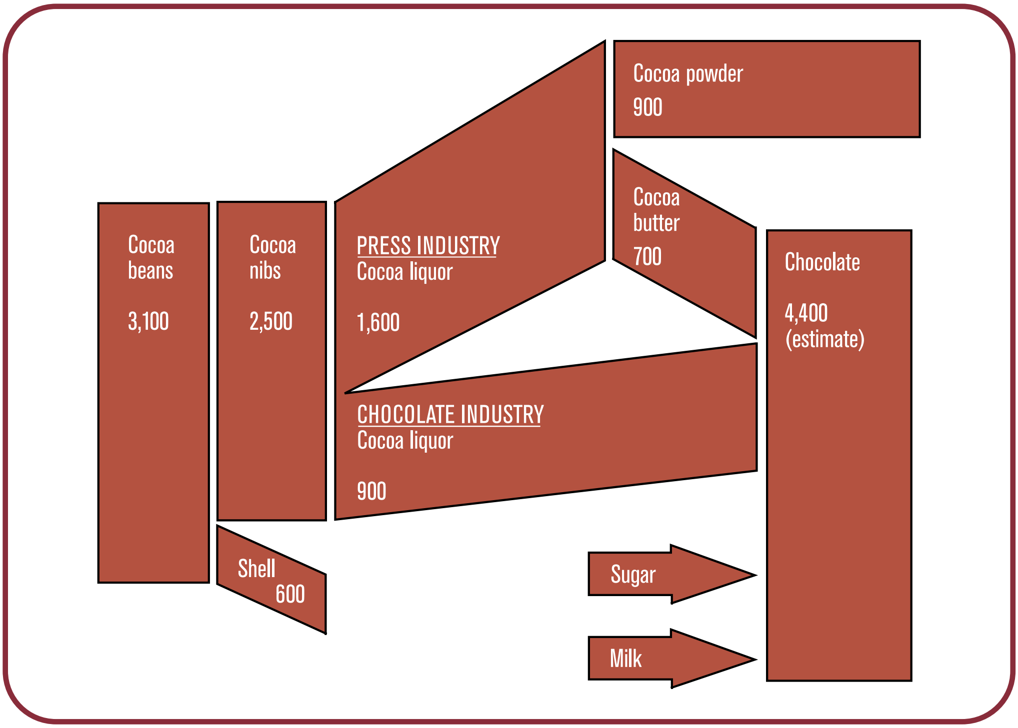
World's cocoa products flow

Three products—cocoa liquor (also called cocoa paste or cocoa mass), cocoa butter, and cocoa powder—are initially made from cocoa beans. Combining cocoa liquor and cocoa butter creates chocolate.

All beans, after having been cleaned, deshelled, roasted, and ground, are first processed into cocoa liquor. Any change in the supply position of one product has an effect on the availability of the others.

For example, in the case of an increase in chocolate consumption, a larger quantity of liquor and butter will be required to satisfy that increase in demand. Consequently, a larger volume of cocoa powder will become available to the market, which may not necessarily coincide with a simultaneous increase in the demand for cocoa powder.

DIAGRAM OF WORLD'S COCOA PRODUCTS FLOW



It is estimated that some 65% of the world grind is pressed into about 55% of cake (powder) and about 45% of butter. The other 35% is processed into cocoa liquor and almost entirely used directly for the manufacture of chocolate.

This interlocking relationship between liquor, butter, and powder not only has a direct influence on their physical supply and demand positions, but also on their relative pricing against the raw material: the cocoa bean.

This book basically deals with the functional aspects of the three intermediate products (cocoa liquor, cocoa butter, and cocoa powder) in their respective applications. To dwell extensively on issues of commercial or legislative considerations would go beyond its purpose.

Worth mentioning though, is the new Cocoa and Chocolate Directive of the European Union (2000/36/EC), allowing up to 5% of six specific vegetable fats other than cocoa butter to be used in chocolate; this substitution has a quantitative and adverse effect on the supply and demand positions of cocoa butter and cocoa powder.

The price of cocoa butter relative to the cocoa bean also remains under pressure.

Whatever the extent of the individual effects of these two aspects, the combination causes an imbalance in the product flow. As no cocoa butter can be made without obtaining a similar quantity of cocoa powder (and vice versa), an adjustment will then clearly have to occur. This can be quantitative (less butter produced leads to less powder available), by means of a price adjustment (a lower butter price must lead to a higher powder price), or through a combination thereof. Competitive market forces, as usual, will ultimately lead to the most practical solution.

Cocoa Processing 2

1. Introduction

Module 1: History and Supply of Cocoa gives a brief account as to where and how cocoa is grown, harvested, and shipped from the major cocoa growing areas. In this module, we deal with cocoa processing into the three products that are highlighted in this book: cocoa liquor, cocoa butter, and cocoa powder.

As the prime purpose of *The De Zaan® Cocoa Manual* is to be a practical guide to the user of cocoa products, this module focuses on those elements of the production process most likely to be relevant to users of such products. For them it is important to know what stages of the process are critical in view of the key features of the cocoa products that they buy as ingredients for application in their products.

Basically the principle of processing cocoa beans into cocoa products has not changed in the past 150 years. Today, the beans are still cleaned, deshelled, roasted, and sometimes alkalized, then ground into cocoa liquor, which is subsequently pressed into butter and cake. Finally, the cake is pulverized into powder. Of course, over time mechanical efficiency and the quality and risk management have vastly improved. Particularly the knowledge and expertise with regard to controlling the intrinsic potential of the raw material have expanded significantly in the past decades. Like many other food processing industries, cocoa product manufacturing has also become a highly automated, capital intensive, high-tech industry.

Before describing the basic features of cocoa processing, however, the role of the raw material in that process must first be discussed.

2. The raw material

Standards

Certainly the condition of the starting material, the cocoa bean, determines the ultimate characteristics of the end products. Close scrutiny of the raw material is essential, and several aspects have to be taken into account.

Cocoa is traded on terminal markets around the world, and standard contracts define a number of quality requirements. An average shipment of cocoa should comply with the following:

- Fermentation - adequately fermented (if fermented)
- Foreign matter - nil
- Waste - < 2%
- Moisture content - < 7.5%
- Smoky or foreign odors - absent
- Bean size uniformity - reasonably uniform
- Packing weight, bag quality, and marking - should be as defined (if applicable)

These standard characteristics, applied in the various grading systems in the countries of origin, are generally limited to those that can be observed by the eye or nose (insect infestation, mold, slatiness, violet beans, flat beans, off-flavors) and to characteristics that can be defined with simple equipment (number of beans per 100 g, moisture content).

For the cocoa processing industry, other characteristics have to be taken into account. A distinction must be made between those characteristics of significance to quantity or yield, like percentage of shell, moisture, and fat, and characteristics that are significant to the quality of the products finally obtained from the beans. For cocoa butter, for example, the free fatty acids and the triglyceride composition of the fat present in the bean are of great importance. For liquor and powder, the flavor and color potential are essential.

Once released from the pod, cocoa beans are subjected to a spontaneous fermentation process, causing a bacterial load to build up. Subsequent drying of the beans does not lead to a microbial improvement, and some bacteria are activated to form spores. The fermentation and drying processes usually take place in the open air on the farms.

During harvesting, post-harvesting, and collection, the beans, like any agricultural commodity, are subject to contamination with filth and foreign matter.

Selection

Whenever possible, bean parcels are selected and analyzed by ADM Cocoa prior to shipment from the country of origin. This is of particular importance in respect to bulk shipment of cocoa, which today is more and more the standard method of bean transportation.

The importance of bean selection with regard to the ultimately desired flavor profile of cocoa liquor, as well as the further development of color and flavor during the alkalization step in the manufacture of cocoa powder, is discussed in Module 4: Flavor and Flavor Development and in Module 5: Color and Color Development.

3. The quality factor

Definition

At ADM Cocoa, we have defined our purpose as: to supply cocoa products, consistent in their attributes, based on mutually defined functional specifications with accompanying services to the worldwide market at competitive prices. Because quality is subject to individual judgment, covers many disciplines, and involves many individuals of an organization, the disciplined management of quality standards is essential.

Customer requirements

ADM Cocoa concentrates on the specific wishes of its industrial customers. Our standards and internal control procedures are upgraded and adapted constantly, bearing in mind the given, unavoidable, natural variability of an agricultural commodity.

In the manufacturing world, the concept of quality has long been understood and defined as the way a physical product compared to some defined ideal. Close to the ideal, the quality of a product or service was considered good; below the ideal, then quality was poor. Quality tended to be restricted solely to physical attributes.

However, today the concept of quality has expanded to mean the way a product or service responds to the expectations of clients, not only in terms of product safety and attributes but also in such areas as delivery reliability, after-sales service, user support, and, of course, overall value. This extension of the meaning of quality has brought changes within food manufacturing organizations. Not only are all departments involved; every individual employee is involved as well. The concept of the quality factor today is how an organization like ADM Cocoa is able to respond in full to customer demands.

ADM Cocoa realizes that just like its own business, the businesses of its customers are constantly evolving. To maintain its position of leadership in the supply of cocoa ingredients, ADM Cocoa takes customers' current and anticipated requirements into account, whereby customers are:

- creating more new products with cocoa ingredients

- requesting more data on the properties and applications of products
- becoming more critical, asking for ever-stricter product consistency
- asking for more non-material added value, which means attention, service, and followup
- asking for support in rationalizing the number of cocoa products required for their growing businesses
- becoming oriented toward keeping low stocks, demanding speedy and flexible just in time deliveries
- trying to eliminate dependence on product inspection of incoming materials

In practice, this often means that identifying particular requirements, be it on product specifications or any other aspect, becomes a matter of close cooperation with the customer that ultimately leads to jointly defining these requirements.

4. The production process

Flow sheet

Cocoa processing at ADM Cocoa is described in the simplified diagram below. The various production steps and critical control points are then discussed.

Bean blending

On the basis of the analysis of the individual bean lots, an optimal blend is prepared. In this way, fluctuating characteristics can be reduced or evened out before the beans are further processed. An alternate approach is to process specific lots of beans and blend the resulting cocoa liquors.

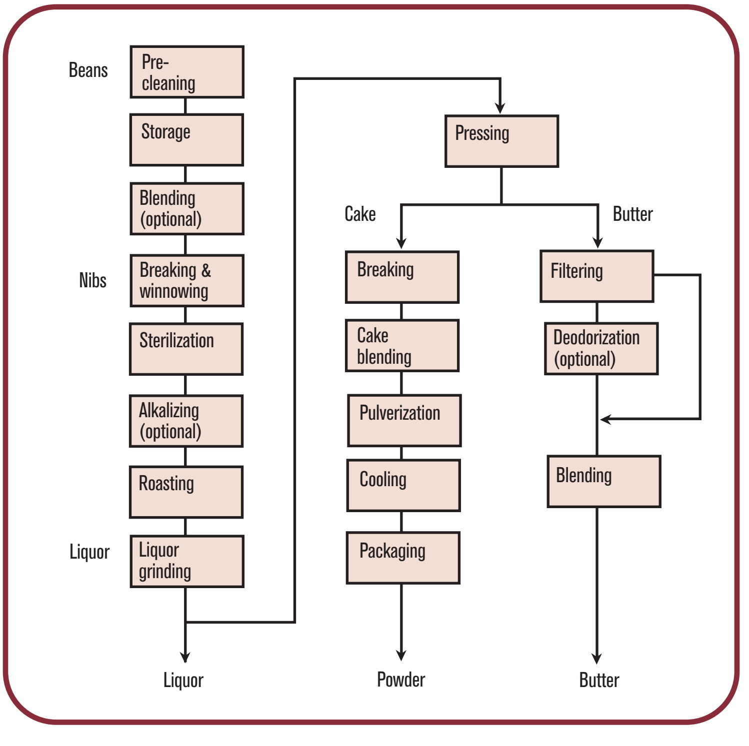
Cleaning, breaking, and winnowing

The actual production process starts with the following three steps: cleaning, breaking, and winnowing. Their objective is to obtain clean, broken, deshelled kernels. These kernels must be as uniform in size as possible in order to achieve constant quality.

First, the beans are sieved, and foreign matter such as bamboo, twigs, string, stones, and magnetic materials is removed. The clean beans are then broken to loosen the shells from the nibs.

The breaking process takes place in multiple steps to avoid an excess of fine particles. After

Production Flow Sheet



the breaking step, the product is sieved into a number of fractions to reach optimal separation during winnowing.

These fractions then go to the winnowing cabinets where the "lighter," broken shell is removed by a stream of air. The breaking and winnowing steps separate the essential ingredient of the cocoa bean, the kernel, most often described as the nib, from its shell. Strong magnets remove magnetic foreign matter from the nib. The nib may then be stored, awaiting further processing. The separated shell is often sold to agricultural mulch or fertilizer producers.

Sterilization and alkalization

The microbiologically contaminated nib is sterilized in a batch or a continuous process by wetting and heating with steam: the Total Plate Count (TPC) is normally reduced to less than 500 per gram, and all pathogenic bacteria are killed. After sterilization, the nib can be roasted directly (natural process) or can be alkalized first (Dutch process).

Alkalizing or Dutching consists of treating the cocoa nibs with an alkali solution such as potassium carbonate. It is practiced primarily to modify the color and flavor of cocoa powder or cocoa liquor; for the effects of alkalization on the formation of flavor and color of cocoa products, see Module 4 and Module 5.

Alkalization can be conducted at various points in the production process. Depending on the stage at which alkalization takes place, different results will be obtained. Nib alkalization is often preferred, as it combines optimal flavor and color development with minimal alkali usage.

Roasting

The roasting process has the objectives of reducing the water content and further developing flavor. Roasting is particularly important to the final flavor because the nib's flavor is formed from the precursors that developed during fermentation. (See Module 4: Flavor and Flavor Development). Roasting temperatures range from 95-145° C (200-295° F) depending on the process, equipment, type of nib processed, and the end product required.

Exposure of the nib to such temperatures during roasting causes an additional reduction in the number of microorganisms. A low level of those organisms after sterilization and roasting is essential for ultimately obtaining excellent food-grade products (cocoa powder, butter, and liquor) with stringent microbiological specifications.

ADM Cocoa does not carry out post-process sterilization by means of fumigation or irradiation at the end of the production process, as post-process sterilization often serves to hide poor hygienic process conditions and contamination with foreign matter, which is not eliminated by post-process sterilization. Further fumigation may leave toxic residues, and irradiation may cause an undesired change in the flavor (oxidation).

Nib grinding

The roasted nib is typically ground in a multi-stage process. During grinding, the broken kernels change from a solid to a fluid mass of cocoa particles suspended in cocoa butter. This is due to the high fat content of the bean: About half of the nib is fat. Grinding breaks up the cell structure of the cocoa nibs and releases the cocoa butter.

Cocoa liquor

After the last stage of the grinding process, the mass is passed through sieves and over strong magnets to remove any remaining coarse cocoa or metal particles. This finely ground fluid mass, the cocoa liquor, can either be stored in tanks to await pressing, or it can be shipped and used by chocolate manufacturers for further processing into chocolate.

Pressing

Cocoa butter constitutes about half the weight of the cocoa nib. This fat is partially removed from the cocoa liquor by means of hydraulic presses applying pressures as high as 450 kg/cm^2. Depending upon the pressing time and the setting of the press, the resulting cakes may have a fat content of 10 to 24%.

Cocoa cake

After pressing, the cakes are broken into kibbled cake. The pressing operation is microbiologically vulnerable, as this is the only part of the process when the product is not in a closed system and is thus exposed to the surroundings. Hygienic procedures are therefore of particular importance in the pressing department.

Kibbled cake is typically stored by fat content and degree of alkalization and may be blended before pulverization to obtain the desired type of cocoa powder. The cocoa butter is filtered and stored in tanks.

Cocoa powder

The powder grinding lines, usually hammer-and-disc or pin mills, pulverize cocoa cake particles into the defined fineness levels. After pulverization, the powder is cooled so that the fat of the cocoa powder crystallizes into its stable form. This prevents any discoloring (fat bloom) and lump forming in the bags later, a phenomenon that is caused by insufficient crystallization of the fat at the moment of filling. Next, the free-flowing powder is passed through sieves and over magnets prior to packing in paper bags or in bulk containers.

Cocoa butter

The cocoa butter from the presses is filtered and stored. Upon request, the butter can be partly or wholly deodorized. Delivery of the various types of cocoa butter can be either in liquid form or in solid form (plastic-lined cardboard boxes).

Storage and packaging of cocoa products are discussed further in Modules 7-9 for Cocoa Liquor, Cocoa Butter, and Cocoa Powder.

5. Process control

Fluctuating bean characteristics

Cocoa is a natural product with considerable quality variations from year to year, from country to country, and from lot to lot. Sometimes certain types of cocoa may not be available at all. As customers expect to receive a consistent final product, fluctuation of quality characteristics of our end-products has to be eliminated or reduced. So the bean mix and the processing conditions can be adapted based on experience, technological expertise, and knowledge of the properties of the raw material.

Therefore, the critical points in processing of cocoa beans into wholesome, safe, and consistent cocoa ingredients are:

- the quality of the cocoa beans; they should be at least well-fermented and clean.
- the production process; the process must be carried out according to the specified norms, with strict hygienic standards.

Assessing the quality of the cocoa beans has been described on page 21 under "The raw material." Further in the process, the roasting and alkalization stages can be adapted to the specific characteristics of the particular cocoa bean mix. In Module 7 and Module 9, the influence of these stages of the production process with respect to the desired flavor and color development of cocoa liquor and cocoa powder is extensively discussed.

Variations, for example in color, flavor, and pH of cocoa powder, can be reduced. Blending of different cocoa cakes or powders may control the characteristics of the resultant cocoa powder. In this way, ADM Cocoa is able to supply each type of cocoa powder within the specifications, every time.

Principles of quality assurance

Part of ADM Cocoa's quality assurance is based on supplying the necessary information regarding the production process and the way in which quality control is achieved.

One of the most important objectives of ADM Cocoa is to transform the naturally fermented cocoa beans into wholesome cocoa products with suitable bacteriological specifications. To this end, bean quality is constantly being assessed and controlled.

Good Manufacturing Practices (GMP)

Although the influence of the raw cocoa beans as a source of contamination is greatly diminished by the procedure described above, it is essential to prevent contamination after the roasting step. For this reason, processing in accordance with the principles of Good Manufacturing Practices (GMP) is indispensable.

These rules are of a preventative nature: They rely not so much on the checking of the finished product but concentrate efforts on the production process itself. They call for careful processing and use of specific checks throughout the production process. This principle was introduced by the Food and Drug Administration in the USA and adopted by the Codex (Code of Practice from 1997) and by the European Union (Directive 93/43/EEG).

Hazard Analysis and Critical Control Points (HACCP)

Later, the concept of Hazard Analysis and Critical Control Points (HACCP) was developed, a comprehensive, step-by-step quality assurance program. This goes beyond the hygienic aspects of quality assurance and is a step-by-step outline for the entire production process. Assessments of hazards associated with raw materials, processing, and transport are made.

At ADM Cocoa, the microbiological, chemical, and physical influences of the processing are considered in relation to food safety and quality. After hazard assessment, the Critical Control Points (CCPs) required to control the identified hazards are determined. For each CCP, critical limits, procedures for monitoring, and corrective actions in case of deviations are established and continuously monitored.

Within HACCP special attention is given to prevention of contamination with *Salmonella* after the roasting process. The International Confectionery Association (ICA) offers the industry a code of hygienic practice based on HACCP for the prevention of *Salmonella* contamination in cocoa, chocolate, and confectionery products.

Production coding and sampling

ADM Cocoa's production is planned according to deliveries defined as a quantity of product that possesses a high degree of homogeneity because it is made at the same production unit without significant changes in process conditions and raw material composition. Such a delivery may consist of several homogeneous batches.

Each delivery is given a unique lot identification code that is printed on the individual packing or, in the case of liquid, tank car shipments, indicated on the accompanying documents. Traceability for packaging (bag or carton) is obtained with a production code.

When the food manufacturer wishes to control incoming ingredients, e.g. cocoa products, it is important to ensure that representative samples are taken and examined. It is essential that the manufacturer of the ingredient is able to demonstrate the homogeneity of the delivered quantity. With this in mind, ADM Cocoa welcomes its customers to audit its production facilities in order to assess the confidence that can be placed in the adopted control systems, procedures, standards, and norms.

If the homogeneity of incoming shipments can be assured, then a somewhat simplified random check can be used on the incoming lots. See also the sampling procedure described in Module 3: Methods of Analysis.

Reference samples

Should a customer wish to check, for example, the color and flavor of a powder, a reference sample of the type in question is needed; delivery samples can be checked against such reference samples. Such samples should be packed in a well-sealed container and kept cool and dry. They should also be replaced twice a year. To this end, the expiration date is shown on the reference sample label.

Please note

The preceding information has been given for use as a basis on which customers can make important decisions with regard to the extent cocoa ingredients are examined before use. Based on the delivery history, audits, and additional information from ADM Cocoa staff, the customer may make simplifications in checking deliveries of ADM Cocoa products.

Methods of Analysis 3

1. Introduction

Good methods of analysis are not only essential for upholding the quality specifications and customer requirements but also for process control purposes. ADM Cocoa often uses classic analytical methodology, such as fat content by extraction, moisture content by oven drying, acidity (free fatty acid) by titration, etc. These methods are by definition related to the specification parameters. However, many modern instrumental and automated techniques, like spectroscopy, chromatography, and densitometry, are used for obtaining results faster and for additional information on the products.

Always, but especially for specifications and requirements, it is necessary to define and describe the methods of analysis clearly and in detail; this assures consensus on the results and no analytical bias caused by using different methods. In addition to our own methodology, we rely on the methods of international analytical and standard organizations like the International Organization for Standardization (ISO), the International Union of Pure and Applied Chemistry (IUPAC), and the Association of Official Analytical Chemists (AOAC). Analytical and microbiological experts from the cocoa and chocolate industries, organized in the International Confectionery Association (ICA), developed and approved about 50 analytical methods specifically for cocoa, cocoa products, and chocolate. These methods can be ordered at the ICA-Secretariat, Rue Defacqz 1, B-1050 Brussels, Belgium, or at www.caobisco.com under ICA-publications.

ADM Cocoa uses the official analytical methods as well as simplified, faster, instrumental methods. The latter always have to be calibrated and checked against the often more time-consuming official methods.

The quality of the sampling is often more important for a reliable result than the analysis itself; however accuracy and precision of analytical methods for process control and finished goods analysis have to be known and evaluated regularly. Analytical data are never absolute but have a "natural" uncertainty or variation. The analyst has to check and evaluate each analysis and each result using his experience and knowledge. Are the results as expected, or is reassurance (reanalysis) necessary?

Good Laboratory Practices (GLP) are essential for validation of data. On a regular basis, analysis of control or check samples must be carried out to evaluate the performance of the methods and the analysis.

In this Module the analytical methods advised by ADM Cocoa for the analysis of specification parameters of cocoa liquor, cocoa powder, and cocoa butter are described; a trained analyst should be able to perform the analyses and obtain reliable, accurate results.

References are given to official methods (ISO, AOAC, IUPAC, ICA); many analytical textbooks also have chapters on the analysis of cocoa products.

2. Sampling procedure

Sampling—general

Correct sampling procedures are essential for obtaining good and reliable analytical results. The sampling and sampling conditions may depend on the type of analysis to be carried out, but the sample always has to be representative for the product or lot. Non-sterile conditions are sufficient for such analyses as fat or moisture content, however sterile conditions are essential when the samples have to be analyzed microbiologically.

In processes the sampling is preferably done automatically and in line by taking (and combining) portions of the product stream at regular intervals with automatic samplers (available for liquids as well as solids). In general the sampling procedure can be divided into two steps:

- primary sampling of the production lot and preparation of the "bulk" sample
- secondary sampling or preparation of the laboratory or test sample from the "bulk" sample

Samples should ideally be packed in moisture- and air-tight containers/bags of suitable size and shape, preferably be stored in a cool and dark place, and be labeled with the product and sample information. This will protect the product from any change in the relevant parameters for as long as the sample is needed for analysis or as evidence (counter samples). This includes no increase in moisture (cocoa powder is very hygroscopic), no change in color (by temperature variation or effect of light), no effect on flavor (too high temperature and influence of air and light), etc.

Deliveries of ADM Cocoa products can be in liquid (tank containers) and solid (bags or cartons) forms. Liquid deliveries should preferably be sampled at regular intervals during unloading of the tank. The "bulk" sample can be sub-sampled to give the laboratory or test sample. The solids in liquid cocoa liquor may partly sediment, so when the delivery is not well stirred many samples have to be taken and recombined (e.g. for analysis of fat content and fineness).

Solid deliveries can be sampled by taking primary samples from a number of pallets with cartons or bags. This process is intended to assure that all units on a pallet (with the same production code) represent the same homogeneous product. The size of a primary sample has to be at least 50 g to be representative for the pallet and to allow the necessary analyses. By comparing primary samples of a delivery, the customer can evaluate its consistency.

Sampling—bags or FIBCs

For cocoa powder, the following procedure is advised, based on one sample per pallet or flexible intermediate bulk containers.

Check the dry (external) color immediately. Only a limited color variation both from sample to sample as well as between samples and reference is allowed.

Next, other parameters can be determined, for instance, fat content, moisture content, or pH. Microbiological analysis is generally carried out separately.

Primary sampling of a bag of cocoa powder from a pallet is as follows:

- Make an inverted U-shaped cut in the shrink-wrap or foil wrap.
- Make a similar but smaller cut in the bag, such that the bag can easily be resealed with tape.
- Take a sample of 50-250 g with a clean sampling spoon (penetrating 5-10 cm into the bag).
- Place the sample in a plastic bag or sterile container. Close carefully and label with product type, lot number, production code, sampling date, and name of sampler.
- Close the bag and then the wrap with adhesive tape.
- Primary sampling of the flexible intermediate bulk container is done by opening the filling tube, taking a sample of 5-10 cm under the surface and subsequently closing the filling tube.

Samples for microbiological analysis must be taken aseptically: The bag surface, the knife used to cut open the bag, and the sampling spoon must first be cleaned and disinfected with 70% alcohol on cotton wool.

Secondary sampling depends on customer requirements:

- Composite samples can be prepared by taking and blending identical quantities of the primary samples.
- Single primary samples may be subsampled and analyzed for specific parameters.

3. Cocoa liquor/ cocoa powder

Flavor evaluation

DEFINITION

The flavor of cocoa liquor and cocoa powder is evaluated by trained panel members under standard conditions, using a standard sample as a reference.

EQUIPMENT/MATERIALS

- sugar, granulated and powdered
- tap water, 55° C (131° F)
- beakers, glass, 400 ml
- disposable cups, approx. 30 ml and 150 ml, with lid, (odor free)
- stirrers, measuring cylinders, thermometer (0°-100°C/32-212° F)
- hot plates
- balance, 0.1 g accuracy

GENERAL TEST CONDITIONS

For effective flavor evaluation, a trained panel of five to eight members is necessary, and test conditions must be standardized.

TASTE PANEL ROOM

The test conditions require a special and separate taste panel room for concentrated, undisturbed, and unobserved testing under comfortable sitting conditions with good lighting and temperature. Smells, sounds, and disturbances should be excluded. It must be possible to spit out the sample and rinse the mouth with warm tap water. Clear written instructions are supplied to each panel member. At each sample booth, general test guidelines should be present.

PANEL MEMBERS

Panel members are selected and trained to discriminate between basic tastes and essential cocoa flavors and off-flavors. In addition, panel member performance is evaluated regularly by flavor analysis supervisors.

The following basic rules apply to taste panel members:

- no tasting when feeling unwell
- no smoking, eating, or drinking for half an hour before tasting
- no tasting on an empty stomach

PROCEDURE

Sample preparation

1. Weigh 21 g of liquid cocoa liquor or 12 g of the cocoa powder to be tested and 15 g of sugar into a 400 ml glass beaker.
2. Add 300 ml of tap water at 55° C (131° F) and stir to a homogeneous suspension.
3. Pour about 50 ml of the suspension into each of the six cups (150 ml) and close with a lid.
4. Repeat these steps with the reference sample (see remarks).
5. Place the samples on hot plates to keep the contents at 50° C (122° F).

TESTING TECHNIQUE

Each panel member evaluates a sample against the reference, separately judging different aspects of odor and flavor.

1. Before starting an evaluation: The mouth is rinsed with lukewarm water.
2. The odor of the reference is judged first, then the sample, and again the reference.
3. The nature and intensity of any differences perceived are recorded on the test form supplied.
4. The flavor of the reference is tested, then the sample, and again the reference, rinsing the mouth with lukewarm water each time before tasting. The sample is then spit out, after swirling in the mouth for 5-10 seconds to evaluate and memorize the different flavor aspects.
5. The nature and intensity of any differences perceived are noted on the test form.

RESULTS

The panel members' evaluation forms are collected; the members are interviewed further if necessary, and the forms are interpreted to obtain an overall impression of the differences against the reference. The overall impression is reported, if possible, in a numerical way for purposes of historical comparison.

REMARKS

Reference samples should be carefully selected, kept under cool (15° C/59° F), dark, and dry (relative humidity below 50%) storage conditions and not be more than six months old.

REFERENCE

ICA method 6/1963 (formerly 2/1963).

Determination of fat content

DEFINITION

The fat content of cocoa liquor and cocoa powder according to the Soxhlet extraction method is the percentage by mass of fat and other components extractable with petroleum ether (p.e.).

EQUIPMENT/MATERIALS

- Soxhlet extractors, siphon capacity about 100 ml, NS 29 at the bottom and NS 45 at the top
- condensors, Dimroth with NS 45 and Call$_{2-}$ tube
- Erlenmeyer flasks, 250 ml with NS 29
- hot plate for flasks (fire-safe)
- desiccator with desiccant
- vacuum drying oven set at 80° C/176° F
- defatted glass beads, extraction thimbles, round filters (Ø 15 cm) cotton wool and boiling stones (see Remark 1)
- residue-free petroleum ether (p.e.), bp. 40°-60° C/104-140° F (see Remark 1)
- analytical balance, 0.1 mg accuracy
- sand, acid-washed at 60° C (140° F)
- glass stirring rod, length 10 cm

PROCEDURE

1. Place a dry and clean Erlenmeyer flask with a few boiling stones for 30 minutes in the drying oven.
2. Let the flask cool in the desiccator for 30 minutes.
3. Weigh the tare weight of the flask to the nearest 0.1 mg (M_1 in g).
4. Weigh approx. 5 g of cocoa powder to the nearest 1 mg (M_2 in g), and transfer the powder into an extraction thimble weighted down with glass beads in which a round filter has been folded to form a bag inside the thimble wall (see Remark 2), or
5. Bring about 10 g of sand into an extraction thimble with a stirring rod; weigh approx. 3 g of well-mixed liquid cocoa liquor to the nearest mg (M_2 in g) into the thimble, and mix the liquor and sand homogeneously with the stirring rod.
6. Fill the thimble with a solid wad of cotton wool and place the thimble in the Soxhlet extractor. Add about 50 ml of p.e. to the tared Erlenmeyer flask, and connect this flask to the extractor.
7. Add slowly more p.e. (about 100 ml) to the extractor until the solvent starts to siphon (see Remark 3).
8. Connect the condenser to the extractor, and place the assembly on the heating plate.
9. Extract the powder/liquor plus sand in the thimble for at least eight hours with 10-15 siphonings per hour (see Remark 4).
10. Disconnect the Erlenmeyer flask and distill off the p.e.
11. Dry the flask with the residue under vacuum in the drying oven at 80° C (176° F), for the first 15 minutes at 400 mm Hg, followed by one hour at less than 10 mm Hg.
12. Cool the flask in the desiccator for 30 minutes and weigh the flask.
13. Repeat the drying, cooling, and weighing until the difference between two successive weighings is less than 1 mg (M_3 in g).

RESULTS

1. Calculation

The fat content of the cocoa liquor/ powder sample is:

$$\frac{M_3 - M_1}{M_2} \times 100\% \ (m/m)$$

Where:
M_1 = mass in g of Erlenmeyer flask (tare)
M_2 = mass in g of the cocoa liquor/ powder sample
M_3 = mass in g of the Erlenmeyer flask with residue

The result should be expressed to two decimal places.

2. Repeatability
The difference between the results of two independent determinations should not exceed 2% of the fat content (0.2% with 10% fat, 0.4% with 22% fat, and 1.1% with 55% fat).

REMARKS

1. Materials and solvent have to be residue free; a complete blank extraction without cocoa liquor/powder should be performed regularly, and the residue should be less than 2.5 mg (0.05% fat in the sample); when the residue is larger than 2.5 mg, the cause of this increase should be investigated. The p.e. should have an evaporation residue of less than 1 mg per 150 ml.
2. The round filter folded to the shape of a bag around a clean rod permits the repeated use of the extraction thimble. It also prevents very small particles from passing through the thimble into the flask and adding to the residue.
3. During extraction the quantity of solvent in the flask should always be at least 50 ml.
4. For the complete extraction of the fat, at least 80 siphonings are needed, each of them effectively emptying the extractor. Completeness of the extraction can be checked by an additional extraction with fresh solvent in a new flask; after two to three hours or 20-40 siphonings the residue after evaporation and drying should be less than 1 mg.

REFERENCE

ICA method 37/1990 (formerly 115/1990).

Determination of pH

DEFINITION

The pH of cocoa liquor and cocoa powder is the pH (negative logarithm of the hydrogen ion concentration) of a suspension of these products in water, prepared and measured according to this method.

EQUIPMENT/MATERIALS

- pH meters with combined glass electrodes readable to 0.01 pH unit
- thermometer, 0°-100°C (32-212° F) with 1° C graduation
- buffer solutions of pH 4.00, 7.00, and 9.00
- distilled or demineralized water, carbon dioxide free on hot plate
- glass beakers (150 ml) and measuring cylinder (100 ml)
- balance, 0.01 g accuracy

PROCEDURE

1. Calibrate one pH meter at 20° C (68° F) using buffers of pH 4.00 and 7.00 and another pH meter at 20° C (68° F) using buffers of pH 7.00 and 9.00.
2. Weigh 10.00 g cocoa powder to the nearest 0.01 g into a 150 ml glass beaker.
3. Slowly add, while stirring, 90 ml of boiling hot distilled (or demineralized) water with a measuring cylinder.
4. Leave to cool to 20°-25° C (68-77° F), e.g. in a cold water bath, stirring occasionally.
5. Measure the pH with both pH meters, and use the pH reading nearest to the buffer range.

RESULTS

The results should be expressed to two decimal places. The difference between the results of two independent determinations should not exceed 0.1 pH unit.

REFERENCE

ICA method 15/1972 (formerly 9/1972).

Determination of sieve residue

DEFINITION

1. The "wet" sieve residue (or "coarseness") of cocoa liquor and cocoa powder is defined as the mass percentage of the product that does not pass a plate sieve with apertures of 75µ x 75µ according to this method.

2. The fineness of cocoa liquor and cocoa powder is expressed as 100% minus the % sieve residue (the fraction remaining on the sieve).

EQUIPMENT/MATERIALS

- plate sieves with apertures of 75µ x 75µ ± 2µ (200 mesh), diameter 6 cm, height 7 cm, open area 25-40% (see Remark 1)
- drying oven, well ventilated, set at 103°-105° C (217-221° F)
- desiccator with desiccant
- glass beakers (400 ml), glass stirring rod, mechanical stirrer
- watch glasses, diameter about 8 cm
- squeeze bottles of 500 ml (for hot water) and 250 ml (for acetone)
- graduated cylinders of 25 ml and 250 ml
- analytical balance (accuracy 0.1 mg) and weighing balance (accuracy 0.01 g)
- hot water 75° C (167° F) ±5° and acetone (water free)
- detergent (surface active agent—concentrated)

PROCEDURE

1. Weigh a dried, clean sieve (75µ) on a dry watch glass to the nearest 0.1 mg (M_1 in g).
2. Weigh approx. 10 g of well-mixed cocoa liquor or cocoa powder to the nearest 0.1 g in a glass beaker (M_2 in g).
3. Add with cocoa liquor 2 g of detergent or with cocoa powder 1 g of detergent.
4. Add 20 ml hot water (see Remark 2), stir the mixture with a stirring rod until all lumps have disappeared.
5. Add 280 ml of hot water and stir mechanically for 2 minutes without producing a vortex and with the propeller near the bottom of the beaker.
6. Pour the hot suspension slowly through the sieve, meanwhile moving and swirling the sieve in a circular manner over the sink (see Remark 3).
7. Rinse the beaker, stirrer, and rod into the sieve, and rinse the sieve with up to 1.5 l of hot water until no more particles pass the sieve.
8. Rinse the sieve and residue with 15-25 ml of acetone to remove water and fat residues.
9. Place the sieve on the watch glass in the oven for 45 minutes (see Remark 4), cool the sieve and glass in the desiccator for 45 minutes.
10. Weigh the sieve and residue and watch glass to the nearest 0.1 mg (M_3 in g).

RESULTS

1. Calculation

The "wet" sieve residue (or "coarseness") of the cocoa liquor or the cocoa powder sample is:

$$\frac{M_3-M_2}{M_1} \times 100\% \text{ (m/m)}$$

Where:
M_1= mass in g of the dried sieve + watch glass
M_2= mass in g of the sample
M_3= mass in g of the dried sieve + residue + watch glass
The result should be expressed to two decimal places.

The fineness percentage is:

$$\{1- \underline{(M_3-M_2)}\} \times 100\% \text{ (m/m)}$$

M_1

2. Repeatability

The difference between the results of two independent determinations should not exceed 0.04% on a 75µ sieve.

REMARKS

1. Plate sieves are very delicate; they may not be touched, not even with a brush. Dirty sieves can be cleaned with a detergent solution in an ultrasonic bath. Sieves should be inspected regularly for damage with a magnifying glass.
2. The detergent dissolves the fat of the cocoa liquor or the cocoa powder.
3. When the sieve becomes clogged, tap the side of the sieve gently.
4. The watch glass collects cocoa particles passing through the sieve on drying, cooling, and weighing.

REFERENCES

ICA method 38/1990 (formerly 116/1990).

Determination of moisture content

DEFINITION

The moisture content of cocoa liquor or cocoa powder is the percentage of mass lost drying for 4 hours at 105° C (221° F).

EQUIPMENT/MATERIALS

- drying oven, well ventilated, set at 103°-105° C (217-221° F)
- desiccator with desiccant
- glass weighing flask for cocoa powder, always with ground glass stopper, Ø 50 mm (see Remark 1)
- alumina weighing dish with lid for cocoa liquor, Ø 70 mm
- glass stirring rod, length 10 cm
- sand, ashed at 600° C (1112° F)
- ethanol p.a.
- analytical balance, accuracy 1 mg

PROCEDURE

1. Dry a clean and empty weighing dish or flask with stopper side by side in the drying oven for 60 minutes at 103°-105° C (217-221° F)
2. Let the dish/flask cool in the desiccator for 30 minutes.
3. Weigh the tare weight of the dish/flask to the nearest 1 mg (M_1 in g).
4. Weigh to the nearest 1 mg approx. 5 g of well-mixed cocoa powder into the tared flask (M_2 in g) (see Remark 2), or
5. Add approx. 20 g of sand into the alumina dish with lid and weigh the tare weight of the dish plus sand to the nearest 1 mg (M_1 in g).
6. Weigh to the nearest 1 mg, 5 g of well-mixed liquid cocoa liquor into the tared dish (M_2 in g); saturate the sand with ethanol, and mix the sand homogeneously with the liquor using a stirring rod.
7. Dry the dish/flask with stopper beside it in the oven for four hours at 103°-105° C (217-221° F). Then remove and place the stopper on the dish/flask (see Remark 3).
8. Let cool and weigh as described above (M_3 in g).

RESULTS

1. Calculation

The moisture content of the sample is:

$$\frac{M_2-M_3}{M_2-M_1} \text{ X } 100\% \text{ (m/m)}$$

Where:

M_1 = mass in g of the empty stoppered dish/flask (tare)

M_2 = mass in g of the stoppered dish/flask with sample

M_3 = mass in g of the stoppered dish/flask with dried sample

The result should be expressed to one decimal place.

2. Repeatability

The difference between the results of two independent determinations should not exceed 0.2%.

REMARKS

1. The flask should always be weighed with the stopper (on or beside it) and only after conditioning in the desiccator. With more than four flasks, the cooling time should be 45 minutes instead of 30 minutes. The correct weighing practices have to be adhered to.
2. Cocoa powder is very hygroscopic; the lab sample has to be stored in an air- and moisture-tight container, and the sample transfer has to be carried out rapidly and carefully.
3. Drying should last exactly four hours, and the oven should not be opened during this period.

REFERENCE

ICA method 1/1952 (formerly 3/1952).

4. COCOA POWDER

Visual color evaluation

DEFINITION

The color of cocoa powder can be evaluated as such (the dry or extrinsic color) or as suspension in milk or water (the intrinsic color) against reference and other samples, using the methods below.

EQUIPMENT/MATERIALS

- beakers, 100 ml and 150 ml, glass
- spoon
- stirring rod, length approx. 15 cm
- grease-proof paper sheets, 20 x 12 cm
- pasteurized milk
- color evaluation flasks of colorless, clear glass with flat sides and screw tops, 45 ml
- color evaluation cabinet with standard light, with daylight lamp of 6500° K (see Remark 3)
- hot plates
- balance, 0.001 g accuracy

PROCEDURE

1. Dry (extrinsic) color

1. Place approx. 0.5 g of the cocoa powder on the table surface of the cabinet.
2. Place one or more reference cocoa powder(s) in a similar way beside or around the sample to be evaluated.
3. Put a grease-proof paper over the samples and flatten them by gently stroking the sheet with a flat hand until they touch each other.
4. Remove the sheet carefully.
5. Evaluate the color difference(s) with two or more persons (see Remarks 1 and 2).

2. Color (intrinsic) in milk

1. Weigh 1.20 g of cocoa powder to be evaluated in a 100 ml beaker to the nearest 0.01 g.
2. Add 5 ml of pasteurized milk and mix until a homogeneous paste is achieved.
3. Add 45 ml of milk, heated to about 60° C (140° F).
4. Stir thoroughly and fill a color evaluation flask with the suspension.
5. Repeat the above steps twice using the reference cocoa powder, filling two flasks with the suspension.
6. Close the three flasks properly and shake them prior to the evaluation (see Remark 4).
7. Place the suspension to be evaluated between the reference suspensions.
8. Evaluate the color under standard light conditions in the cabinet with two or more persons (see Remarks 1 and 2).

3. Color (intrinsic) in water

1. Weigh 1.20 g of the cocoa powder to be evaluated in a 150 ml beaker to the nearest 0.01 g.

2. Add 100 ml of water and bring it to a boil on a hot plate.
3. Allow to boil for a moment, stirring the suspension with a stirring rod.
4. Fill one color evaluation flask with the suspension.
5. Repeat the above steps twice, using the reference cocoa powder, and fill two flasks with the suspension.
6. Close the three flasks properly and shake them prior to the evaluation.
7. Place the suspension to be evaluated between the reference suspensions.
8. Evaluate the color under standard light conditions in the cabinet with two or more persons (see Remarks 1 and 2).

REMARKS

1. The visual evaluation of the color should be carried out by people who have successfully passed an eye test (e.g. the S. Ishihara test).
2. There should be unanimity about the terminology used for the evaluation of the colors: expressions such as "too light," "too dark," "redder," "greyer," etc. should have the same meaning for all evaluators.
3. The lamps of the color evaluation cabinet should be replaced regularly to ensure the consistency of the standard light conditions.
4. To prevent the rapid sedimentation of the suspension, the following modifications can be used:
   - Weigh 1.20 g of cocoa powder, 20 g of sugar, and 0.035 g of the gelling agent carrageenan E407 in a 100 ml beaker.
   - Add 10 ml of pasteurized milk and stir the contents to a paste with a stirring rod.
   - Add 40 ml of pasteurized milk heated to approx. 60° C (140° F).
   - Proceed as described in 2. Color (intrinsic) in milk.

Instrumental color evaluation

DEFINITION

The instrumental color evaluation of cocoa powder as such or as a slurry in water is expressed in L*-, C*-, and h-values measured with a color meter.

The L*-, a*-, and b*-values are calculated from the CIE X-, Y-, and Z-values using the CIE 1976 equations. C*- and h-values are calculated from the a*- and b*-values according to the following:

$$C^* = (a^{*2}+b^{*2})$$

$$h = arcig(b^*/a^*)$$

L* value – the lightness/darkness coordinate; a low value indicates a dark color, a high value indicates a light color

a* value – the red/green coordinate, with +a* indicating red and -a* indicating green

b* value – the yellow/blue coordinate, with +b* indicating yellow and -b* indicating blue

C* value – the chroma coordinate, indicating brightness; a higher value indicates a brighter color

h value – the hue angle; a lower value indicates more redness, a higher value indicates more yellowness

EQUIPMENT/MATERIALS

- Datacolor Spectraflash SF 450 X color spectrophotometer (or equivalent)
  - measuring geometrics d/8 - specular excluded
  - illuminant D65
  - observer angle 10°
- quartz cuvette
- tubing pump system
- magnetic stirrer
- beakers, 400 ml, glass
- balance, 0.1 g accuracy
- demineralized water

PROCEDURE

1. Dry (extrinsic) color

1. Fill a cuvette 3/4 full with the cocoa powder sample and tamp the powder down carefully.
2. Then add cocoa powder until it is heaped above the rim.
3. Level the powder evenly by using the edge of a spatula with tapping movements.
4. Remove the surplus powder carefully with the spatula to produce a flat surface in line with the rim (see Remarks).
5. Place the cuvette carefully against the illuminated window of the calibrated meter.
6. Read and record the L*-, C*-, and h-values.
7. Compare the values found with those of a standard sample.

2. Intrinsic color measurement

1. Weigh 7.5 ± 0.1 g of cocoa powder in a 400 ml beaker.
2. Add 100 ml demineralized water of 50° C (122° F) and stir with a stirring rod until a smooth slurry is obtained without lumps.
3. Continue stirring using a magnetic stirrer for 10 minutes.
4. Add 50 ml demineralized water at room temperature.
5. Continue stirring for at least 1 minute.
6. Pump the suspension through the quartz flow cuvette, while stirring.
7. Read and record the L*-, C*-, and h-values with a calibrated color spectrophotometer.

REMARKS

The flow rate during pumping of the water/cocoa powder suspension should be so that settlement of cocoa particles is prevented. If the cocoa powder is lumpy, the surface will be irregular when evaluating the dry color. It is then advisable to sieve the cocoa powder through a 500µ sieve and carefully break down the lumps. Mix the powder thoroughly.

REFERENCES

1. Schulze: "Farbelehre und Farbemessung," 1966 (Springer-Verlag, Berlin).
2. Clydesdale: "The measurement of color," Food Technology 23 (1969), 16-22.
3. CIE, 1978: "International Commission of Illumination. Recommendations on uniform colour spaces, colour difference equations, psychometric colour terms." (Bureau Central de la CIE, Paris).
4. Instruction manual: Datacolor Spectraflash SF 450 X Colour spectrophotometer.
5. DataFacts Technical bulletin nr. 004-96 from Datacolor International.

5. Cocoa butter

Refractive index

DEFINITION

This method describes the determination of the refractive index of cocoa butter. The refractive index is expressed as nD (40° C/104° F).

EQUIPMENT/MATERIALS

- water bath, thermostatically controlled at 40° C (104° F) ± 0.5º and with a circulation pump
- refractometer, e.g. Abbe type, connected to the water bath
- light source (sodium vapor light)

PROCEDURE

1. Bring the prisms of the refractometer to 40º C (104° F) by connecting the refractometer to a water bath.
2. Place a drop of clear, filtered cocoa butter on the surface of the prisms and close the prisms.
3. Wait a few seconds to allow the butter to obtain the temperature of the prisms.
4. Adjust the refractometer in such a way that a clear contrast line can be read where it crosses the scale.
5. Read the refractometer at the nearest 0.0001.

REMARKS

The prisms should be handled with care.

REFERENCES

1. IUPAC Standard Methods of the Analysis of Oils, Fats and Derivatives, 6th Edition, Method 2.102.
2. ISO 6320:1995 - Animal and Vegetable Fats and Oils - Determination of Refractive Index.

Melting point

DEFINITION

This method describes the determination of the melting point of cocoa butter. The melting point is expressed as Slip Point (the butter starts to melt) and/or as Clear Point (the butter is fully liquid/molten).

EQUIPMENT/MATERIALS

- magnetic stirrer with hot plate
- stirring bars
- exterior water bath
- inner water bath
- plate with two holes: one for fixation of the inner water bath
- movable rubber ring for adjusting the inner water bath
- rubber plate to cover the inner bath
- thermometer, range 0°-50° C (32-122° F), graduation of 0.1º
- U-tubes for melting point according to H. Fincke
- thermometer for exterior water bath, graduation of 0.5º
- water baths thermostatically controlled at 25° C (77° F) and 32°-33° C (90-91° F)

PROCEDURE

1. Pretreatment of cocoa butter

1. Heat >50 g of cocoa butter to 50°-60º C (122-140° F), and filter through a fluted filter, Whatman no. 3, Ø 15 cm.
2. Pour 50 g of this filtered butter into a glass beaker of 100 ml and immerse the glass beaker in a water bath, which is thermostatically controlled at 25º C (77° F).
3. Cool the butter while constantly stirring until it assumes a pasty consistency.
4. Prevent the inclusion of air bubbles.
5. Subsequently, immerse the glass beaker into a water bath that is thermostatically controlled at 32°-33° C (90-91° F). Continue to stir until the

butter has come to the same temperature. This takes about 30 minutes.
6. Pour the cocoa butter into a metal tray and allow to stand for at least two hours at room temperature (20°-22° C/68-72° F).

Note: Seeding crystals (grated cocoa butter) should in no case be added.

2. The melting point of cocoa butter
1. Press a 1 cm column of pretreated cocoa butter into the longer side of the U-tube.
2. Use a very fine metal rod to push the column of cocoa butter down to 1 cm before the bend of the tube.
3. Fix the shorter side to the thermometer (0°-50º C/32-122° F) by means of the rubber ring, and make sure that the bend of the tube is on the same level as the bulb of the thermometer.
4. Introduce the thermometer with the U-tube into the inner water bath of the melting point equipment. The water level of the inner water bath has to be 1 cm below the level of the exterior water bath, which has a level of about 9.5 cm high.
5. Slowly heat the exterior water bath while constantly stirring by means of the magnetic stirrer. Up to 30º C (86° F), the maximum increase in temperature of the inner water bath may be 1º per minute. Over 30º C (86° F), the increase in temperature may not exceed 0.2º per minute.
6. Read the temperature when the column of solid cocoa butter moves (slips) down; this is the Slip Point.
7. Read also the temperature when the column of cocoa butter is completely molten (clear); this is the Clear Point.
8. Give the temperature of both the Slip Point and the Clear Point in ºC (or °F) and to one decimal place.

REFERENCES

1. ISO 6321: Animal and Vegetable Fats - Determination of Melting Point in Open Capillary Tubes (Slip Point).
2. ICA Method 4/1962: Determination of the Melting Point of Cocoa Butter (formerly 8b/1962).

Lovibond color

DEFINITION

This method describes the determination of the color of liquid cocoa butter with the Lovibond Tintometer and Yellow, Red, and Blue color glasses.

EQUIPMENT/MATERIALS

- Lovibond Tintometer, type 1A with two identical lamps of 60W (to be replaced after 100 burning hours or after three years)
- magnesium carbonate blocks as standard white (clean surface by rubbing the cubes together)
- 1-inch glass cuvette for the Tintometer
- set of Yellow, Red, and Blue Lovibond color glasses (clean regularly with lens paper)
- neutrally hued filter (Grey)

PROCEDURE

1. Switch the lamps on and fill a 1-inch cuvette with clear-filtered cocoa butter of approx. 40º C (104° F).
2. Place the cuvette against the opening at the rear side of the color compartment in the Tintometer, covering the entire opening.
3. Compare the color of the cocoa butter with Lovibond color glasses: start with 40.0 Yellow and add Red (units and tenths) and, if necessary, Blue until the combination of color glasses matches the color of the cocoa butter.
4. If a color cannot be matched by means of the color glasses, then use the neu-

trally hued filter (Grey).

5. The color is expressed in a sum of units and tenths used from the Yellow, Red, and Blue color glasses.

REFERENCES

ISO 15305: Animal and Vegetable Fats and Oils - Determination of Color - Tintometer Method.

Extinction values

DEFINITION

This method describes the determination of the extinction values of cocoa butter before and after washing with alkali.

PRINCIPLE

The extinction values at 270 nm and 325 nm of a 1% cocoa butter solution in cyclohexane, before and after washing with alkali solution, are measured in a 1 cm cuvette; the difference in extinction values at 270 nm and 325 nm is an indication of the purity of the cocoa butter. The maximum extinction value at 270 nm for cocoa butter is 0.5, whereas after washing with alkali the extinction value should be maximum 0.14; the difference is caused by the removal of the alkaloids (caffeine and theobromine) with the alkali washing.

The cocoa butter extinction values are indicative of the degree of contamination and aging of cocoa butter. During oxidation of cocoa butter, products such as conjugated dienes and diketones are formed. Measurement of the absorbance of dienes can take place at about 232 nm, and that of diketones can be measured at 268 nm. Absorbance of conjugated trienes can be measured at approx. 270 nm. Pure prime pressed cocoa butter does not contain any dienes, trienes, or products of decomposition. Consequently, the extinction value must be low. Any higher extinction value could, for example, be an indication of refined cocoa butter or expeller butter.

If at approx. 270 nm several peaks are observed, this would mean that the cocoa butter has been treated with bleaching earth.

EQUIPMENT/MATERIALS

- cyclohexane (for spectroscopy)
- diethyl ether (p.a.)
- potassium hydroxide solution (4 N)
- sodium sulfate (anhydrous)
- pipette (5 ml)
- graduated measuring cylinder
- separating funnels (100 ml)
- Erlenmeyer flasks (25 ml with ground-glass stopper)
- fluted filters (Ø 7 cm, e.g. S&S no. 597)
- water bath
- pH-indicator paper
- quartz-cells (1 cm)
- UV spectrophotometer
- glass beakers

PROCEDURE

Measurement of the extinction values:

1. Weigh 0.1 g cocoa butter to the nearest 0.1 mg into a 25 ml Erlenmeyer flask (weight: G in g).
2. Add 5 ml of cyclohexane by means of a pipette and mix.
3. Fill a 1 cm quartz-cell and scan the UV spectrum between 220 nm and 290 nm by means of the UV spectrophotometer.
4. Use cyclohexane as blank (reference).
5. Register the UV curve by means of a recorder.
6. Read the extinction values at 270 nm and 325 nm.

Alkali washing and measurement of the extinction values:

1. Weigh about 2 g of cocoa butter into a 100 ml glass beaker.
2. Add 5 ml of diethyl ether and mix.
3. Pour the solution into a separating funnel of 100 ml.

4. Rinse the glass beaker with 5 ml of diethyl ether and pour into the separating funnel.
5. Add 3 ml of potassium hydroxide (4 N) and shake for 2 minutes.
6. Draw off the alkali layer and thoroughly wash out the ether layer by means of 3 ml of distilled water.
7. Continue to wash out (five times on average) until the water layer has become alkali free.
8. Check by means of the indicator paper.
9. Add 5 ml of diethyl ether and draw off the solution into a 25 ml Erlenmeyer flask with stopper.
10. Add about 2 g of anhydrous sodium sulfate and allow to dry for about one hour.
11. Filter through a fluted filter (Ø 7 cm) into a glass beaker of 25 ml and completely evaporate the ether on a water bath.
12. Proceed by carrying out steps 1-6 as described in "Measurement of the extinction values."

CALCULATION

Calculate the extinction values with the following formulas:

$$\frac{E270 = \text{Ext at } 270 \text{ nm}}{20 \times G}$$

$$\frac{E325 = \text{Ext at } 235 \text{ nm}}{20 \times G}$$

Express the extinction values with two decimal places.

REFERENCES

1. ICA method 18 and 19, 1973: UV Extinction Values for Cocoa Butter (formerly 8d + 8c/1973).
2. ISO 3656: Animal and Vegetable Fats and Oils - Determination of UV Absorbance.

Saponification value

DEFINITION

This method describes the determination of the saponification value (S.V.) of cocoa butter. The S.V. is the number of mg of potassium hydroxide required to saponify 1 g of fat.

EQUIPMENT/MATERIALS

- 0.5 N KOH in ethanol (clear, colorless solution, stored in a brown glass bottle with a rubber or Teflon stopper)
- 0.5 N hydrochloric acid (accurately standardized)
- phenolphthalein, 1% w/v solution in 95% ethanol
- Erlenmeyer flask, NS 29
- spiral reflux condenser NS 29
- volumetric pipette
- boiling stones chips
- hot plate

PROCEDURE

1. Weigh about 2 g of cocoa butter to the nearest 1 mg into a 200 ml (NS 29) Erlenmeyer flask.
2. Add 25.0 ml of ethanolic KOH solution by means of a pipette.
3. Add some boiling stones and attach the reflux condenser to the Erlenmeyer flask.
4. Place the flask on the hot plate and gently boil for 60 minutes.
5. Add 1 ml of phenolphthalein to the hot soap solution and titrate with 0.5 N hydrochloric acid until the color changes to colorless (V1 in ml).
6. At the same time, carry out a blank (without cocoa butter) determination (V2 in ml).
7. Calculate the saponification value with the following formula:

$$\frac{56.1 \text{ x } N\ (V_2 - V_1)}{G}$$

Where:

N = normality (0.5 N) hydrochloric acid
V_1 = ml hydrochloric acid (0.5 N) determination
V_2 = ml hydrochloric acid (0.5 N) of the blank
G = cocoa butter weight in g.

Express the result with one decimal place.

REFERENCES

IUPAC Standard Methods for the Analysis of Oils, Fats, and Derivatives, 6th Edition, Method 2.202.

Iodine value by Wijs method

DEFINITION

This method describes the determination of the iodine value (I.V.) of cocoa butter by the Wijs method. The I.V. of a fat is the number of grams of halogen absorbed by 100 g of fat and expressed as the weight of iodine. The I.V. is a measure of the degree of unsaturation of fat.

EQUIPMENT/MATERIALS

- equipment has to be clean and dry
- Erlenmeyer flasks of 300-500 ml with NS29 and ground stoppers
- burette, graduated in 0.1 ml
- pipette, 25 ml
- demineralized water
- N sodium thiosulfate solution (standardized)
- Wijs solution 0.2 N
- glacial acetic acid/cyclohexane solution, ratio 1:1
- potassium iodide (KI) solution in water, free from iodine or iodate
- starch solution in water
- reference sample of cocoa butter

PROCEDURE

1. Weigh 0.32-0.38 g of the cocoa butter to be analyzed to the nearest 1 mg into an Erlenmeyer flask; weigh also 0.32-0.38 g of the reference sample into an Erlenmeyer flask (m in g).
2. Dose 15 ml of the glacial acetic acid/cyclohexane solution into the flasks, stopper the flasks, and dissolve the cocoa butter.
3. Pipette 25.0 ml of 0.2 N Wijs solution into the flasks, stopper, and mix carefully.
4. Place the flasks in the dark for at least one hour but not more than 1.5 hours (exclusion of daylight is essential).
5. Add after this time 20 ml of KI solution and 150 ml of demineralized water.
6. Titrate the free iodine in the contents of the flasks with the sodium thiosulfate solution (Normality T) from the 50 ml burette; add 5 ml of starch solution (indicator) at the end of the titration and continue the titration under vigorous shaking till the blue color just disappears (V_2 in ml).
7. Carry out a blank test simultaneously under the same conditions and without cocoa butter (V_1 in ml).

EXPRESSION OF RESULTS

Calculate the I.V. with the formula:

$$\text{I.V.} = \frac{12.69 \times T \times (V_2 - V_1)}{m}$$

Where:

V_1 = ml of standardized sodium thiosulfate solution used for the blank determination
V_2 = ml of standardized sodium thiosulfate solution used for the cocoa butter samples
T = the exact Normality of the sodium thiosulfate solution used
m = the mass, in g, of the cocoa butter samples

REMARKS

Determination of the I.V. by an automatic titration often gives better reproducibility and repeatability than manual titration. The reference sample is used to check the performance of the methodology.

REFERENCES

1. IUPAC Standard Methods for the Analysis of Oils, Fats, and Derivatives, 6th Edition, Method 2.205.
2. ISO 3961 - 1996: Animal and Vegetable Fats and Oils - Determination of Iodine Value.

Unsaponifiable matter

DEFINITION

This method describes the determination of the % of unsaponifiable matter of cocoa butter.

PRINCIPLE

The unsaponifiable matter is that part of the cocoa butter which, after saponification, is still soluble in a non-polar solvent. The unsaponifiable matter consists of lipids of natural origin present in press butter, such as sterols, alcohols, and hydrocarbons. The % of these substances is <0.3% in pure prime press cocoa butter. When the unsaponifiable matter is >0.3%, the butter is contaminated with non-volatile (at 103° C/217° F) organic matter foreign to press butter (for example mineral oils or shell fat).

EQUIPMENT/MATERIALS

- KOH p.a.
- petrol ether (p.e.) b.p. 40°-60° C (104-140° F), p.a. (free from residue)
- ethanol 96%
- ethanol/water mixture 1:1 (v/v)
- Erlenmeyer flask of 200 ml NS 29 with reflux condenser
- Erlenmeyer flask of 100 ml
- separating funnel 500 ml

- oven 103° C/217° F (± 3°)
- heating bath—fireproof and spark-free
- desiccator with blue silica gel
- fume cupboard
- phenolphthalein solution, 1% (w/v) in ethanol

PROCEDURE

1. Weigh approx. 5 g of cocoa butter to the nearest 10 mg into an Erlenmeyer flask of 200 ml (NS29) (G_1 in g).
2. Add approx. 5.5 g of potassium hydroxide and 50 ml of ethanol.
3. Attach the Erlenmeyer flask to a reflux condenser and boil gently in a heating bath for one hour.
4. Add 50 ml of distilled water through the top of the condenser.
5. Mix and cool down.
6. Transfer the contents of the flask into a separating funnel of 500 ml.
7. Rinse the flask several times with a total of 50 ml of p.e.
8. Transfer these p.e. rinsings into the separating funnel.
9. Shake the separating funnel vigorously for 1 minute.
10. Allow to stand until there is complete separation of the two phases.
11. Draw off the soap solution (the lower layer) into a second separating funnel of 500 ml.
12. Add small amounts of ethanol (96%) or concentrated potassium hydroxide solution if an emulsion has formed that must be broken.
13. Extract the soap solution twice more, each time with 50 ml of p.e.
14. Draw off the soap solution into the original Erlenmeyer flask.
15. Collect the three p.e. layers in the first separating funnel.
16. Wash out the p.e. at least three times, each time with 50 ml of the ethanol/water mixture (1:1), until the ethanol/water mixture reacts neutral. Check this by means of a drop of phenolphthalein.
17. Transfer part of the p.e. into an Erlenmeyer flask of 100 ml with boiling stones. The flask must previously be dried and tare weighed to the nearest 0.1 mg (G_2 in g).
18. Evaporate the p.e. on the heating bath in the fume cupboard.
19. Transfer the remainder of the p.e. quantitatively into the Erlenmeyer flask and rinse the separating funnel with small amounts of p.e.
20. Evaporate the p.e. completely in the heating bath.
21. Dry 100 ml flask with residue in an oven at 103° C (217° F) for 15 minutes, placing the flask in a horizontal position.
22. Cool in a desiccator for approx. 30 minutes and weigh the flask to the nearest 0.1 mg.
23. Repeat the drying for successive 15 minute periods until the weight loss between two successive weighings is less than 2.0 mg (G_3 in g).
24. Calculate the % of unsaponifiable matter with the following formula:

$$\% \text{ unsaponifiable matter} = 100\,(G_3 - G_2) / G_1$$

REFERENCES

1. IUPAC Standards Methods for the Analysis of Oils, Fats, and Derivatives, 6th Edition, Method 2.401.
2. ISO 3596-2: Animal and Vegetable Fats and Oils - Determination of Unsaponifiable Matter, part 2: rapid method using hexane extraction.
3. ICA method 23/1988: Determination of Unsaponifiable Matter in Cocoa Butter (formerly 102/1988).

Blue value

DEFINITION

This method describes the quantitative determination of the blue value (B.V.) of cocoa butter; a B.V. of >0.05 is indicative of a too high % of shell in the nibs from which the cocoa butter is obtained.

PRINCIPLE

The B.V. of cocoa butter is the extinction of a blue-colored solution that is formed after oxidation of the reaction product of behenic acid tryptamide with p-dimethyl aminobenzaldehyde. The reaction takes place under acid conditions. Behenic acid tryptamide is only found in the shell of cocoa beans.

EQUIPMENT/MATERIALS

- carbon tetrachloride (p.a.)
- p-dimethyl aminobenzaldehyde (p.a.)
- hydrochloric acid (32% p.a.)
- hydrogen peroxide (30% p.a.)
- pentanol-2 (p.a.)
- demineralized water
- volumetric flasks (10 ml)
- water bath (40° C/104° F ±1°)
- spectrophotometer
- cuvette (3 cm)
- graduated pipette (1 ml)

PROCEDURE

1. Dissolve 0.2 g of p-dimethyl aminobenzaldehyde in 20 ml of carbon tetrachloride (1% solution).
2. Add 1 ml of hydrogen peroxide (30%) to 60 ml of demineralized water (0.5% solution).
3. Weigh approx. 0.2 g of liquid cocoa butter to the nearest 0.1 mg in a volumetric flask of 10 ml (G in g).
4. Add 1 ml of carbon tetrachloride, dissolve the cocoa butter, and successively add 0.5 ml of p-dimethyl aminobenzaldehyde solution and 0.05 ml (1 or 2 drops) of 32% hydrochloric acid.
5. Mix and shake the volumetric flask in a water bath of 40° C (104° F) continuously for 5 minutes.
6. Add 0.05 ml (one or two drops) of 0.5% hydrogen peroxide solution.
7. Heat, under continuous shaking, in the water bath of 40° C (104° F) for another 3 minutes.
8. Make up the volumetric flask with pentanol-2 to 10 ml and mix.
9. Also carry out a blank determination (steps 4-8).
10. Measure the extinction of the pentanol-2 solution in a cuvette of 3 cm compared to the blank sample (step 9) at 500, 630, and 680 nm.
11. Calculate the B.V. with the formula:

$$\frac{0.4[E_{630} - (E_{500} + E_{680})/2]}{3G}$$

Where:
E_{500} = measured extinction at 500 nm
E_{630} = measured extinction at 630 nm
E_{680} = measured extinction at 680 nm
G = weight of the cocoa butter in g

Express the result in two decimal places.

REMARKS

1. If tetrahydrofuran is used instead of pentanol-2, the extinction must be measured at 510, 625, and 675 nm. Although tetrahydrofuran has a higher M.A.C. value than pentanol-2, the latter is preferred because of its low vapor pressure. Both liquids are poisonous.
2. For the B.V., the extinction is converted into that of a 2% solution (2 g in 100 ml) measured in a cuvette of 2 cm.

REFERENCES

ICA method 29/1988: Method for Determination of the "Blue Value" (formerly 108/1988).

Moisture and volatile matter

DEFINITION

This method describes the determination of the moisture and volatile matter in cocoa butter by heating the butter at 125° C (225° F).

EQUIPMENT/MATERIALS

- boiling stones
- glass beaker with flat bottom, 100 ml
- thermometer 100°-150° C (212-302° F)
- hot plate
- balance (accuracy 1 mg)
- watch glass

PROCEDURE

1. Put some boiling stones into a beaker and, subsequently, add 20 g of butter to the nearest 1 mg. The weighed amount of butter is G_1 in g, the weight of the glass beaker plus butter is G_2 in g.
2. Heat the beaker on a hot plate.
3. During heating, continuously stir the fat with a thermometer, which has been weighed together with the beaker glass and the butter.
4. Raise the temperature to 125° C (225° F) and keep at this temperature until there is no vapor escaping anymore.
5. Check this by covering the beaker with a cold watch glass. The glass may not steam up.
6. Allow the beaker to cool down and weigh again to the nearest 1 mg (G_3 in g).
7. Calculate the percentage of water and other volatile constituents with the help of the following formula: $(G_2 - G_3)/G_1 \times 100\%$. Express the value obtained in two decimal places.

REFERENCES

1. IUPAC Standard Methods for the Analysis of Oils, Fats, and Derivatives, 6th Edition. Method 2.601.
2. ISO 662 - Animal and Vegetable Fats and Oils - Determination of Moisture and Volatile Matter Content.

Peroxide value

DEFINITION

This method describes the determination of the peroxide value (P.V.) of cocoa butter. The P.V. of a fat is the number of m.eq of active oxygen (peroxides) per kg of fat; the P.V. relates to the oxidative stability (rancidity) of the fat.

EQUIPMENT/MATERIALS

- chloroform, p.a.
- glacial acetic acid, p.a.
- saturated KI solution in water (140 g/100 ml of water), free of iodine and iodates
- sodium thiosulfate 0.002 N, freshly prepared from a 0.1 N stock solution
- starch solution 0.5%
- Erlenmeyer flask (200 ml) with NS29 and glass stopper, clean and dry
- micro-burette according to Bang 5 ml with 0.01 ml graduations

PROCEDURE

1. Homogenize the liquid cocoa butter by stirring without introducing air.
2. Weigh 1.2-2.0 g of cocoa butter to the nearest 1 mg into an Erlenmeyer flask of 200 ml (weight G in g).
3. Add 10 ml of chloroform and dissolve the cocoa butter by shaking.
4. Add 15 ml of glacial acetic acid and, subsequently, 1 ml of KI solution.
5. Shake for 1 minute and allow the Erlenmeyer flask to stand in the dark at room temperature for 5 minutes.
6. Add 75 ml of distilled water and 3 ml of starch solution.
7. Titrate, while shaking vigorously, the released iodine with the sodium thiosulfate solution 0.002 N. (V in ml), Normality thiosulfite = N.

8. At the same time, carry out a blank determination, during which no iodine may be released.
9. Calculate the peroxide value with the formula:

P.V. = (1,000 x V x N) / G.

REMARKS

1. It is essential to reduce presence of air (oxygen) during steps 1-7 of the procedure, so the flask has to be stoppered as much as possible or nitrogen can be introduced into the flask regularly. Direct daylight also must be prevented.
2. The P.V. must be determined as quickly as possible. If this is not possible, the sample must be stored in a cool and dark place.
3. The P.V. can be expressed in m.eq as well as in m.mol or mg of active oxygen per kg.

Conversion factors	multiply the P.V. with
m.eq/kg	1
m.mol/kg (Lea value)	0.5
mg/kg	8

REFERENCES

1. IUPAC Standard Methods for the Analysis of Oils, Fats, and Derivatives, 6th Edition. Method 2.501.
1. ISO 3960: Animal and Vegetable Fats and Oils - Determination of Peroxide Value.

Free fatty acid content

DEFINITION

This method describes the determination of the percentage of free fatty acid (ffa) of cocoa butter, expressed as % oleic acid (then also called acidity). The ffa can be recalculated into Acid Degree (m.eq KOH required to neutralize 100 g of cocoa butter) or into Acid Value (mg KOH required to neutralize the ffa in 1 g of cocoa butter).

EQUIPMENT/MATERIALS

- Erlenmeyer flasks of 250 ml
- burette of 25 ml, graduated in 0.1 ml
- ethanol (p.a. 96%)
- diethylether p.a.
- KOH solution in water, approx. 0.1 N. accurately standardized
- diethylether-ethanol (3:2) mixture, neutralized before use with KOH solution against phenolphthalein
- phenolphthalein solution, 1% in ethanol

PROCEDURE

1. Weigh 5-10 g of liquid cocoa butter to the nearest 1 mg into a 250 ml Erlenmeyer flask (m in g).
2. Add 50 ml of the diethylether-ethanol mixture and dissolve the cocoa butter by swirling.
3. Add a few drops of phenolphthalein solution and titrate with 0.1 N KOH (Normality T) to the end point. (The pink color persists for at least 10 seconds.)
4. Register ml KOH used (V in ml).

RESULTS

The ffa, expressed as oleic acid, is calculated with the formula:

ffa = 28.2 x T x V / m

Where:
T = the Normality of the standardized KOH solution
V = ml of the standardized KOH solution
m = the mass (g) of the cocoa butter sample

The Acid Value can be calculated with the formula:

Acid Value = 56.1 x T x V / m

The Acidity can be calculated with the formula:

Acidity = 100 x T x V / m

REFERENCES

1. IUPAC Standard Methods for the Analysis of Oils, Fats, and Derivatives, 6th Edition, Method 2.201.
2. ISO 660 - Animal and Vegetable Fats and Oils - Determination of Acid Value and Acidity.

6. Microbiological

Introduction

The microbiological specifications are based on the IOCCC methodology: method 39/1990 (formerly 118/1990), which is the reference method used for arbitration and calibration of other methods.

For the microbiological control of finished goods and process samples (microbiological - HACCP), large numbers of samples have to be analyzed per day. Special methodology has been developed and optimized for efficiency and rapid availability of the results.

- Determination of total plate count (TPC), molds/yeasts, and *Enterobacteriaceae* starts from the same sample suspension in lactose broth (1:10 dilution).
- *Salmonella* determination starts with pre-enrichment of 4 x 375 g = 1,500 g of product per production day in sterilized skimmed milk. These samples could be composed of 15 x 25 g samples or bigger samples from automatic sampling.

Sample preparation for total plate count (TPC), molds/yeasts, and *Enterobacteriaceae*

1. Mix 13 g of lactose broth (LB, commercially available) with 1,000 ml of demineralized water in a glass bottle.
2. Sterilize the broth in an autoclave at 121° C (250° F) for 30 minutes.
3. Allow to cool to about 45° C (113° F) and check the pH (6.9 ± 0.1).
4. Weigh 2 g of cocoa powder in a sterile (glass) flask, add 18 ml of lactose broth or 10 g of cocoa butter or liquor in 90 ml of lactose broth. Close the bottle and shake well.
5. Let the suspension stand for about 30 minutes and continue with method TPC, method Molds/Yeasts, or method *Enterobacteriaceae*.
6. Always carry out the same analysis with a blank sample containing lactose broth only.

Determination of total mesophilic aerobe plate count

DEFINITION

The TPC or total number of viable mesophilic aerobe microorganisms is defined as the number of microorganisms per grams of product that develop into colonies on a non-selective agar medium by incubation at 30° C (86° F) ± 1° for 48 hours.

MEDIA

- (LB): see sample preparation.
- Plate Count Agar (PCA) (commercially available): Mix 8-13 g of PCA (depending upon supplier) with 500 ml of demineralized water, sterilize for 15 minutes at 121° C (250° F), and cool to about 48° C (118° F).

PROCEDURE

1. Take the sample suspension (1:10 dilution) and shake.
2. Pipette 2 ml of this suspension into a sterile test-tube with 8 ml of LB (1:50 dilution), and mix.
3. Pipette in each of two petri dishes 1 ml of the 1:50 dilution.
4. Add about 15 ml of liquid PCA (about 48° C/118° F). Mix the suspension with the PCA in the dish and allow the mixture to solidify (cool).
5. Check the sterility of the PCA by

pouring the last remains of each bottle into a petri dish.
6. For the blank LB samples no dilution has to be made.
7. Incubate the petri dishes bottom up at 30° C (86° F) ± 1° for 48 hours.
8. Count the number of colonies and multiply this by 50.
9. Calculate the average of the two petri dishes per sample.

Determination of mold and yeast count

DEFINITION

The number of molds and yeasts is defined as the number of molds and yeasts per g product that develop into colonies on selective agar media by incubation at 25° C (77° F) ± 1° for three days (72 hours).

MEDIA

- (LB): see sample preparation.
- Rose-Bengal Chloramphenicol Agar (RBC) (commercially available): Mix 16.1 g of RBC with 500 ml of demineralized water, sterilize for 15 minutes at 121° C (250° F), and cool to about 48° C (118° F).

PROCEDURE

1. Shake the sample suspension (1:10 dilution), and also analyze the blank LB.
2. Pipette 1 ml of this suspension into each of two petri dishes.
3. Add about 15 ml of liquid RBC (about 48° C/118° F), mix the suspension with the RBC in the dish, and allow the mixture to solidify (cool).
4. Check the sterility of the RBC medium by pouring the last remains of each bottle in a petri dish.
5. Incubate the petri dishes bottom up at 25° C (77° F) ± 1° (for 72 hours).
6. Count the numbers of mold and yeast colonies.
7. Multiply the count by 10 and calculate the average of the two petri dishes per sample.

Qualitative determination of *Enterobacteriaceae* incl. *E. coli*

DEFINITION

Enterobacteriaceae and/or *Escherichia coli* are considered to be present if microorganisms develop on selective media and show positive responses according to a specific pattern of reactions.

MEDIA

- LB: see sample preparation.
- Violet Red Bile glucose agar (VRBD) (commercially available): Mix 17-21 g of VRBD (depending on supplier) with 500 ml demineralized water; heat to boiling and pour 6 ml into sterile tubes and cool to room temperature.
- Tryptone water (TW): Mix 7.5 g of TW (commercially available) with 500 ml of demineralized water, pour 6 ml into test tube and sterilize for 15 minutes at 121° C (250° F).
- Brilliant Green Bile Lactose Broth (BGL): Mix 20 g of BGL (commercially available) with 500 ml of demineralized water, pour into reagent tubes with Durham tubes (about 6.5 ml liquid should fully immerse the Durham tube) and sterilize for 15 minutes at 121° C (250° F).
- Kovacs' reagent.

PROCEDURE

1. Take the remaining sample suspension (1.6 g sample in about 16 ml LB) and shake.
2. Incubate this suspension and a blank LB sample at 37° C (99° F) ± 1° for 20-24 hours.
3. Inoculate a VRBD tube from the incubated suspension by stabbing with an inoculation wire down the center to the

bottom of the tube.
4. Incubate the VRBD tube at 37° C (99° F) ± 1° for 24 hours.
5. A sample is considered positive when the whole VRBD agar has become turbid and colored purple-red to yellow, while gas formation may also cause the agar to lighten.

Positive readings have to be confirmed and tested for the presence (quantitative) of *E. coli*.
1. Inoculate from the positive VRBD tube into:
   - a TW-tube (indol formation)
   - a BLG-tube (lactose formation)
2. Incubate both tubes at 42° C (108° F) ± 1° for 24 hours.
3. Add Kovacs' reagent to the TW-tube: Formation of a red ring indicates the presence of indol.
4. A gas bubble in the Durham tube indicates a positive BGL.
5. *E. coli* was present in the VRBD tube when the indol (TW) as well as the lactose BGL-tests were positive.

REMARKS

In case of a positive reaction, the determination has to be repeated with 1 g of cocoa powder in 10 ml of LB.

Determination for presence of *Salmonella*

DEFINITION

Salmonellae are considered to be present if microorganisms develop on the selective media and show positive responses to a specific number of tests (biochemical and serological).

This method includes the motility test, which allows for a negative detection within 48 hours. (In case of a positive motility, test isolation and confirmation have to take place.)

Suspect	Non suspect
XLD: Pink to red colonies with/without black centers, black colonies, yellow colonies with/without center surrounded with transparent medium	White colonies
MLCB: purple-black colonies, mauve-grey colonies with cratered centers, colonies with black centers	No growth
MSRV: Growth, with a clear, milk-white zone around the drop	No growth

MEDIA

1. Pre-enrichment medium
- Sterilized milk, pre-heated to 35-38° C (95-100° F).

2. Selective enrichment medium
- Rappaport-Vassiliadis Broth (RV) (commercially available): Mix 30-43 g of RV broth (depending on supplier) with 1,000 ml of demineralized water, pour into 10 ml tubes, and sterilize for 15 minutes at 121° C (250° F).

3. Selective media
- Modified semi-solid Rappaport-Vassiliadis medium (MSRV).
  - Novobiocin solution (2%); dissolve 200 mg of Novobiocin into 10 ml demineralized water.
  - Dissolve 31.6 g of the MSRV agar into 1,000 ml demineralized water.
  - Bring to boil to sterilize (do not autoclave).

Flavor and Flavor Development 4

Research into the flavor of cocoa has been a fruitful topic in the past decades. Modern analytical techniques have contributed to a better understanding of the composition and the formation of the cocoa flavor components. However, even with all of the new and additional information recently gathered, we still do not know exactly what constitutes cocoa flavor. More than 480 different volatile components divided among some 20 different chemical classes have, to date, been identified in roasted cocoa, making it one of the most complex flavors known to mankind.

1. Formation of cocoa flavor

The most important factors in the formation of the cocoa flavor are:

- cocoa bean variety
- fermentation and drying
- alkalization
- roasting

Cocoa bean variety

In Module 1: History and Supply of Cocoa, we mentioned the major cocoa bean growing countries of today. Not all countries produce the same variety or type of cocoa. It is very important to distinguish between the various types with regard to their differing flavor formation characteristics.

The oldest-known type is the Criollo, which means “native.” This variety was already cultivated by the Aztecs and Mayans in Central and South America. Later, new varieties from the Amazon region were imported, called Forastero, which means “foreign.” These were appreciated particularly for their greater resistance to diseases and pests.

Therefore, it was chiefly the Forastero type that was exported to other parts of the tropics in West Africa and East Asia. However, the flavor of the Forastero was less appreciated by chocolate manufacturers. In trying to combine the advantages of the Forastero and the fine flavor of the Criollo, new hybrids were cultivated. These are known under the variety name of Trinitario. More recently, hybrids have been cultivated by crossing Trinitario and newly collected varieties from the upper Amazon, which give higher yields and are more resistant and faster growing.

Each bean variety has its own specific potential flavor profile.

However, growing conditions like climate, amount and time of sunshine and rainfall, soil conditions, ripening, time of harvesting, and the time between harvesting and fermentation of the beans all contribute to the flavor formation.

Differing conditions may lead to significantly different flavor profiles. A good example is the difference in flavor profile between cocoa produced from beans growing in Ghana and Sabah. Although the variety cultivated in Sabah was originally imported from Ghana, their flavors are completely different.

Fermentation and drying

During fermentation, enzymatic reactions play a principal role in the formation of the cocoa flavor precursors. Peptides and amino acids are generated by proteolytic enzymatic breakdown of proteins. Sugar from the pulp is split into glucose and fructose. The peptides and amino acids and reducing sugars are the precursors for the formation of the volatile flavor components formed by Maillard reactions during the later stages of the processing of the cocoa beans. Enzymes are also responsible for the conversion of the flavonoids into tannins, leading to a decrease in astringency of the cocoa and changing the original purple color of the fresh beans into the typical brown color of cocoa.

The chemical processes involved in fermentation are complex and not completely understood.

Two phases can be distinguished. In the first phase the conditions are more or less anaerobic. The pulp sugars are converted into alcohols by yeasts, and lactic acid bacteria and pectins are broken down by pectinases, which results in liquefaction of the pulp. The liquefied pulp drains from the mass and allows aeration of the mass, which starts the second aerobic phase of fermentation. Acetic acid bacteria take over and the temperature in the mass is increased to about 50° C (122° F). The combination of acid and heat kills the germinal force of the bean. This is accompanied by the loss of cellular integrity, which permits the mixing of substrate and enzymes leading to the reactions that produce the precursors of the cocoa and chocolate flavor.

The proteins in the beans are broken down in two stages. In the first stage, early in the fermentation at a pH <4, the proteins are split into hydrophobic peptides by proteases. Later, during the fermentation at a pH >5, these peptides are converted by carboxypeptidases into hydrophilic peptides and free amino acids. The conversion of the flavonoids by polyphenol-oxidases into tannins takes place during the aerobic stage of the fermentation as oxygen is needed for the reaction. At that stage, the saccharose from the pulp penetrates into the bean and is broken down into the reducing sugars by enzymatic hydrolysis. During sun drying, after fermentation at moisture contents below 12%, the Maillard reaction starts.

Good fermented

Unfermented, violet

Unfermented, slaty

All these reactions have to take place for the ultimate development of a good cocoa flavor. The degree of fermentation of the cocoa bean is therefore considered of paramount importance.

The cut test is used to determine the degree of fermentation of the bean. In this test, each bean out of a sample of 300 beans is bisected, and the color of the interior of the bean is assessed by counting the percentage of slate-colored and violet-colored beans. Slaty beans are not fermented, and violet beans are incompletely fermented. Non-fermented beans do not lead to cocoa flavor development. To qualify as being "good fermented," the percentage of slaty beans should not be more than 5%.

Cocoa beans can also be overfermented. In this case, the beans begin to decompose, and the pH rises sharply as proteins in the beans start to break down. During this process, very dark pigments are formed. They are reaction products of flavonoids with amino acids. The beans are then very dark colored and brittle. Overfermented beans lead to a hammy off-flavor.

Alkalization

Alkalization is not a common step in the manufacture of chocolate. However, in the manufacture of cocoa powder, alkalization has a number of distinct benefits. It will influence both the color and the flavor of the end product.

In the alkalization process, the cocoa is treated with an alkaline solution. A number of different alkalis are permitted and the process conditions can vary considerably. Among other criteria are the kinds of beans, the type and quantity of alkali used, ratio of the active ingredients, time, and temperature. Alkalization can take place in the cocoa nib (preferably) or in the cocoa cake/powder.

Literature reveals little of the numerous and complicated chemical reactions taking place during alkalization. It is assumed that further reactions take place as were earlier described during fermentation. In an alkaline medium, the polyphenolic components are converted into phenoxides, which easily oxidize into quinones. The active role of the polyphenolic components during alkalization is demonstrated by analysis of the components before and after alkalization.

Alkalization reduces the acidity of the flavor of cocoa as well as its astringency. Flavor aspects like typical cocoa and bouquet are enhanced and intensified. The lowering of the astringency is caused by a further polymerization of the flavonoids during the alkali treatment.

Roasting

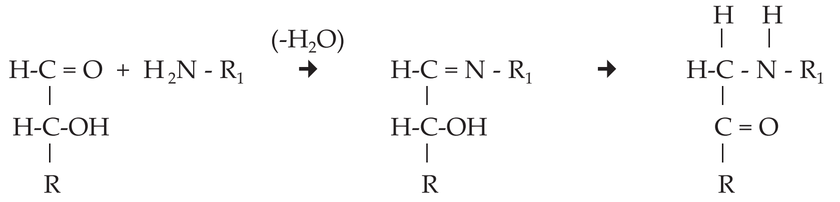
The roasting process is of great importance for the ultimate flavor profile of the end-product. The roasting step is also important because it allows the manufacturer to influence the flavor development to a significant degree. By adapting the roasting conditions, a variety of flavor profiles can be obtained for cocoa liquor, the base flavor component for chocolate and cocoa powder.

During the drying after fermentation, the Maillard reactions cause the first meta-stable components to be formed, the Amadori compounds, which are condensation products of amino acids and reducing sugars like fructose. A direct correlation has been demonstrated between these compounds and the formation of the volatile cocoa flavor components.

2. Chemistry of Roasting

Most of the various compounds found in the flavor of cocoa are generated by the Maillard reactions. The aldehydes and pyrazines in particular, are considered to be important for the character of cocoa

Formation of an Amadori Compound from a Reducing Sugar and an Amino Acid



Reducing sugar + amino acid (Intermediate) Amadori compound

flavor.

The Maillard reactions play a major part in all food preparations in which the flavor is developed by a heating process like baking, frying, or roasting. It is essentially a reaction between a reducing sugar like glucose or fructose with an aldose-group and a compound with an amino-group. In food, this is usually an amino acid, peptide, or protein. Initially the aldose group reacts with the amino-group by removal of a molecule of H_2O.

In cocoa, a large part of the Maillard reactions already take place during sun drying after fermentation, and in the first stage of roasting, the Amadori compounds are formed. The Amadori compounds are reacting further in different ways depending on the reaction conditions. For cocoa, the so-called Strecker Degradation is considered to be very important for the development of the cocoa flavor.

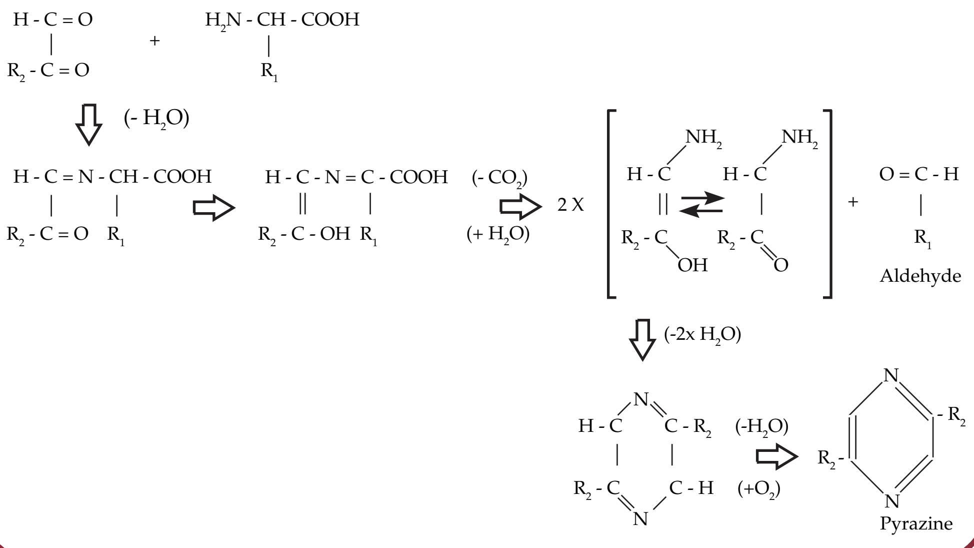
First, the Amadori compounds are converted into dicarboxylic compounds by further removal of H_2O molecules. These compounds reduce the α-amino acids into aldehydes, and during further dehydration, the heterocyclic components like pyrazines are formed.

From these mechanisms, it is quite apparent that the formation (and removal) of water is the driving force in these reactions. Therefore, they can only take place in a rather dry medium and at

Compounds Found in Cocoa Flavor (Flamant, 1989)

Component	Number
Aliphatic, Alicyclic	
Hydrocarbons	39
Organic acids	51
Amines	45
Alcohols	25
Aldehydes	22
Ketones	24
Esters	58
Lactones	7
Ethers	8
Sulfides	10
Phenols	6
Heterocyclic	
Furans	19
Thiazols	8
Thiophenes	1
Pyridines	12
Pyrroles	18
Oxazoles	15
Pyrazines	95
Total	463

Maillard Reactions: Strecker Degradation



higher temperatures. However, particularly in the first stages, some free water should be available in order to make contact between the various reactants.

The roasting process is required to further develop the desired flavor. For cocoa, the roasting conditions are rather mild. The product temperature at the end of the roasting process should not exceed 110°-120º C (230°-248° F), and the final moisture content should be between 1 and 2%. If the roasting is continued for too long, then the more volatile components like aldehydes, esters, and low molecular acids like butyric acid will be removed, leaving only the pyrazines and the non-volatile acids. This results in a burnt flavor.

Another important reaction during roasting is the change in the organic acid composition. The major acids in cocoa are acetic, lactic, and citric acid. Acetic acid is volatile; the others are not. During roasting, the pH increases due to the removal of acetic acid.

In general, cocoa products made from Malaysian beans have a more acidic flavor compared to products made from African-type beans. Also, in Malaysian and South American beans, the content of lactic acid is usually higher. During roasting, lactic acid is not removed, which might explain the higher acidity of cocoa made from these beans.

The beans from Venezuela and Ecuador contain a relatively high amount of esters, which contributes to fruity wine-like flavor top notes, expressed as bouquet. They are already present in the fermented cocoa beans before roasting. Because these esters are rather volatile, they are easily removed during roasting. Therefore, these beans should be subjected to a very light roast in order to keep these bouquet flavors in the cocoa.

The chocolate and cocoa industries use a wide assortment of equipment, methods, and conditions for roasting cocoa. Differences in roasting conditions have a distinct effect on the flavor development.

3. Sensory evaluation of cocoa flavor

Introduction

People have a flavor memory that allows both instantaneous judgment as well as comparison with experiences from the past. The consumer's sensory evaluation of foods is a process that can offer information often difficult to obtain from an instrument and is critical in the assessment of a food product's acceptability.

Sensory evaluation is, in the first place, an individual's judgment of a taste or smell of a food product. Because it is largely a subjective process, it must be transformed into an objective assessment to be of use to a food manufacturer in the areas of new product creation or improvement and quality control. In essence, flavor evaluation is a tool with which a food processor is able to convert the subjective judgment of consumers into measurable data from which an objective analysis can be made.

Sensory evaluation may be defined as analysis performed using the senses: taste, smell, touch, sound, and sight. In this context, the concept of "taste" should be interpreted in a much wider sense than the direct impression on the tasting sense when eating. To avoid confusion between the wider and the narrower concepts of "taste," the word "flavor" is often used. "Flavor" encompasses the total impression of taste (gustation), smell (olfaction), and trigeminal nerve sensations such as touch, temperature, pain, and chemical irritants (giving a heat or cooling response) obtained when eating a product. Sensory evaluation is used in quality control, product development, and consumer tests. Sensory evaluation can, for example, provide the answer to the question of whether a change in raw material or process conditions results in a flavor change in the end-product. Recent development of flavor selective sensors, also called "electronic noses," could be helpful in increasing the number of discriminatory tests, but the calibration and internal control of such equipment will always require a panel of flavor experts.

Flavor release

One of the most important factors to be considered when judging the properties of a flavor is how it ultimately manifests or releases itself in the final product during consumption. Flavor release is the perceived intensity of a certain aspect of the flavor as a function of time, when the product is sensorially evaluated. It is determined, for example, by the physical and chemical properties of the flavor itself, by the location in the mouth and the nose where the flavor is perceived as well as by the texture and the temperature of the product in which the flavor is incorporated.

In many products, fat is an important transmission medium for flavor. In such products, the amount of fat and its melting point and melting behavior are important for the flavor release, as the fat must first melt before the flavor becomes available. This is one of the reasons why the cocoa flavor in different end-products shows a different flavor profile. With cocoa butter melting rapidly at body temperature (in the mouth), the flavor release is relatively fast, allowing a variety of different flavors, each having a different time-intensity curve, to be expressed in unique ways. For a full flavor evaluation, it is important to keep the product in one's mouth for some time before it is swallowed. Contact with saliva is also essential.

Appearance, sound, mouthfeel, texture, taste, smell

The importance of products' appearance is evident. Size, weight, shape, and color are the most important contributing characteristics. In the case of cocoa, this is even more obvious, as the intensity of the color will initiate a corresponding flavor expectation. Packaging also serves to enhance the expectations for a food item.

Sound can also play a crucial role. With some products, the sound generated during consumption can lead to a more positive or negative judgment. Consider the "crunch" of a fresh apple or the "snap" of a good chocolate bar—both are necessary for a positive valuation.

The mouthfeel of a product is determined by its texture, viscosity, and behavior during the (often short) period of residence time in the mouth. This can be described in such terms as hard, smooth, crunchy, watery, powdery, greasy, waxy, or dry. The melting behavior of the fat phase can be of influence also. A product can be liquid, half liquid, paste, or solid, all forms in which cocoa-flavored products are available to the consumer.

Chewing refines the product. In the meantime, the texture of the food is evaluated, and its temperature is adapted to that of the mouth. It creates the desired particle size and allows the release of the less volatile components of a food. As a result, the flavor of a product can be appreciated to its fullest extent. This is of particular importance to the cocoa flavor as it releases comparatively little volatile flavor components by itself.

Taste is appreciated by taste receptor cells present mainly on the tongue and soft palate. The taste buds (2,000-5,000) situated in papillae on the tongue (except in the middle, where the filiform papillae only have a tactile function) each contain 50-150 taste cells that respond to all taste stimuli; only the sensitivity (threshold value) varies for the types of papillae or position on the tongue. The four classical taste sensations are salt, sweet, sour, and bitter; a fifth sensation, umami, associated with monosodium glutamate (MSG), is getting acceptance, while terms like metallic and astringent are also named. The receptor cells in the taste buds regenerate about every 10 days, so damage is repaired, though sickness or ill health may temporarily delay this.

The role of saliva is very important for tasting as the nonvolatile taste stimuli have to be dissolved before they can contact the taste pores of the taste buds. A "dry" mouth or reduced saliva flow, e.g. caused by drugs or medication, results in loss of taste.

The ability to taste declines slightly as people age, as does, to a larger extent the ability to detect smells, especially for males. It has been established that elderly people develop a preference for more bitter and stronger, but less sweet, chocolate-flavored products. This is primarily due to the fact that their threshold for bitter compounds is higher and, therefore, they perceive the bitterness less in foods.

The nose can detect the most ephemeral of sensory messages. If the nose is pinched closed while eating, mostly touch; temperature; texture; and the basic salt, sweet, bitter, or sour tastes can be detected. No other flavors of a food can be perceived. (Smell forms about 75% of the flavor impression.)

High up in the nose, against the nasal wall, lies the olfactory organ. The olfactory organ is lined with a mucous membrane, about 2-5 cm^2, which has to be penetrated by the volatile odor molecules in order for them to be perceived by the olfactory receptor cells, regenerating about every 50 days. The olfactory organ lies out of the direct stream of air that we inhale when we breathe. Only 2% of the air we breathe reaches the receptors.

Odoriferous molecules (stimulants) can reach the olfactory organ either via the normal respiratory passages or in a retronasal manner. During eating, the flavor of a food is primarily perceived in the retronasal manner. Sensitivity differs considerably per substance and per person. Individuals can display differences in olfactory sensitivity by factors up to 1,000 for the same substance. About 150-200 odor qualities containing about 10,000 different odors can be recognized by trained persons.

Adaptation, synergism, total impression, judgment

Adaptation, or fatigue, is the decrease in response with constant stimulation and is observed both with smell and taste (and with many other senses). So, the sensitivity to a certain stimulant declines as a result of previous exposure to that stimulant. At complete adaptation, the sensitivity to the stimulant involved is completely lost. In cross adaptation, the reduction of sensitivity is caused by exposure to another stimulant. Adaptation is time dependent (a few minutes), and it can be neutralized by removing the stimulant (rinsing with fresh air or clean, warm water).

Synergism is the enhanced impression of taste. It is the taste impression above that or different from two individual components, so a mixture with subthreshold levels of its components will produce a strong taste sensation. Inhibition or mixture suppression is the opposite effect, where taste sensations are reduced or changed in a mixture of stimulants.

It is important to realize that sensory sensitivity and capability differ strongly between individuals. The population consists of about 25% “supertasters” and 25% “non-tasters.” For evaluation purposes, the “non-tasters” and persons with taste or smell defects (temporarily or definite) have to be excluded from panels by adequate screening and training sessions.

When we evaluate a food product, each of our five senses are used: sight, sound, taste, touch, and smell. The information is gathered and integrated into a total sensory picture or impression by the brain. This judgment process is immediate and is the way in which the brain interprets this impression.

The process by which a consumer makes a judgment on a food involves three separate phases. The first is the input phase to the brain. The second is the comparison of the input with what exists in the flavor memory. The third is the output presented in the form of an opinion. It is this opinion that is critically important for the food technologist to be aware of. This is where the acceptability of a new formulation will first be visible. And this opinion is very clearly a function of what happens after that initial tasting. Does it taste good?

Flavor memory

The brain has a powerful memory for flavor, retaining the most subtle features of a flavor with amazing accuracy. It is this flavor memory that represents the reference against which a new flavor is compared. The memory contains details of thousands of flavors that range from delicious to unpalatable.

Experience has taught that if a product offers a totally new sensory picture, it runs a high risk of rejection. It is unknown. For a new flavor to be successful, it should be reasonably close to a familiar and trusted flavor impression. Moreover, the expectation of the consumer should be confirmed in the actual tasting experience. In creating new formulations, emphasis is often placed on adapting known and trusted flavors rather than creating completely new ones. This is very much the case in the cocoa, chocolate, and confectionery industries. The flavor of cocoa is well known and has proven to be immensely successful.

Sensory evaluation

Sensory evaluation as we know it today was developed after World War II. Almost all food companies carry out sensory evaluation, notably on the product lines that carry and represent their own particular house flavor. The number of measurement methods for sensory research has increased over the past years, partly due to the opportunities that computers offer to process complex data.

Methods for analytical sensory evaluation can be divided into two groups: difference tests and descriptive tests. In difference or discrimination tests, samples are always judged in comparison with another sample or a standard; in descriptive tests, a sample is examined on its own to determine its sensory qualities and the intensities of these qualities.

Difference (discrimination) tests

Some well-known methods are the Triangle Test, Paired Comparison Test, Ranking Test, and Two-Out-of-Five Test. These indicate only whether or not there is a significant difference between samples. Difference tests are easy to carry out. It is not necessary for the members of the test panel to have intensive training, and the cumulative results will indicate whether or not there is a significant difference between the samples. Therefore, it is not surprising that difference tests are often used. However, unlike descriptive techniques, the nature of the difference is not always established.

Descriptive tests

The first, and for a long time the only, descriptive method was the Flavor Profile Method (FPM). The panel leader would determine the aspects of the samples to be tested, usually with four to five panel members. A disadvantage is that the panel members have to undergo fairly intensive and lengthy training before they can participate. They also need regular retraining to keep the variations in individual judgments within narrow limits.

The '70s saw the development of the Quantitative Descriptive Analysis test (QDA). In this method, the aspects to be tested are jointly determined by all members. Eight to 10 panel members perform the testing.

A QDA variant is Free Choice Profiling (FCP). In this method, panel members individually indicate only those aspects they want to test.

The principal component analysis (PCA) is a methodology that is further described in Module 7: Cocoa Liquor under "Flavor."

Sensory evaluation in the food industry

Sensory evaluation, as a management tool to improve a company's operations, requires a systematic approach. Current findings suggest strongly that Descriptive Analysis Tests provide the best information, which tells investigators what they want to know, can be related to results obtained from instruments, can be stored for future reference, and can be collected systematically.

Some of the activities to which systematic sensory evaluation can contribute include:

- quality control
- quality assurance
- shelf-life determination
- product reformulation
- new product development - R&D
- marketing
- evaluating competitive products

Sensory evaluation contributions to company operations can best be made through a team of specially trained personnel—the Sensory Evaluation Panel.

Its evaluation work must be independent and totally free from interference. It must provide an objective testing medium and should communicate adequately with all company departments that are going to use the information obtained.

ADM Cocoa uses a combination of a descriptive test (the QDA test) and a difference test (the paired comparison test). It involves the following three steps:

- creating a glossary of terms used to describe different sensory aspects (cocoa flavor and flavor notes)
- training panels to judge and rate those aspects
- evaluating the ratings

The methodology for the sensory evaluation of cocoa powder can be found in Module 3: Methods of Analysis under "Flavor Evaluation."

Basic cocoa flavor notes

As part of the flavor evaluation, panel members can use the following as the glossary of terms for cocoa products:

Cocoa
The basic cocoa note, which is derived from a good fermented, deshelled, roasted, and ground cocoa bean

Bitter
One of the four basic tastes perceived most sensitively at the back of the tongue, stimulated by solutions of caffeine, quinine, and other alkaloids (ASTM)

Rich or Full
A full-flavor intensity contrasting with watery. It indicates the "overall" or total flavor intensity of the product.

Bouquet
General term covering all flavor elements over and above the cocoa character, e.g. aromatic, floral, and fruity notes

Acid (Sour)
One of the four basic tastes perceived on the tongue, associated with acids (ASTM) like citric acid

Astringent
The chemical feeling factor perceived on the tongue and other oral surfaces, described as puckering or drying, elicited with tannins or alum (ASTM)

Acrid
A burnt, harsh, aromatic taste often associated with burnt wood, smoke, or roasted beans (ASTM) or a pungently bitter note often associated with astringency and acidity, when tasted it gives a sensation of dryness

Cocoa off-flavor notes

Burnt
Tar-like flavor

Earthy/Moldy
Stale, a flavor suggestive of a badly ventilated cellar

Hammy
A flavor suggestive of smoked bacon/ham

Smoky
A burnt wood note

Metallic
A note suggestive of iron and copper

Rancid
A flavor suggestive of oxidized butter or oil

Cardboard
A note suggestive of paper or cardboard

Baggy/Raw
A note suggestive of raw beans and/or burlap bags

Color and Color Development 5

After vanilla, cocoa is the most popular food flavor in the Western hemisphere. Cocoa, however, fulfills two primary functions in foods: as a colorant and as a flavor ingredient. In many cases, the flavor function dominates. In practice, this double role has led to a wide range of cocoa powders adapted to applications in a very large range of foods.

1. Formation of the cocoa color

The formation of the color of cocoa passes through a number of stages. It starts with the formation of precursors by biochemical processes that take place in the cocoa beans during the growth and ripening of the fruit on the tree. This process is largely determined by the bean varieties and the climatic conditions during growth. The next stage takes place subsequent to harvesting during fermentation and drying of the beans. This is a very important phase, as it is here that the characteristic brown color of cocoa is formed. The ultimate color of cocoa, however, is reached after further processing of the beans, where alkalization is the critical step. Depending on the process conditions and the alkali used, the initial yellowish-brown color develops into a variety of hues from light brown to red or even black.

Controlling the influence of the various stages of production on the color development of cocoa powders is complicated and difficult.

The color of the beans arriving from their countries of origin is beyond the immediate control of the manufacturer. The only direct control the cocoa powder producer exercises is at the stage of bean selection and blending, which is very important for providing the raw material for a consistent product. Users of cocoa products like liquor and powder, however, can set their own standards in purchasing specifications.

It is the combination of expertise in bean selection, blending, and successful management of the production process that offers the cocoa products buyer the confidence of a product that will fulfill the requirements of both the manufacturer and the final consumer.

Precursors of the color component

Flavonoids, a sub-group of polyphenols, are the primary precursors of the pigment in cocoa. They occur widely in the plant kingdom and have a variety of functions: as pigments, as protective agents against disease, and as disinfectants when a plant is wounded. Their concentration in fresh, unfermented cocoa beans may be approximately 15%. The anthocyanidines and procyanidines are flavonoids of particular interest as color precursors.

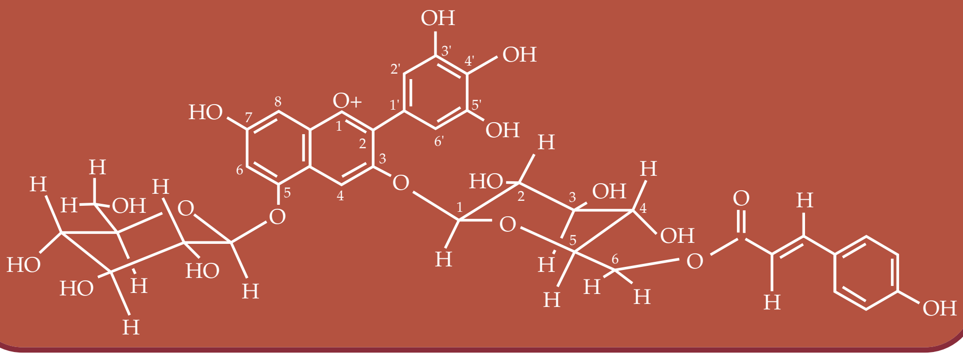
The purple color in fresh, unfermented beans is due to anthocyanines.

These are esters of anthocyanidines and sugars. Procyanidines are present in cocoa as mono-, di-, and trimers of epicatechin.

They are also found in the form of sugar ester derivatives. During fermentation, the sugar esters are hydrolyzed by enzymes. The free antho- and procyanidine molecules are then oxidized by enzymes to quinones. The quinones are reactive agents and behave as oxidizing agents, oxidizing other organic molecules, which, in turn, react themselves. Quinones react with amino acids and proteins, forming covalently bonded complexes. In this way, they form various strongly colored pigments.

They also react with other flavonoids,

Stereostructure of an Anthocyanin Glycoside (Goto et al. 1978)



forming high-molecular weight condensed tannins. If the molecular weight of the tannin is above 3,000, it forms complexes with proteins by hydrogen bonding. As oxidation is involved, the reactions take place during the second oxidative stage of fermentation and during sun drying of the beans. The result is a brown pigment that is stable and insoluble in water.

The conversion of flavonoids into brown tannins can be demonstrated easily by cutting a fresh, non-fermented cocoa bean in half. The cells on the surface are destroyed, freeing the enzymes to react with the phenols. In a few seconds, the color of the surface turns from deep purple to brown.

The concentration of anthocyanidines and epicatechin are lowered during fermentation because the anthocyanines (the purple pigment) react, and the purple color almost vanishes. Therefore, these color precursors are probably the controlling factor in this enzymatic browning.

In certain *Theobroma cacao* species, such as the Criollo, the beans do not contain this purple pigment, and after fermentation the beans are still very lightly colored. In the cut test, the color is used to assess the quality of the bean.

When a consignment of beans is of good quality, only a small percentage of the beans will show these defects. They are not so important for the color formation but may indicate that insufficient or suboptimum flavor will develop on roasting.

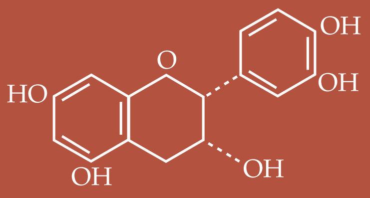
Alkalization and color development

Reactions taking place during the alkalization process are complex. It is practiced in many different ways by different producers, and many aspects influence the color of the final product. As mentioned above, the kind of beans, type and quantity of alkali used, ratio of the active ingredients, time, and temperature are all of influence.

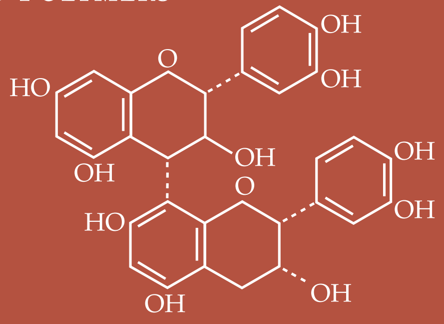
Although alkalization in itself appears to be essentially a simple process, in practice the greatest challenge is to consistently keep the color and flavor within a desired range. In particular, the production of dark and red cocoa powders without the sacrifice of flavor demands great skill and advanced technology.

At ADM Cocoa, the available technological expertise allows the alkalization process to be easily adapted to the differences in the various types of cocoa beans, resulting in a wide range of end-products with consistent colors. The color range varies from light brown to reddish brown to very dark brown tints.

Structure of Flavonoids in Cocoa
Mono- and Polymers



Epicatechin



Procyanidin B

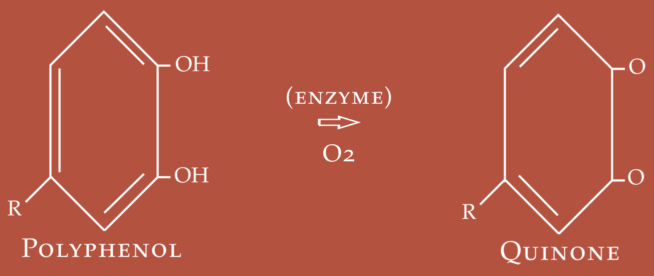
Color of cocoa butter
Flavonoid-based pigments are insoluble in cocoa butter. The color of cocoa butter is a result of another group of natural pigments called carotenoids. This natural coloring occurs in such products as carrots. Vitamin A is one example of this group of compounds. The amount of ß-carotene in cocoa butter can vary and, depending on the amount, the butter will have a more or less yellow-orange, transparent color. Pure prime pressed cocoa butters are not bleached and therefore retain their typical ivory color.

Refining and bleaching are applied to cocoa butters with high free fatty acid contents. These butters are usually extracted from waste material and second-grade cocoa beans. The carotenoids are then removed, rendering the butter colorless.

2. Elements of color

The three dimensions of color
A quantitative and most accurate definition of color is a recent development. The foundation for the color theory was laid out by A.H. Munsell. He was the first to describe

Browning During Fermentation
Polyphenol-oxydase enzyme



Secondary Reactions

Oxidation	: Quinone + RH2 ⇨ Phenol + R
Complexation	: Quinone + Amino Acid/Protein ⇨ Complexes
Polymerization	: Quinone + Phenol+ O2 ⇨ Tannins
	Tannin + Protein ⇨ Complexes

color by means of three parameters.
Lightness (L): The light or dark aspect of a color. The lower the L value, the darker the cocoa powder will appear.

Chroma (C): The intensity of a color by which one distinguishes a bright or gray color. The higher the C value, the brighter the powder will be.

Hue (H): Color in daily speech, such as red, yellow, or blue. For cocoa powders, a low H value indicates a red color, and a high H value indicates a brown color.

Munsell classified all colors and shades on maps with color areas in an atlas according to the coordinates above. This meant that by comparing an object with one of the color areas in the atlas, colors and color differences could objectively be described.

The CIE color coordinates

A next step in the color theory was the quantification of colors that would enable color calculations. This development was based on the idea that colors are made by mixing the additive primary colors: red (R), green (G), and blue (B), corresponding with the three types of cones in the retina of the eye.

The disadvantage of this system was that certain colors had to be indicated with negative figures. This is why the Commission Internationale d'Eclairage (CIE) created three primaries, or tristimuli, indicated with the letters X, Y, and Z. These do not exist in reality but are derived mathematically from the original R, G, and B primaries, with which all colors can be expressed with positive figures.

The translation of X, Y, and Z values to L*, a*, and b* values according to the CIE system can be expressed as follows:

$L^* = 116 \times Y\%^{1/3} - 16$

$Y\% = Y/100$

$a^* = 500 \times (X\%^{1/3} - Y\%^{1/3})$

$X\% = X/98.072$[1]

$b^* = 200 \times (Y\%^{1/3} - Z\%^{1/3})$

$Z\% = Z/106.892$[1]

([1] 2º Standard Observer, Standard Illuminant D65)

Color differences

Although a mathematical description of the spectral colors was now available, the XYZ coordinate system still had difficulties with the color differences calculated. These did not correspond to visual observation. The human eye is less sensitive to color differences in the light area than in the dark area. A calculated identical color difference in the dark area was therefore experienced as greater than in the light area. Attempts to overcome this transformed the XYZ coordinate system with the help of conversion factors. An example is the Hunter color system, with coordinates L, a, and b, which can be calculated from X, Y, and Z as follows:

$$L = 10\sqrt{Y}$$

$$a = \frac{17.5\,(1.02\,X - Y)}{\sqrt{Y}}$$

$$b = \frac{7.0\,(Y - 0.847\,Z)}{\sqrt{Y}}$$

A number of transformed coordinate systems are still in use. However, none of them is completely satisfactory, so no universal agreement has been reached. This is why it is always necessary to determine which coordinate system is being used when discussing color.

The L coordinate is consistent with the Value of Lightness then introduced by Munsell, and from the a and b coordinates, the Chroma and Hue can be calculated as follows:

$$C = \sqrt{(a^2 + b^2)}$$

$$H = \operatorname{arctg}(b/a)$$

3. Measuring color

The source of light

The spectral color is the result of the source of light and the reflecting surface. So for a good reproducible measurement of color, it is essential that the source of light is standardized.

The CIE has defined four standard sources:

Source A: Incandescent light
Source B: Simulated noon sunlight
Source C: Simulated overcast sky daylight
Source D65: Daylight

A distinction is made between the following concepts:

- a source that defines the physical source of light, for instance, an electric bulb (source A)
- an illuminant that defines the theoretically defined division of spectral energy of the source of light. This is an index of numbers as a function of the wavelength. Of course, “source” has to be as close to “illuminant” as possible

In practice, “A” and “D65” are mainly employed as the light sources. Because the color measured depends on the light source used, this should always be stated with the measurement.

The reflecting surface of the sample

Reflection is largely determined by the morphology of the sample. When a light beam strikes a surface, it is partly passed through, partly absorbed, and partly reflected. Light reflects at an angle of incidence of 90°, and it is diffused at an angle of 45°.

When a surface is smooth, much light will be reflected. With a rough surface, the light will mainly be diffused, i.e. light is absorbed and re-emitted.

When using color meters, there are two ways in which the light should be directed onto the surface of the sample to minimize reflection:

- by means of a focused light source at an angle of 45° to the sample surface. Reflection is then minimized. However, the measurement can be susceptible to the orientation of the sample relative to the light source. Certain surface effects can result in differences in measurements.
- by means of an "integrating sphere," so that the light is directed onto the subject from all sides from the interior surface of a white sphere. Then, the color measurement is not dependent on the position of the sample relative to the light source. However, light is still reflected. In practice, this can be eliminated by making a hole in the sphere at the place where this light is reflected most.

Color measuring

There are two basic approaches for measuring color.

Visual judgment of color

Because of the natural human tendency to trust only one's own eyes, colors are still frequently judged only visually. To be able to do this in a reproducible manner, certain standard conditions have to be met:

- the light source, preferably one of the earlier mentioned CIE standards
- the position of the sample relative to the light source, preferably at an angle of 45° to each other
- the background of the sample, uniform and preferably gray
- the distance between the eyes and the sample
- the size of the sample

In practice, color cabinets are mostly used with standard light sources.

Instrumental color measurement

Color meters can be distinguished by their two measurement principles:

Tristimulus colorimeter

The diffuse reflected light that passes through four filters is measured with a photometer. The filters are made in such a way that they come as close to the spectral distribution of the Standard Observer as possible. The fourth filter is used to account for the correction in the second filter between 400 and 500 nm. One can then read the X, Y, and Z color coordinates directly. These instruments are mostly linked to a small computer. The color differences between samples and standards in one of the other coordinate systems can be calculated as desired.

Color spectrophotometer

Using this principle, the whole visible spectrum can be measured. The X, Y, and Z color coordinates are calculated by combining the measured spectrum and the theoretical spectra of the Standard Observer (CIE).

The spectrophotometer has a number of advantages:

- No filters are required. (These have to meet very high standards and are very hard to manufacture.)
- The color with different light sources can be calculated from the measured spectrum. From the spectra of the individual components, one can calculate the color of a mixture.

Color measurement is dealt with in Module 3: Methods of Analysis.

Health and Nutritional Aspects 6

1. Introduction

To the Aztecs, cocoa was not only a stimulant, but first and foremost a magical medicine, through which the properties of the four elements, Fire, Water, Air, and Earth, exercised their beneficial influence on humans. When cocoa initially became popular in Europe, it was also attributed quite a few beneficial factors. For example, in 1717, a German physician recommended cocoa as a product that: "strengthens the stomach, stimulates the spirits. It increases the venus lust, stimulates the working of the brain, and eases pain. It cannot be recommended enough both as a food and as a medicine." Quite a broad statement, and one that would not be acceptable today without elaborate support from scientific facts.

This chapter gives an overview of the current state of affairs with regard to the health and nutritional aspects of cocoa and cocoa products. A clear distinction is made between facts and fiction on one of the most popular foods known to mankind.

2. Manufacturer's responsibility

The increasing awareness of the relationship between the quality of the food we eat and the effects that food may have on our health understandably means that increasing demands are being placed on the food manufacturer to provide assurances that the products offered to the consumer are of high quality. This awareness has resulted in many countries creating legislation that holds manufacturers legally responsible for the safety of their products.

In this respect, ADM Cocoa is very much aware of its responsibility to its customers. Our products lose their identity as soon as they are incorporated in a customer's final product. From that moment on, they bear the name and reputation of that customer.

In Module 2, Cocoa Processing, we indicate how this responsibility is realized.

3. Indicative nutritional information

The nutritional data on cocoa liquor (Table 1 on page 76), cocoa butter (Table 2 on page 76), and cocoa powder (Table 3 on page 77) are provided. It should be kept in mind that the values are indicative. They may occasionally show significant variations due to natural fluctuations in the raw material.

Table 1: Indicative Nutritional Information on Cocoa Liquor

Main components	per 100 gram
fat	55.0 g
moisture	1.0 g
crude protein	11.1 g
theobromine	1.5 g
caffeine	0.1 g
sugars	0.3 g
starch	8.5 g
total dietary fiber	17.5 g
soluble dietary fiber	3.5 g
insoluble dietary fiber	14.0 g
flavonoids	3.5 g
organic acids	1.5 g
ash	3.0 g
Minerals	
potassium	1.0 g
sodium	<0.01 g
calcium	0.08 g
magnesium	0.3 g
phosphorus	0.4 g
chloride	<0.01 g
iron	12.5 mg
zinc	3.5 mg
copper	2.0mg
Vitamins	
- A (retinol)	1.0 mg (3,300 IU)
- B1 (thiamine)	0.1 mg
- B2 (riboflavin)	0.3 mg
- B3 (niacin)	0.5 mg
- C (ascorbic acid)	0.1 mg
- E (tocopherol)	15.0 mg
- pantothenic acid	1.0 mg
Energy (Atwater system)	
Kcalories	520
Kjoules	2,175
Kcalories from fat	460
Kjoules from fat	1,925

Table 2: Indicative Nutritional Information on Cocoa Butter

Main components	per 100 gram
total fat	99.9 g
moisture	0.1 g
Fatty acids (%)	
saturated	61.5%
monounsaturated	35.0%
polyunsaturated	3.5%
Fatty acid composition (%)	
palmitic	(C16:0) 26.0%
stearic	(C18:0) 34.5%
arachidic	(C20:0) 1.0%
palmitoleic	(C16:1) 0.3%
oleic	(C18:1) 34.5%
linoleic	(C18:2) 3.2%
others	0.5%
Minerals	
calcium	0.25 mg
copper	0.01 mg
iron	0.03 mg
magnesium	0.45 mg
phosphorus	50.0 mg
potassium	20.0 mg
Vitamins	
- A (retinol)	1.8 mg (6,000 IU)
- E (tocopherol)	20.0 mg (18 IU)
Energy (Atwater system)	
Kcalories	835
Kjoules	3,495
Kcalories from fat	835
Kjoules from fat	3,495

Table 3: Indicative Nutritional Information on Various Cocoa Powder Types			
	Non-alkalized	Lightly alkalized	Strongly alkalized
Main components	per 100 gram	per 100 gram	per 100 gram
fat	11 g	11 g	11 g
moisture	4 g	4 g	4 g
total N	1.25 g	4.15 g	4.10 g
N from alkaloids	0.80 g	0.80 g	0.80 g
N from crude protein	3.45 g	3.35 g	3.30 g
crude protein	21.5 g	21 g	20.5 g
theobromine	2.5 g	2.5 g	2.5 g
caffeine	0.25 g	0.25 g	0.25 g
sugars	0.5 g	0.5 g	0.5 g
starch (complex CHO)	16 g	15.5 g	15 g
total dietary fiber	34 g	33 g	32 g
soluble dietary fiber	7 g	7 g	6.5 g
insoluble dietary fiber	27 g	26 g	25.5 g
flavonoids	7 g	6 g	4 g
organic acids	3 g	3 g	2.5 g
ash	6 g	8.5 g	11 g
Minerals			
potassium	2.0 g	4.0 g	5.0 g
sodium	0.01 g	0.03 g	0.04 g
calcium	0.15 g	0.15 g	0.15 g
magnesium	0.55 g	0.55 g	0.55 g
phosphorus	0.7 g	0.7 g	0.7 g
chloride	0.01 g	0.04 g	0.05 g
iron	25.0 mg	25.0 mg	25.0 mg
zinc	7.0 mg	7.0 mg	7.0 mg
copper	4.0 mg	4.0 mg	4.0 mg
Vitamins			
- A (retinol)	0.2 mg (660 IU)	0.2 mg (660 IU)	0.2 mg (660 IU)
- B1 (thiamine)	0.2 mg	0.1 mg	0.05 mg
- B2 (riboflavin)	0.5 mg	0.4 mg	0.3 mg
- B3 (niacin)	1.0 mg	0.6 mg	0.5 mg
- C (ascorbic acid)	0.2 mg	0.1 mg	0.05 mg
- E (tocopherol)	0.3 mg	2.5 mg	2.0 mg
- pantothenic acid	1.5 mg	1.5 mg	1.5 mg
Energy (Atwater system)			
Kcalories	205	200	200
Kjoules	860	840	840
Kcalories from fat	90	90	90
Kjoules from fat	380	380	380

Fat (cocoa butter)

Most commercially available cocoa powders contain between 10 and 24% fat while the 10-12% fat range is the most frequently used. Cocoa butter contains specific flavor ingredients, antioxidants, and, as a vegetable fat, only traces of cholesterol (approx. 3.0 mg/100 g). The fatty acid composition (Table 4) shows that cocoa butter is rich in stearic, palmitic, and oleic acid. Recent publications suggest that cocoa butter is less easily digested, thus possibly influencing actual calorie per gram dietary calculations in the future.

Table 4: Indicative Fatty Acid Composition (%) of Cocoa Butter

palmitic acid	*(C16:0)*	26.0%
palmitoleic acid	*(C16:1)*	0.3%
stearic acid	*(C18:0)*	34.5%
oleic acid	*(C18:1)*	34.5%
linoleic acid	*(C18:2)*	3.5%
arachidic acid	*(C20:0)*	1.0%
others		0.2%
saturated		61.5%
monounsaturated		35%
polyunsaturated		3.5%

From these factors, low digestibility, high levels of stearic and oleic acid, and the presence of tocopherols (vitamin E), it can be concluded that consumption of cocoa butter may not pose a risk to human health. (See “Flavonoids” on page 80 in this module and ADM Cocoa’s technical information bulletin *Nutritional Functions of Cocoa and Chocolate in Human Food*.)

Moisture

The moisture content of cocoa liquor and butter should not exceed the indicated levels.

Cocoa powder is hygroscopic. If a cocoa powder has an excessive level of moisture, flavor may deteriorate, and the possibility of microbiological spoilage will arise. The actual moisture content of cocoa powders is lower than the moisture content found by analysis. The method of analysis used to determine the moisture content does not discriminate against other components that easily evaporate (such as certain organic acids) and disappear from the cocoa powder during the procedure. Because cocoa powder is hygroscopic, good packaging and storage conditions are essential to preventing the takeup of moisture. (See also Module 9: Packaging, Storage, and Transportation of Cocoa Powder.)

Cocoa powder is safe at a moisture content of up to 5%. ADM Cocoa’s production and packaging technology ensures that the moisture content of their cocoa powders is typically below 5%, provided the product is stored under proper conditions.

Proteins

Proteins are essential constituents of all living cells. Biochemically, proteins are built from amino acids as basic building blocks. Proteins are of great nutritional value and have numerous physiological functions.

In the tables, the total nitrogen as well as the nitrogen originating from the so-called crude proteins and alkaloids are given for cocoa liquor and cocoa powder. The crude protein is calculated from the nitrogen content. The Kjeldahl method is used to establish the total nitrogen content from which the nitrogen originating from the alkaloids is then subtracted from the total, and the result is multiplied by 6.25. (A factor based on the average nitrogen content of vegetable proteins.) The protein from cocoa powder is low in digestibility, probably because it forms a complex with certain polyhydroxyphenols (condensed tannins). An indicative amino acid pattern of cocoa protein is shown in Table 5. (Significant differences in amino acid patterns exist depending on the origin of the cocoa.) The effect of the alkalization is illustrated by the difference in the indicative amino acid profile of proteins for a natural process and an alkalized cocoa powder.

Table 5: Indicative Amino Acid Profile of Cocoa Powder Protein (in g/100 g cocoa powder)

Amino acid	Non-alkalized	Alkalized
isoleucine	0.75	0.70
leucine	1.22	1.13
lysine	0.93	0.61
methionine	0.29	0.26
cystine	0.45	0.34
phenylalanine	0.94	0.85
tyrosine	0.70	0.65
threonine	0.83	0.77
tryptophan	0.26	0.24
valine	1.17	1.10
arginine	1.32	1.17
histidine	0.32	0.28
alanine	0.86	0.77
aspartic acid	1.96	1.84
glutamic acid	3.28	3.08
glycine	0.85	0.79
proline	0.89	0.85
serine	1.05	0.93

Sugar and starch

Sugars are commonly occurring carbohydrates characterized by the presence of the saccharide group. They are a primary source of energy for the human body.

Whenever cocoa products are manufactured from good fermented cocoa beans that are roasted in the correct manner, they will contain only traces of mono- and disaccharides.

Starches, as complex polysaccharides, are the form in which carbohydrates are stored in plants. They are broken down during digestion.

The starch in cocoa liquor and powder consists of approx. 36% amylose and 64% amylopectin.

Dietary fiber

Dietary fiber in cocoa products is the collective term for the structural parts of plant tissues that are not or only partly digested. It is the modern term for what used to be referred to as “roughage” or “bulk.” In recent decades, it has been established that a diet high in fiber is recommendable. Dietary fiber has been found to reduce the risk of cancer in the digestive tract. See also ADM Cocoa’s technical information bulletin *Nutritional Functions of Cocoa and Chocolate in Human Food.*

The quantities of dietary fiber found in a product are largely dependent on the analytical method chosen to determine them. In theory, dietary fiber consists of the following components:

Structural polysaccharides
- cellulose
- hemicellulose
- pectic substances

Structural non-carbohydrate
- lignin

Non-structural polysaccharides
- gums
- mucilages

From the various analytical methods that are published for the determination of dietary fiber, ADM Cocoa uses the method developed by Prosky et al. for the following reasons:

- It gives an optimal picture of the dietary fiber.
- The method is relatively simple.
- It is the official method of the United States Food & Drug Administration (FDA) and the Association of Official Analytical Chemists (AOAC).

Flavonoids

From a nutritional standpoint, the most interesting components of cocoa powder are possibly the flavonoids. These are complex aromatic compounds widely found in nature as pigments in flowers, fruits, vegetables, and bark. Cocoa products consist of a relatively high percentage of these important components.

During fermentation, roasting, and alkalization of the cocoa, mono- and oligomeric-catechins may be partially polymerized into tannins. They play an important role in color formation and partly influence flavor. In addition, with the increase of molecular weight, reactivity with proteins and peptides increases. As a result, complexes that reduce the digestibility of the protein are created. The determination of flavonoids is not simple, so that the values shown have only an indicative character. These indicative values include a wide variety of polyphenolic compounds, including several flavonoids.

In literature, these compounds are known to possess antioxidative properties. This explains the long shelf life of cocoa powder and chocolate products. Moreover, research carried out in connection with the function of food-borne antioxidants suggests certain potential preventive effects against a number of chronic conditions including cancer and cardiovascular disease.

Organic acids

In the natural fermentation process of cocoa beans, organic acids such as acetic and lactic acid are formed. During further processing, these are partially converted or volatilized, but they represent some 1.5% of cocoa liquor and 3% of cocoa powder (in non-alkalized cocoa powder as the acids in alkalized cocoa powders as salts).

In addition to acetic acid, lactic acid, and citric acid, cocoa contains a small quantity of oxalic acid (approx. 0.5% on fat-free dry matter.)

Methylxanthines

Cocoa products contain theobromine, caffeine, and traces of theophylline. Depending on the degree of fermentation and the type of cocoa bean, the theobromine and caffeine contents will vary from 1.5-3.0% to 0.1-0.5% respectively.

The caffeine proportion of cocoa products made from good, fermented African cocoa beans is in general very low: 0.1% or less.

Despite its close chemical resemblance, theobromine does not possess the stimulant effect caffeine has on the human nervous system.

Ash

The ash content of cocoa products is the residue after the organic matter has been subject to incineration. It indicates a measure of the presence of the inorganic salts in the original material.

The natural ash content of non-alkalized cocoa liquor and cocoa powder is approx. 7.0% of the fat-free dry material. The ash content in alkalized cocoa powder is affected by the type and quantity of alkalis that are used in the alkalization process itself. The EU directive 95/2/EC on food additives other than colors and sweeteners allows max. 7% potassium carbonate (or equivalent on fat-free dry basis) to be added for alkalization. In the U.S., the CFR 163.110 states that 3% of potassium carbonate may be added to cocoa nibs for alkalization.

When the ash content of cocoa powder is determined, it is frequently combined with the determination of the alkalinity of the ash. This is important for certain applications. For instance, in baking, it does have an effect on the characteristics of certain baked products and is a better and more objective parameter than pH. The latter can easily be influenced and is dependent on the production process but also the age. (The pH of alkalized cocoa powder may drop during storage, particularly when moisture has been picked up.)

Minerals

The minerals shown in the tables on pages 76 and 77 are those for which the greatest interest exists. Naturally, there are many other minerals present in cocoa products for which information is available at ADM Cocoa's Technical Service Departments.

Of those mentioned, potassium and sodium are of primary importance. Potassium is generally regarded as beneficial for humans. It fulfills a role in the synthesis of proteins and the formation of glycogen in the human body.

The natural potassium content of cocoa powder is relatively high at approx. 2%. As a result of alkalization with potassium carbonate, this number may rise to 5%.

In the manufacture of dark brown powders, sodium hydroxide is often used. This can raise the natural sodium content of 0.01% to more than 2%. So, in cocoa powders in which these darker components are incorporated, an increased sodium content may be present.

Vitamins

Vitamins are naturally occurring organic substances that are essential in very small quantities for the normal functioning of living cells. Cocoa products are not an important source of vitamins. As shown, vitamin A is negligible; the quantity of vitamin C is very low, and the B-group vitamins are also low and decline further in alkalized cocoa powder as a result of the alkalizing process. The presence of vitamin E (tocopherol) and to a lesser extent, vitamin A, in cocoa butter is an exception.

Energy

Interest in the caloric value of food products is currently high because of consumers' sensitivity to diet.

The amount of cocoa powder in a product is generally low in comparison to, for example, sugars and fats. The caloric value of cocoa powder is also intrinsically low. Cocoa powder thus contributes little to a product's total caloric value and thus has minimal effects on total energy intake. The caloric values for cocoa liquor and cocoa butter are, of course, correspondingly higher.

There are various methods available to calculate the caloric value of cocoa powder. ADM Cocoa follows the U.S. FDA recommendation for the use of either the specific Atwater food factors or the general factors: 4 for protein, 4 for carbohydrate, and 9 for fat in calories per gram, as described by Merrill and Watt.

In the application of Atwater factors, the following calculation of caloric value is used:

% fat x 0.9 (Digestibility Coefficient)
x 9.3 (Heat of Combustion) + % protein
x 0.42 (D.C.) x 4.35 (H.C.)
+ % carbohydrate x 0.32 (D.C.)
x 4.16 (H.C.) = % fat x 8.37 + % protein
x 1.83 + % carbohydrate x 1.33
= caloric value

In this, the following should be considered:

- **Digestibility Coefficient (D.C.)**
  The digestibility coefficient is a measure of the proportion of a food absorbed into the bloodstream. It is measured as the difference between intake and fecal output, with an allowance made for that part of the output not derived from undigested food residues, such as the lining of the intestinal tract, digestive juices, etc.

- **Heat of combustion (H.C.)**
  This is the energy released by the complete combustion or oxidation of a food. With allowances made for materials not oxidized in the body, the values are used to indicate energy availability.
- **Carbohydrate**
  The proportion of carbohydrate is obtained by means of the so-called difference method:
  100 - (crude protein + fat + ash + moisture)
- **Protein**
  In order to not overestimate the content of carbohydrate, not crude protein but total nitrogenous matter (obtained by multiplying total nitrogen by 5.63 (Merrill and Watt)), is used as the basis for calculating carbohydrate by difference.

If the general factors (4, 4, and 9) are used for calculating the caloric value, then the determination of the carbohydrate content is made according to the following difference method:

100 - (crude protein + fat + dietary fiber + ash + moisture)

(Because dietary fiber is not digestible.) The protein content is, in this case, calculated from total N x 6.25.

This last calculation leads to higher energy values than the Atwater approach. Considering the fact that bomb calorimetry measurements compare well with the results of the Atwater calculations, and taking into account recently published information on the lower digestibility of fat-free dry cocoa components, the Atwater system for the energy values are shown in Tables 1-3 on pages 76 and 77.

4. Cocoa and allergies

Food allergy is a phenomenon vastly misunderstood by the general public. For example, the American Academy of Allergy, Asthma, and Immunology has found that as many as one-third of American adults believe they are allergic to at least one food, whereas in reality, less than 2% of Americans actually have a true food allergy. For children, this figure is about 5%; however, many children seem to outgrow their hypersensitivity.

Food allergy is caused by an overreaction of the immune system. It identifies a harmless substance, often a particular protein, as an antigen. To fend off the "invader," antibodies are produced that ultimately lead to symptoms of allergic diseases like asthma, eczema, and hay fever. In some cases, the reactions can be very serious and even life threatening.

Chocolate is often mentioned as being allergenic. More often than not, it must be seen in the light of the above-mentioned gap between perception and reality. Clinical tests have been carried out on a group of adults suspected of allergic reactions to chocolate. From the test results, it was concluded that chocolate allergy is rare in adults.

Nevertheless, food allergies must have the undivided attention of the food and confectionery industries. In chocolate and cocoa-flavored products, a wide range of different raw materials is used in an almost endless variety of consumer products. It is of paramount importance that the food manufacturer properly labels the products (e.g. the presence of nuts, even in trace amounts) to give the consumer the opportunity to select a food on the basis of the presence of possible allergens.

Cocoa Liquor 7

1. Functionality and attributes of cocoa liquor

Introduction

Cocoa liquor is the product from which cocoa butter and cocoa powder are made. It is also the base raw material for making chocolate. No other ingredient in the chocolate formula has such an impact on the ultimate outcome of the product as cocoa liquor. Dark chocolate is basically a mixture of liquor, sugar, and cocoa butter, whereas in milk chocolate, milk powder has also been added.

Typical Chocolate Recipes

	Dark chocolate	Milk chocolate
Sugar	50%	45%
Cocoa liquor	45%	10%
Cocoa butter	5%	25%
Full cream milk powder	Ð	20%

In combination with the chocolate manufacturing process, each of these components has a specific influence on the final characteristics of the chocolate product. However, cocoa liquor is always the dominant factor in determining the chocolate experience of the consumer.

Although cocoa liquor is sometimes used as a flavoring component in other food products, its principal use is as an ingredient in the manufacturing of chocolate. Within the scope of this chapter, we focus particularly on the attributes of cocoa liquor as a raw material for chocolate. A number of these attributes are highlighted as they relate to quality aspects of the end-product, while others are mentioned because they are important to the user of liquor in the chocolate production process itself.

It is not uncommon to use different words for the same product or raw material. This is the case with cocoa liquor. It is also often called cocoa mass, sometimes cocoa paste, and in the United States, it is referred to as unsweetened chocolate, chocolate liquor, or simply chocolate. It was the cocoa press industry that introduced the name "cocoa liquor." As this industry today supplies the bulk of this raw material to the merchant market, we believe that the name "cocoa liquor" has become more familiar to the cocoa and chocolate industry as compared to other industries. In the context of this book, we have chosen to refer to this product as "cocoa liquor" or simply "liquor."

Standard of identity

Most countries provide a definition of cocoa liquor in their food laws. From country to country, the definition may vary somewhat, but in Codex Standard 141-1983, Rev. 1-2001, cocoa mass or liquor is described as "the product obtained from cocoa nib from cocoa beans of merchantable quality which have been cleaned and freed from shell as thoroughly as is technically possible (with/without roasting and with/without removal of or addition of any of its constituents)."

The European Directive 2000/36/EC relating to cocoa and chocolate products does not contain a definition of cocoa liquor. In the U.S., cocoa liquor is described in CFR 163.111 as the solid or semi-plastic food prepared by grinding cocoa nibs (which can be alkalized), allowing a maximum of 1.75% shell based on alkali-free nibs. Legislators have left it up to the chocolate maker to decide in what stage of the production process the roasting takes place. Whole bean roasting, nib roasting, or liquor roasting can be used.

The Federation of Cocoa Commerce (FCC) defines cocoa mass or liquor as obtained from cocoa nib (roasted or unroasted, max. 5% shell and max. 10% ash, both on a fat-free dry basis), mechanically processed to a paste, which retains the natural fat content of the cocoa nib.

In some countries, an important aspect in the marketing of chocolate is that if a certain percentage of the cocoa liquor used is made from so-called fine or flavor beans, the final product may be called fine grade chocolate (*Edelschokolade* in German). The International Cocoa Organization (ICO) listed in the International Cocoa Agreement of 1993 certain cocoa bean origins as flavor beans (*Edelkakao* in German). Cocoa beans from the following countries are designated as fine or flavor beans: Dominican Republic, Grenada, Jamaica, St. Lucia, St. Vincent, Samoa, Surinam, and Trinidad & Tobago. In addition, from the following countries only a portion of the cocoa export may be called fine or flavor beans: Colombia, Costa Rica, Ecuador, Indonesia (Java), Madagascar, Sao Tomé & Principe, Papua New Guinea, Sri Lanka, and Venezuela.

Some chocolate manufacturers emphasize to the consumer that their products are made of a particular cocoa bean origin, aiming at a special market position. However, selection of sound and well-fermented beans of most origins, in combination with proper processing, can result in a whole range of flavors.

The personality of chocolate

When discussing cocoa liquor, it is almost inevitable to directly deal with its prime application: the making of chocolate. It plays such a predominant role in determining the ultimate flavor of the chocolate that it is justified to extensively dwell on the subject of how the flavor in cocoa liquor is developed.

The flavor of cocoa liquor is dependent on three very distinct and equally important factors:

- the type of cocoa bean used (generic background and growing conditions)
- the flavor precursor development in the bean during fermentation and drying, as well as the first steps in further handling
- the flavor formation during subsequent processing

Bean type and bean quality are major factors in determining the flavor characteristics of the final product. Subsequent processing can be further influenced by the choice of equipment and by varying the processing conditions, thereby tailoring to the specific flavor needs of each individual customer. Obviously, that specific flavor has to be reproduced time and again to assure that the customer receives what is expected: that typical, recognizable, and unique house flavor. *In short, the cocoa liquor determines the personality of the chocolate.*

Cocoa bean selection

In Module 1, the various types of beans with their specific characteristics were discussed. Differing cocoa bean types and beans from different origins each have their own flavor potential. Therefore, choosing a particular type of bean to be used for cocoa liquor is of paramount importance. This does not mean simply specifying the origin of the bean, as both short- and long-term influences have an impact on the flavor potential. Among the short-term effects are climatological aspects and crop handling, in particular fermentation and subsequent drying of the beans. Longer-term factors are the genetic history of the bean, soil conditions, the age of the trees, and crop management, all of which must be taken into account. During recent years we have seen significant changes in the availability of certain types of cocoa beans. Industrial processors have had to adjust to a 50% drop in the supply of Brazilian cocoa. Malaysian bean production rose rapidly in the late '80s, only to fall back again in the '90s. The Ivory Coast has increased its output to more than 40% of the total world crop. Indonesia has shown a tremendous increase in cocoa production, but the flavor potential of the beans coming from the various regions is vastly different, as a substantial part is unfermented.

Crop management is another factor: In Ecuador, producer of the unrivaled Arriba beans, there are fewer and fewer true Arriba-yielding trees. They are being replaced by hybrids that yield a far higher bean production per acre but lack the unique flavor of the original Arriba cocoa. Similar examples can be found in other cocoa growing areas.

At the same time, the cocoa trade itself has experienced important changes (e.g. the privatization of the cocoa trade in some countries of origin), making direct control over the selection of beans even more important. Obviously, only ripened, good fermented, and adequately dried cocoa beans will lead to good quality cocoa liquor. During fermentation and subsequent drying of the cocoa beans, the flavor precursors are developed. They will ultimately come to their full flavor during roasting. The initial stages of pretreatment of the beans prior to roasting, as discussed in Module 4, will influence the precursor formation as well.

Even the best starting material will fail to deliver its potential if it has not been treated correctly. For that reason, ADM Cocoa has established itself on every cocoa-growing continent. Having resources and an actual presence in the major cocoa growing areas not only assures that ADM Cocoa is able to procure the cocoa needed to produce the desired products, but also enables participation in rapidly changing local cocoa environments, as well as direct control over bean quality.

Processing equipment

Cocoa processing has progressively developed over the years. Many production systems are available, from whole bean roasting to nib roasting, special steps to reduce the overall plate count, and thin film techniques for even better homogenous roasting.

The two most commonly used roasters are:

- contact roaster, in which batches of cocoa nibs are heated in a large rotating drum
- continuous air roasters, whereby cocoa beans or nibs are roasted by direct contact with hot air

Some prefer liquor from whole bean roasting; others prefer nib-roasted liquor. Both methods are very adequate and can produce similar but also distinctly different types of cocoa liquor. This can be even further accentuated by pretreatment of the nibs, during which they are wetted and heat treated to reduce the plate count.

Temperature, moisture content, and air throughput are very different in both types of equipment, resulting in quite different types of liquor. Nib contact roasters and whole bean roasters are particularly suitable for delicate top-note flavors that mark the bouquet and richness of cocoa. On the other hand, if full-bodied chocolate flavors with pronounced cocoa and bitter notes and lower acidity and astringency are required, an air nib roaster is the better system. Nib contact roasters and whole bean roasters are recommended for processing the fine flavor beans and for low and medium roasting of West African beans. Air roasters are excellent for West African cocoas that require full development of their typical cocoa and bitter potential. See Figures 1-4 below.

If subsequently the cocoa liquor is subjected to a thin film treatment, a process whereby the astringent and acid notes are significantly reduced, the conching time of the chocolate can also be reduced considerably. See Figure 5 on page 89.

In the manufacturing of chocolate, the conching process allows some of the natural volatile flavoring components that do not have a favorable effect on the taste of the chocolate to escape.

Each of the different types of equipment has specific features. By combining them in the appropriate manner, the best can be brought out of each of the different bean origins and particular bean blends. ADM Cocoa produces a range of liquors, with and without subsequent thin film treatment.

Figure 1

Temperature and Moisture Content During Air Roasting of Nibs

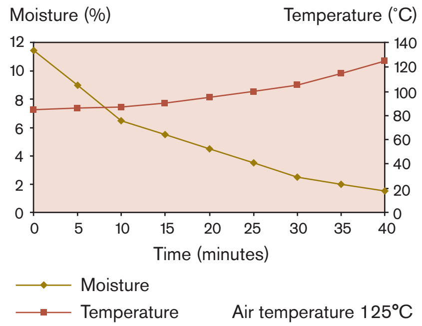


Figure 2

Temperature and Flavor Index During Air Roasting of Nibs

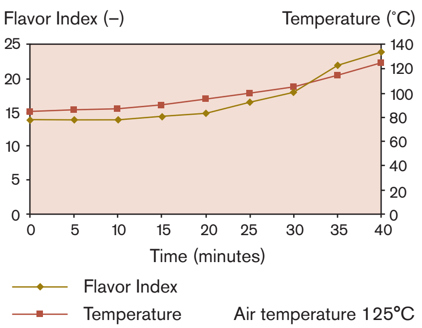


Figure 3

Temperature and Moisture Content During Contact Roasting of Nibs

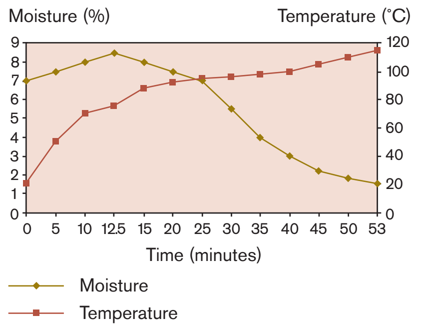


Figure 4

Temperature and Flavor Index During Contact Roasting of Nibs

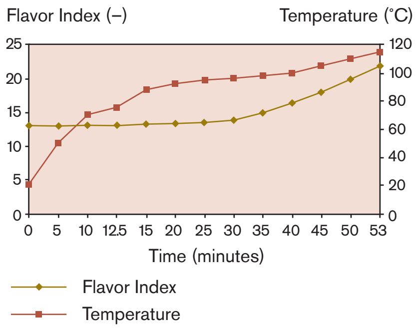
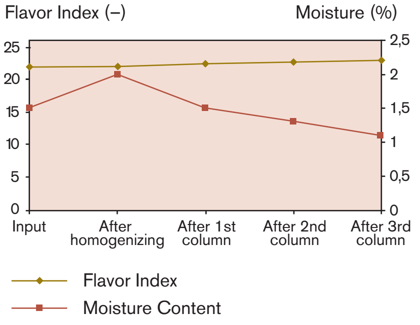


Figure 5

Flavor Index and Moisture Content During Thin Film Treatment of Liquor

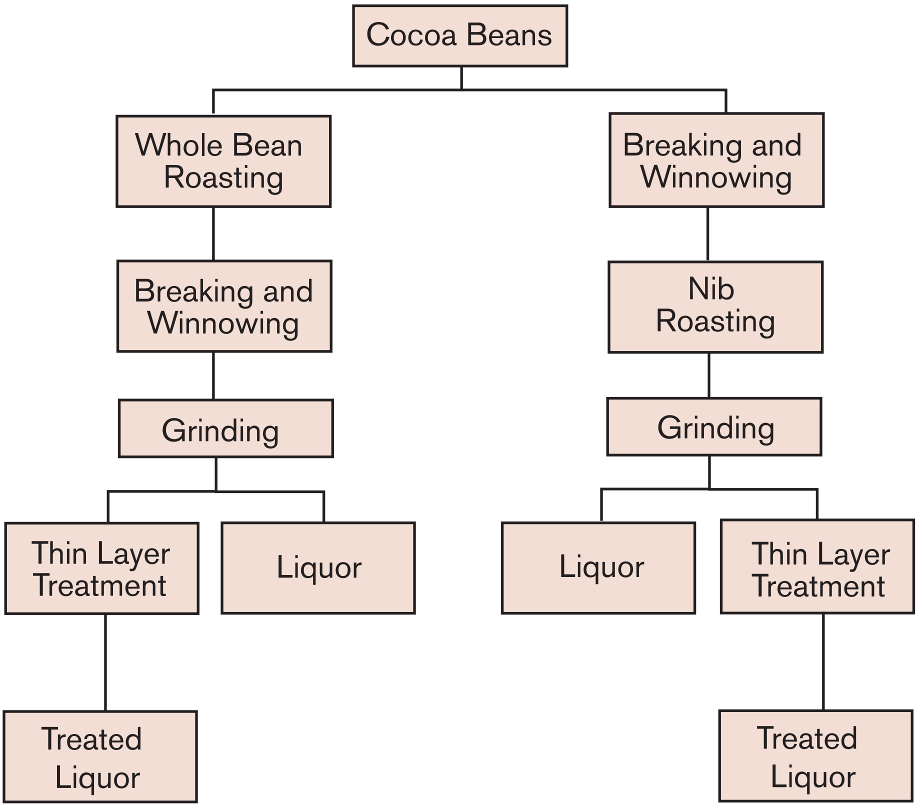


Flavor

To be able to determine the flavor profile of a cocoa liquor, six different descriptors have been defined: favorable ones like cocoa, bitterness, bouquet, and richness/body, and less favorable ones such as astringency and acidity. Off-notes are classified separately under descriptors like burnt, hammy, smoky, moldy, earthy, and woody.

The ultimately desired chocolate flavor may vary considerably, not only from manufacturer to manufacturer but also regionally. Some consumers prefer a robust flavor, whereas others prefer a mild flavor like that of milk chocolate. Principle Component Analysis uses biplots to determine the flavor profile.

Cocoa Liquor Processing Methods



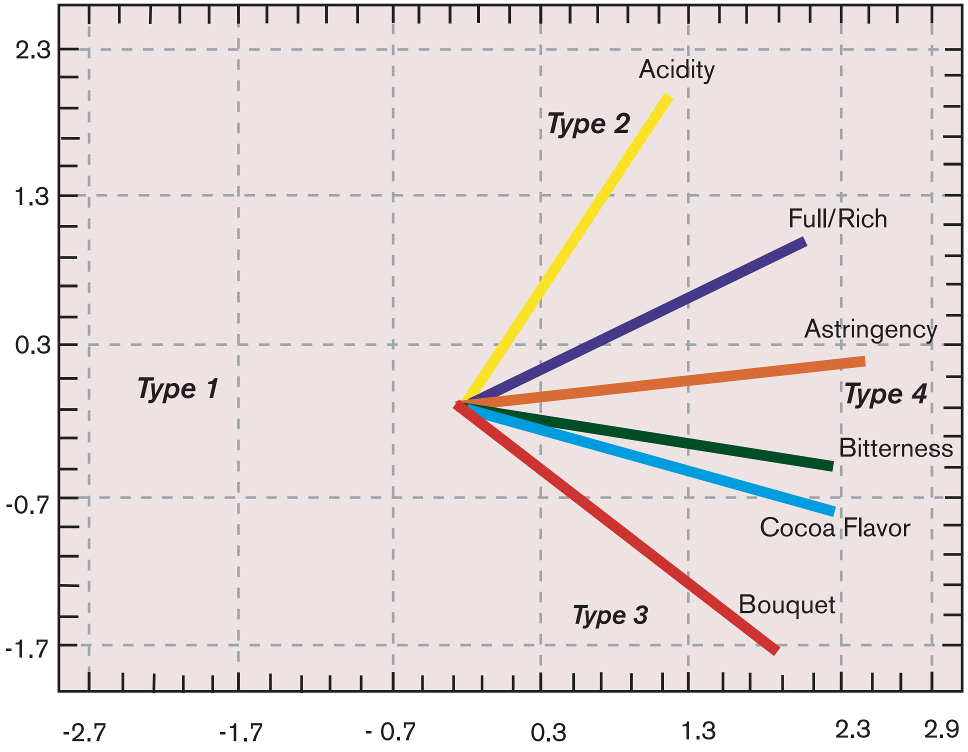
An example, based on four differently processed cocoa liquors made from the same blend of West African main crop cocoa beans, is given in Figure 6.

Principle Component Analysis is a method used to easily gain insight into the complex connections between many variables, such as in the case of a sensoric analysis. The information contained in the variables is reduced by grouping the most important variables on the basis of their inter-related connection. By means of these groups of variables (dimensions), a graph can be drawn to show the essential information of all the data.

The variables in the graph are indicated as lines. The angle between two lines indicates the degree to which the variables are inter-related, whereas the length of the line indicates the significance of the variable. The placing of the products in the graph emphasizes the variables applicable to that product. In order to be meaningful, however, the two dimensions shown in the graph must explain the greater part of the variation.

As can be deduced from the biplot, very different flavor profiles can be obtained to meet the needs of the individual chocolate maker, from low roast, thin

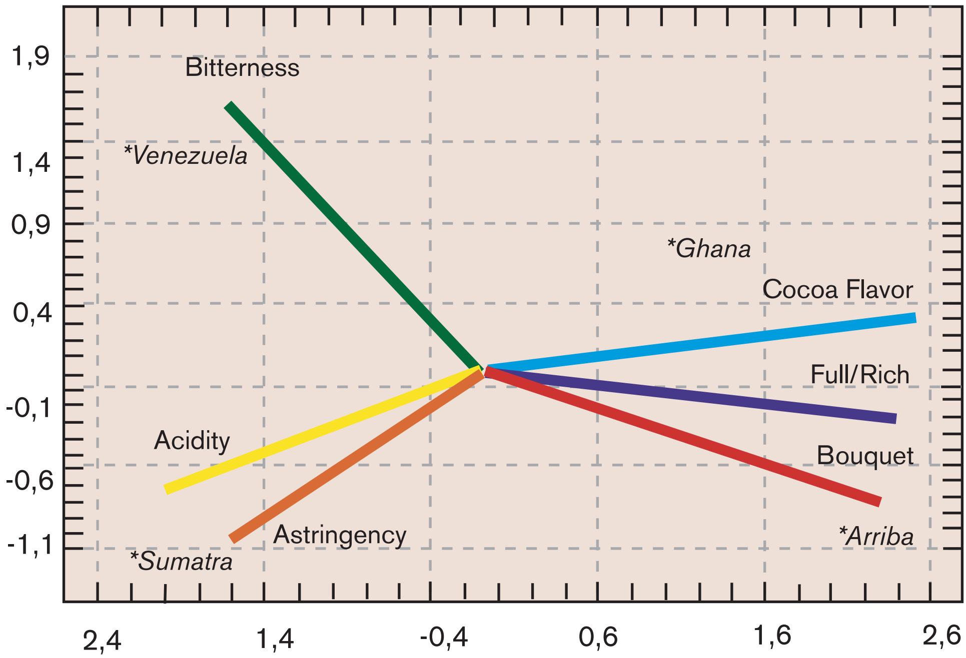
Figure 6: Principle Component Analysis of Four Cocoa Liquor Types Based on the Same Bean Blend of West African Origin



Horizon axis: Component 1
Vertical axis: Component 2

Type 1 - Low roast + thin film treatment
Type 2 - Medium roast
Type 3 - Full roast + thin film treatment
Type 4 - Full roast

Figure 7: Principal Component Analysis of Various Cocoas



Horizon axis: Component 1
Vertical axis: Component 2

film-treated to fully roasted cocoas.

When using different cocoa bean sources, the rich palette of different flavor characteristics can be enlarged. In Figure 7, the flavor profiles for four different cocoa liquors are shown, each produced under similar conditions and made from cocoa from the same source.

Clearly, the typical flavor aspects come forward:

- Arriba, known for its unique bouquet, with flowery, honey, and nutty top notes
- Venezuela, with its characteristic cheesy, nutty bitterness
- Sumatra, with its extreme acidity and astringency
- Ghana, known for its full chocolate flavor

Color

The roasting process of good fermented beans renders a characteristic brown color to the cocoa liquor. Differing roasting conditions may lead to color differentiation in the liquor. A low-roasted liquor will have a slightly lighter color compared to a high-roasted liquor. In chocolate, however, these color differences will not be very distinctive. The color of Criollo beans is somewhat lighter than the Forasteros' color, but this difference mostly disappears after roasting.

Some bean types, the so-called light breaking beans such as from Java and from Madagascar, are substantially lighter in color compared to others. Both of these bean types are classified as fine flavor beans, and they not only enable the manufacturer to produce a chocolate with typical value-added top flavor and color notes, but they may also call their chocolate fine-grade chocolate (*Edelschokolade*) in the European Union. Thus, both the applied technology and the chocolate formula make it possible to influence the color of the end-product.

Fat content

Usually, cocoa butter is the most expensive ingredient in the chocolate recipe. Cocoa liquor contributes a significant amount of cocoa butter to the chocolate formula, so using cocoa liquor favorably affects the total raw material cost of the chocolate.

Depending on the bean origin and its quality, the fat content of the nib usually varies between 50 and 57%. Small beans contain proportionately less fat and more shell compared to large beans, and main crop beans have a higher fat content than mid-crop beans. Seasonal effects, such as the amount of rainfall, may cause the fat content to fluctuate.

Cocoa liquor made from good quality main crop bulk beans from West African countries such as Ghana, Ivory Coast, and Nigeria have a cocoa butter content higher than 54% of the dry matter. Criollos such as Ecuadorian and Venezuelan beans usually have a somewhat lower fat content. The resulting liquor should normally have a butter content of 50%. The same goes for Asian types such as Java beans.

It should be noted that adverse climatic and growing conditions have a direct negative influence on the butter content of the bean. If the fat content of the liquor fluctuates too much, problems may arise during chocolate production.

Significant fluctuations in fat content will lead to differences in the consistency of the chocolate mass, requiring continuous adjustment of the roller refiners. This will cause problems with respect to the particle size distribution after refining, as the result of which the desired viscosity of the chocolate is not reached. It is therefore necessary to keep the fat content of the cocoa liquor as constant as possible.

Fineness

Cocoa liquor as an ingredient is ground again during the production of chocolate, usually on a five-roller refiner. Therefore, the impression could mistakenly arise that the fineness of cocoa liquor is of secondary importance.

For two reasons, the fineness of the cocoa liquor itself is of paramount importance in the production of chocolate:

- the availability of free fat
- the maintenance cost of roller refiners

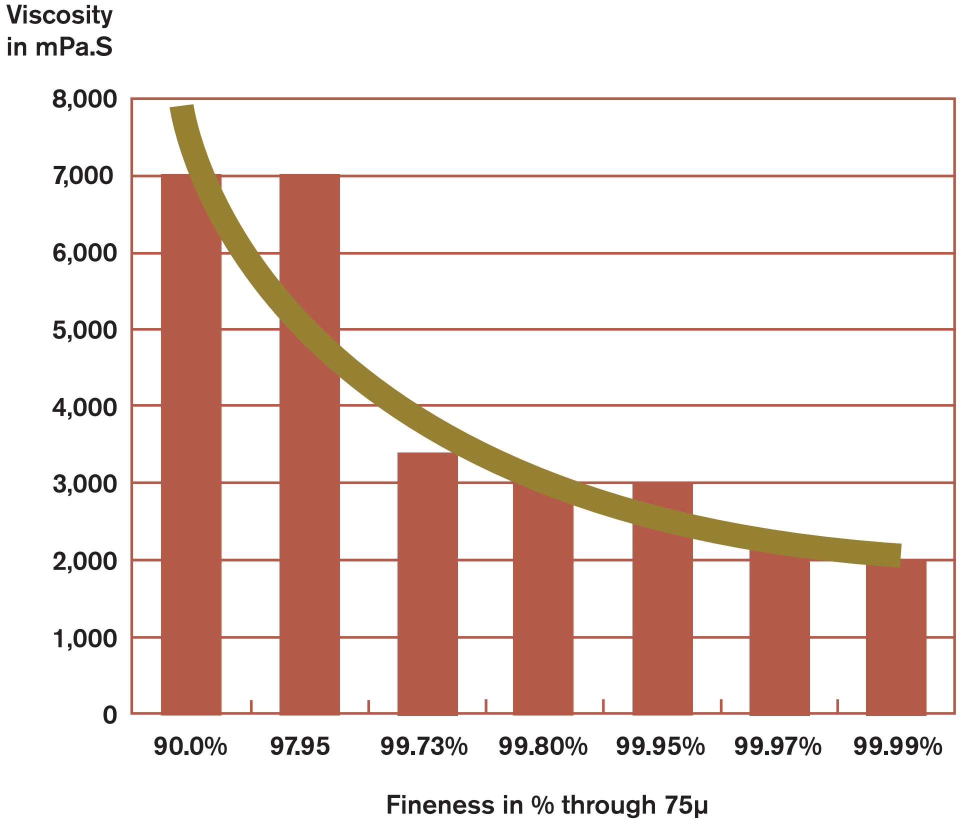
Free fat

In the nib, the cocoa butter is encapsulated in the plant cells. During the grinding of the nib into cocoa liquor, the fat is released, and the physical form of the product, above 35° C (95° F), is changed into a paste. In case the plant cells remain intact, the fat will not be released and thus will not be available to participate in the continuous phase in the cocoa liquor and, later on, in the chocolate.

It would be optimal if all of the cocoa butter in the liquor were already present as free fat in the kneader. The fat can, of course, still be released during the refining stage of the process, but this may lead to extra slip of the upper rollers, then to undesirable extra fine particles in the chocolate. In Figure 8, the influence of the fineness on the viscosity of a West African cocoa liquor is demonstrated.

There is, however, an optimum fineness and particle size distribution of the cocoa liquor. If too many very fine particles are present, increasing the specific surface of the fat free matter exponentially, the viscosity of the liquor would increase as well, thereby creating the opposite result.

Figure 8: Influence of the Fineness on the Viscosity of a West African Cocoa Liquor



Maintenance cost

The fat-free dry matter of cocoa liquor consists mostly of fibrous material. Fiber material is difficult to disintegrate. The grinding of cocoa liquor demands not only a vast amount of energy, it also causes significant wear on equipment. In particular, the five-roller refiner is subjected to this wear. Repair or maintenance of such refiners is costly. In cases where the cocoa liquor being processed is too coarse, further disintegration of the particles will take place on the roller refining equipment, leading to excessive wear. The difference between an adequate and an insufficient fineness of cocoa liquor can lead to a difference in terms of downtime of the refiner of a factor 4 to 5.

Furthermore, in chocolate recipes with very high liquor contents, part of the liquor has to be added in the conching stage, as the total fat content would be too high to pass through the refiners without causing problems. However, this can only be done if the cocoa liquor is sufficiently fine. If the cocoa liquor contains too many coarse particles, these particles will appear in the chocolate as separate specks.

Rheology
Obviously, both the fat content and the fineness of the cocoa liquor have a direct influence on the viscosity of the product. Other factors, however, are also of importance, such as the moisture content, the time and intensity of processing, and the shear forces to which the liquor is subjected during production. From this, one can safely conclude that the lower the viscosity of the cocoa liquor, the better the rheological properties in the chocolate, with minimal fat content.

Microbiology
Certainly, all ingredients to be used in food products should be of excellent microbiological quality, regardless of whether these ingredients will be subjected to an adequate reduction of microorganisms during further processing into a finished product. Similarly, it is no longer sufficient for a supplier to specify only a maximum plate count for a particular food ingredient.

The water activity of cocoa liquor and chocolate is usually too low to permit development of microorganisms. On the other hand, pathogenic organisms such as *Salmonellae* can survive in the fat medium of both these products.

Furthermore, cocoa liquor, and the chocolate made from that liquor, can be used in combination with other products in which microbial growth conditions are favorable. Therefore, ADM Cocoa specifies that all of our cocoa liquors comply to strict microbiological values. For flavor beans that are usually subjected to mild roasting conditions, a maximum plate count of 25,000/g is specified, whereas for standard liquors a maximum of 5,000/g is given. In both cases, the median value is normally a factor 10-20 lower, and the presence of certain pathogens, including *Salmonellae*, is monitored.

Lipase activity and cocoa liquor
Enzyme activity forms an integral part of live seeds, and the cocoa bean is no exception to this. In particular, the fat-splitting lipase enzyme is undesirable in most food products. Splitting or hydrolization of fats (triglycerides) produces free fatty acids and di- and monoglycerides. Short chain fatty acids in particular produce strong off-flavors at very low concentrations. For instance, when lipase is introduced to lauric fats such as coconut oil and sufficient water is available, saponification may occur. The resulting soapy flavor is caused by the lauric acids formed. In a similar way, if lipase catalyzes the hydrolysis of butter fat, strong rancid notes will become apparent.

This normally will not occur in cocoa liquor and chocolate, but in products such as ice cream coatings and filled chocolates (bonbons), conditions may be appropriate for enzymatic activity. Thus, when lauric fats are present in chocolate product formulations, lipase-free ingredients should be used.

2. The application of cocoa liquor

Chocolate
The overall taste perception of chocolate is, to a large extent, the result of a balance between the sweetness of sugar and the bitterness of the cocoa liquor. Relatively small variations may have a significant influence on that balance. The degree of roasting as well as the origin of the cocoa can change the perception of the bitterness of the cocoa liquor substantially. A chocolate product that is perceived as too bitter can be corrected by using cocoa liquor with a milder flavor. Such a correction, however, can often also be achieved by merely increasing the sweetness of the product. Similarly, a chocolate product that is found to be too sweet can be harmoniously balanced without having to

reduce the sugar content by adding a somewhat stronger-flavored cocoa liquor.

Supporting flavor ingredients such as vanillin are often instrumental in rounding off the total flavor impression. Quite a large number of spices and herbs have been described in literature as enhancing the overall chocolate flavor.

The fineness of chocolate is an important factor in both the color and the flavor of the product.

The finer the chocolate, the lighter its color will be. The flavor experience of such a product will also be more rounded and more harmonious. This is particularly true for chocolate with a median particle size (<18μ). In coarser material (>25μ), the harsher flavor components, like bitterness, will come forward in a more pronounced manner.

As a rule, chocolate with a high liquor content is very finely ground. When the high amount of cocoa liquor causes the fat content of the chocolate mass to become too high, this mass can no longer be fed over the roller refiners. In such a case, part of the cocoa liquor must be directly added to the conching equipment. This can only be done if the liquor has a sufficient fineness.

Other applications

Apart from chocolate, cocoa liquor is also used in other applications, though only in modest amounts. In ice cream, ice cream coatings, bakery products, chocolate drinks, and desserts, the use of cocoa liquor is sometimes preferred over that of cocoa powder. Usually, it is then a matter of weighing the chocolate flavor against the flavor of cocoa powder.

Adding a proportionate amount of cocoa butter to cocoa powder will not provide a comparable flavor to the flavor produced from cocoa liquor. The conditions to which the liquor is subjected during the press operation lead to a certain loss of the typical chocolate flavor notes in the resulting cocoa powder.

If cocoa powder is not able to give an adequate chocolate flavor in a particular end-product, then either chocolate or cocoa liquor can replace it. Notably, in Europe, labeling a product "made with real chocolate" is a strong consumer marketing tool. In that case, chocolate must indeed be the ingredient used. In other parts of the world, the use of the word "chocolate" seems to be of lesser importance, and consequently, the alternative ingredient could instead be the thin film pre-treated cocoa liquor, which resembles the flavor of a liquor that has been subjected to a conching treatment.

3. PACKAGING, STORAGE, AND TRANSPORTATION

Cocoa liquor as a rule is used in liquid form. Large users accept the product in tank trucks in liquid form as soon as this is logistically feasible. Transportation must take place in clean, odor-free, dry tanks that are exclusively used for food-grade products and that have proper insulation. Loading temperature of the cocoa liquor should be between 55°-65° C (131°-149° F). During transport, depending on the distance, the temperature of the liquor may drop somewhat, but at the point of discharge, the temperature should not be below 45° C (113° F).

Cocoa liquor is a dispersion of very fine particles in cocoa butter. When it is stored in tanks, these particles will settle to the bottom of the tank (the lower the viscosity, the quicker this will happen).

In order to avoid settling on the bottom part of the tank and prevent the liquor from dehomogenizing, it is necessary to stir the liquor regularly.

Usually, an intermittent scraping/stirring device is installed to keep the liquor moving during the entire storage time and protect it from overheating and settling.

Special care must also be taken to prevent condensation in the storage tank. This may especially occur near the manhole or the lid of the tank. These should be properly insulated or traced.

Cocoa liquor is a very stable product. Still, for prolonged optimal storage in liquid form, it is advisable to keep the temperature of the product, under stirring, between 40°-45° C (104°-113° F). Storage tanks can be heated by hot air in a hot room where the tank is located, by a jacket, or by an internal hot water spiral. Steam heating should be avoided, as this may raise the contact temperatures too high, causing after-roasting.

Designating tanks for the exclusive storage of cocoa liquor is recommended. They need not be made of stainless steel. As long as the tanks are used properly and regularly, it is also not necessary to clean them. If, for whatever reason, a tank has to be cleaned, the inside must be completely dried and rinsed with cocoa butter before it is put in use again.

When cocoa liquor cannot be received in liquid form, it can be supplied in cartons in solid blocks of 25 kg or in kibbled form in bags of 25 kg.

In solid form, the liquor must be protected against direct sunlight and other heat radiation sources during transportation. Store in cool (15°-20° C/59°-68° F), dry (RH <50%), dark conditions.

Temperature fluctuations should be avoided. During melting of the liquor, avoid overheating and be sure the contact temperature does not exceed 90° C (194° F). In the spirals of the melting tank, use warm water rather than steam, as this would raise the contact temperature too high.

Cocoa liquor is a product with a high fat content—about 50% of it is cocoa butter. Like all high fat products, cocoa liquor easily absorbs foreign odors. During storage, be sure no undesirable odors are directly exposed to the cocoa liquor, as the product will quickly absorb these.

4. Specification for cocoa liquor

The standard specification of a natural-process (non-alkalized) cocoa liquor is based on West African cocoa beans and applies to an average sample of a consignment leaving the production plant, determined with the company's standard

Standard Specification	
Flavor	up to standard
Fat content, extraction with petroleum ether	50-51% or 52-54% or 54-56%
pH	5.3-6.0
Fineness (%), 75µ sieve, water-suspension	99.0 min. (or micrometer fineness 10-12)
Moisture content (%)	1.5 max.
Standard plate count	5,000 max. (or up to 25,000 max.)
Molds per g	50 max.
Yeasts per g	50 max.
Molds and yeast per g	100 max.
Enterobacteriaceae *in 1 g*	negative
E. coli *in 1 g*	negative
Salmonellae	negative

methods of analysis (shown in Module 3).

Cocoa Butter 8

1. Functionality and attributes of cocoa butter

Introduction

If it had not been for John Fry, it is debatable whether chocolate as we know it today would ever have come into existence. In 1847, he discovered one of the confectionery industry's greatest inventions by adding cocoa butter to a mixture of cocoa liquor and sugar.

Chocolate was born, and it was here to stay. Like many inventions, his discovery seems like a relatively simple matter today.

Cocoa butter was the key to John Fry's chocolate invention. Probably no other edible fat available at the time would have produced a consumer product that, right from the beginning, proved to possess such commercial staying power globally. Particularly, the functional properties of cocoa butter in the initial recipe made it possible to formulate the chocolate into a product with the specific characteristics that it still has today.

This module deals with the functionalities and attributes of cocoa butter in its almost sole application: the manufacture of chocolate.

Standard of identity

Cocoa butter is one of the most expensive commodity-based vegetable fats available. Therefore, it is not surprising that over the years legislators have been very particular in defining its standard of identity.

Current legal definitions around the world are very similar. The Codex Standard (Codex Stan 86-81, Rev. 1-2001) and the European Directive 2000/36/EC, for instance, define the standard of cocoa butter in almost identical wording. In the USA, cocoa butter is not separately defined, but it is described in CFR 163.112 as the cocoa fat removed from ground cocoa nibs.

It seems logical that cocoa butter is made from cocoa beans, but some legislators have gone one step further by stipulating that cocoa butter can only be made from cocoa beans, cocoa nibs, cocoa liquor, cocoa cake, or cocoa dust. In other words: from nothing else.

Relevant factors for cocoa butter and its production are:

- use of sound cocoa beans to obtain cocoa butter with max. 1.75% of free fatty acids (FFA)
- reduction of shell content in the cocoa nibs (max. 1.75% on alkali-free nibs), resulting in max. 0.35% unsaponifiables in press cocoa butter but in max. 0.5% unsaponifiables in expeller and refined cocoa butter (larger portion of shell)
- processing like filtering and/or centrifuging, degumming and/or deodorizing, neutralization, and bleaching

Based on these factors, some legislation and several trade contracts on cocoa butter, e.g. of the Federation of Cocoa Commerce (FCC), recognize four defined types or quality grades of cocoa butter:

- *Press Cocoa Butter*, obtained by means of mechanical pressing of cleaned and ground cocoa nibs and subsequently only filtered/centrifuged and degummed and/or deodorized
- *Expeller Cocoa Butter*, obtained by the expeller process, often with whole beans or nibs with high shell content and only subjected to further processing similar to Press Cocoa Butter

	Press Cocoa Butter	Other Types of Cocoa Butter
Refractive Index n_D(40° C/104° F)	1.456-1.459	1.456-1.459
Slip Melting Point	30°-34° C (86-93° F)	30°-34° C (86-93° F)
Clear Melting Point	31°-35° C (88-95° F)	31°-35° C (88-95° F)
Free fatty acids (as % m/m oleic)	0.5-1.75%	0.5-1.75%
Saponification value (mg KOH/g fat)	188-198	188-198
Iodine Value	33-42	33-42
Unsaponifiable Matter (% m/m)	max. 0.35%*	max. 0.5%

**0.45% for Southeast Asian beans*

- *Refined Cocoa Butter*, obtained by expelling or pressing, subjected to the same treatments as Expeller Cocoa Butter, and neutralized and bleached (refined)

Analytical criteria have been defined for the various types of cocoa butter:

Cocoa Fat forms a separate category. This is defined as fat obtained in any way from part of the cocoa bean that does not necessarily conform to one of the above definitions.

The chocolate industry is almost the sole user of cocoa butter, and usually press cocoa butter is set as the standard. The other types are generally considered to be somewhat lower standard, mostly because they are often made from sub-grade cocoa beans or extracted from cocoa waste material. In this module, we will exclusively deal with the standard of the press cocoa butter.

Flavor

The flavor of cocoa butter should be investigated from two different angles: its own typical flavor characteristics and its flavor stability. Both aspects are dealt with in this module.

Flavor characteristics

After the roasting and alkalizing steps, cocoa butter intrinsically incorporates all of the typical cocoa flavor elements. It will, therefore, have a distinct cocoa flavor. Cocoa butter made from alkalized liquor has a somewhat stronger flavor than butter obtained from non-alkalized liquor. By far, most cocoa butter today is made from alkalized cocoa liquor. Particularly, the bitter and specific cocoa flavor components are accentuated in this type of cocoa butter.

Most often, the term "natural cocoa butter" is used for cocoa butter that has not been subjected to a deodorization step, so it has the full cocoa butter flavor. Sometimes the term "natural cocoa butter" describes the cocoa butter from non-alkalized (natural) cocoa liquor.

The flavor intensity of cocoa butter can be managed by subjecting it to a deodorizing treatment. Depending on the required flavor intensity, cocoa butter can be fully or partially deodorized. A taste panel can help establish to what degree of deodorization the cocoa butter should be subjected in order to obtain the desired flavor profile. The Rostagno Aroma Index can be used as an instrumental aid in establishing the extent of deodorization.

Fully deodorized butter has hardly any cocoa flavor of its own, whereas non-deodorized butter absorbs the cocoa flavor components released during the roasting process. The degree of deodorizing is determined by the flavor intensity the cocoa butter user requires:

- In dark chocolate, which contains a relatively high amount of cocoa liquor and a proportionately lower amount of cocoa butter, the flavor contribution of cocoa butter is acceptable.

However, depending on flavor profile target and customer preferences, fully or partially deodorized cocoa butter is normally used.

- In creamy milk chocolate, which contains much smaller quantities of cocoa liquor in combination with higher quantities of cocoa butter and has a flavor profile that usually avoids strong and bitter notes, fully deodorized cocoa butter is often used.
- In white chocolate, which contains no cocoa liquor at all, the type of cocoa butter will heavily depend on flavor profile and customer targets. For children, who expect a smooth, creamy flavor, fully deodorized butter might be used. For adults, who expect a cocoa flavor experience, partially or non-deodorized butter may be preferred.

In contrast with other refined oils and fats, cocoa butter is deodorized by means of a light treatment with steam under vacuum. As this treatment is very mild, the less volatile flavor components of cocoa butter can still be detected even if it is fully deodorized. Also, tocopherols, the natural antioxidants present in the cocoa butter, are not removed.

The main reason for a mild steam treatment lies in the need to maintain the optimal functional properties of the cocoa butter. More stringent conditions could trigger interesterification of the butter. The unique triacylglycerols composition of the butter, with the unsaturated oleic acid on the 2- position and the saturated fatty acid on the 1- and 3- positions, would be lost due to interesterification, causing the fatty acids to be randomly distributed. This is detrimental to the hardness and the crystallization properties of the cocoa butter, which are sensitive issues for cocoa butter users. Under "Hardness" on page 103, we discuss this subject in more detail.

Flavor stability

Like any fat, cocoa butter can deteriorate. Fat oxidation leads to a variety of off-flavors which, in combination, are usually referred to as rancidity. This can also happen to cocoa butter, although cocoa butter is one of the most stable lipids in comparison with other fats and oils.

The sensitivity for oxidation can be measured in several ways. In the food industry, the Rancimat test is often used for establishing the oxidation stability of oils and fats. The longer the incubation time the more stable the product will be. In Table 1, a comparison is given for a Rancimat test carried out at 100° C (212° F) on a number of natural and processed oils and fats.

Table 1: Rancimat Test at 100° C (212° F)

Cocoa Butter	213
Vegetable Oils	
Canola Oil	6
Olive Oil	20
Peanut Oil	29
Soybean Oil	11
Vegetable Fats	
Coconut Oil	180
Hydrogenated Soybean Oil	174
Palm Oil	43
Palm Kernel Oil	45
Animal Fats	
Butter Oil	17
Lard	3

The reason for the high stability is twofold:

- By nature, the composition and structure of cocoa butter give it outstanding protection. Just over one-third of all fatty acids present in the triacylglycerols are unsaturated. By far, the largest part is oleic acid. Only about 10% of the unsaturated fatty acids is polyunsaturated linoleic acid, whereas the very unstable linolenic acid is virtually absent. In addition, almost all unsaturated fatty acids are located on the 2- position of the triglycerides, which allows for structural protection.
- Cocoa is a rich source of antioxidants. The well-known tocopherols are found in cocoa butter. A typical analysis shows that cocoa butter contains about 200 mg/kg tocopherols, with the larger part (170 mg/kg) consisting of gamma tocopherol and the remainder being alpha and delta tocopherol (15 mg/kg each). Too-stringent deodorization reduces the tocopherol level, resulting in reduced stability.

In addition, cocoa is rich in flavonoids. These substances have attracted attention lately because of their radical binding properties and their effectiveness in retarding the oxidation process. Flavonoids, however, because of their polar character, will remain mainly in the solid phase (cocoa powder), and their positive influence is hardly conveyed to the cocoa butter.

In order to establish oxidative deterioration, the peroxide value determination is sometimes used. (See Module 3: Methods of Analysis.) This test, however, often lacks accuracy, as many oxidative products such as n-hexanal show a much lower detection level than those that can be determined. An experienced taste panel proves to be a very reliable means to detect taste and flavor deviations and is often much more sensitive to these deviations than existing instrumental techniques.

Color and opacity

Cocoa butter has an ivory color in solid form and is yellowish in liquid form. In liquid form, its color should be clear and may not contain any solid particles. In most cases the color of cocoa butter is not relevant with regard to the color of the chocolate made from it. The brown color of the fat-free dry cocoa constituents determines the color of the chocolate, and in this respect the color influence from the butter is negligible. There is, however, one exception: white chocolate. Although here the color of the milk components is dominant, the color of cocoa butter does have its impact as well.

Color is usually measured by means of a Lovibond tintometer. (See Module 3: Methods of Analysis.) For cocoa butter, normally the red color is measured, after having standardized the yellow color on 40 in a 1-inch cell. The red color varies between 1 and 2. For white chocolate, it is desirable to limit the red color to a maximum of 1.6, as otherwise the chocolate tends to become too dark yellow.

When white chocolate is exposed to UV light, the yellow color will disappear. This bleaching effect occurs due to photo-oxidation of the photo-sensibilizers. These are present in cocoa butter (chlorophyll derivatives) as well as in the milk constituents (riboflavines). As the color gradually disappears and the bleaching effect becomes noticeable, the oxidation can also be sensorically detected (rancidity). It is therefore important to protect cocoa butter and white chocolate from direct UV sources such as sunlight.

Clearness of the cocoa butter is of no significance for chocolate. However, it is an indication as to whether proper processing conditions have been applied. It is important that liquid cocoa butter is completely clear and shows no particles, either in suspended form or as a sediment. Turbidity of fat may be caused by contamination with moisture. In the manufacturing of chocolate, this should immediately be corrected to avoid problems in the production process.

Hardness

Due to its typical chemical composition, cocoa butter is a unique fat. In contrast with most other vegetable and animal fats, cocoa butter consists of mainly three triacylglycerol molecules: POS, SOS, and POP (P=palmitic acid, O=oleic acid, S=stearic acid). The uniqueness of these three molecules is that they strongly resemble each other, with the unsaturated oleic acid mainly located on the 2- position and the saturated palmitic and stearic acid on the 1- and 3- positions of the glycerol molecule. Because cocoa butter makes up about 80% of these three molecules, its behavior at a phase transition resembles that of a pure chemical substance: The fat is almost entirely solid up to 27.5° C (81.5° F), quickly becomes softer when the temperature is raised, and is entirely liquid above 34° C (93° F).

The group of symmetric triacylglycerols is often indicated with the letters SUS, meaning saturated-unsaturated-saturated triacylglycerol. Table 2 shows the different types of triacylglycerols (trisaturated= SSS, monounsaturated=SUS/SSU, disaturated=SUU/USU and triunsaturated= UUU) in cocoa butters from various origins, and Table 3 illustrates the differences and variations in monounsaturated (SUS/SSU) triacylglycerols by country of origin.

These tables show that Malaysian cocoa butter contains substantially lower quantities of unsaturated triacylglycerol molecules (SUU/UUU) and much higher quantities of monounsaturated molecules (SUS). This explains why cocoa butter

TABLE 2
ORIGIN COCOA BUTTER AND COMPOSITION OF TRIACYLGLYCEROLS

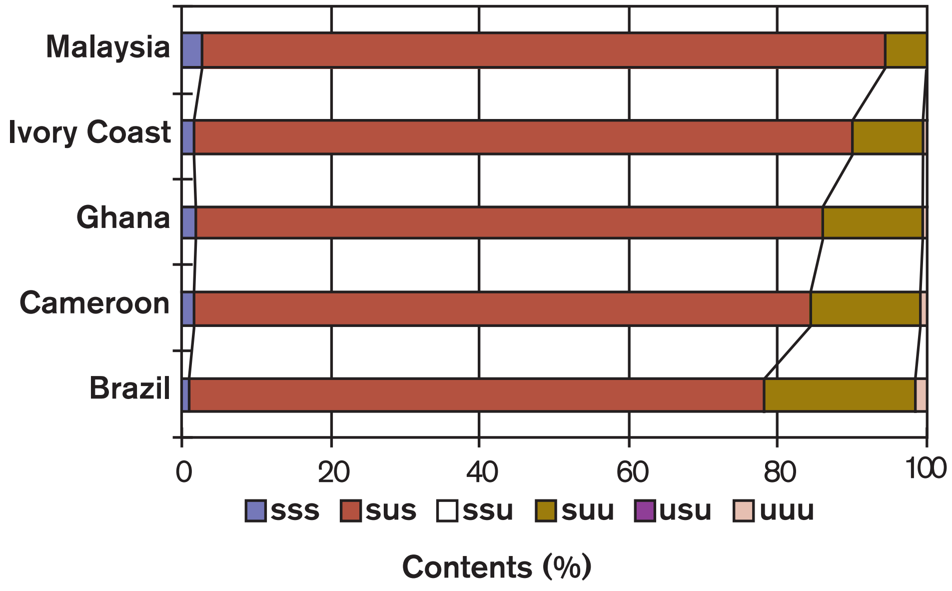


Table 3

Origin Cocoa Butter and Monounsaturated Triacylglycerols

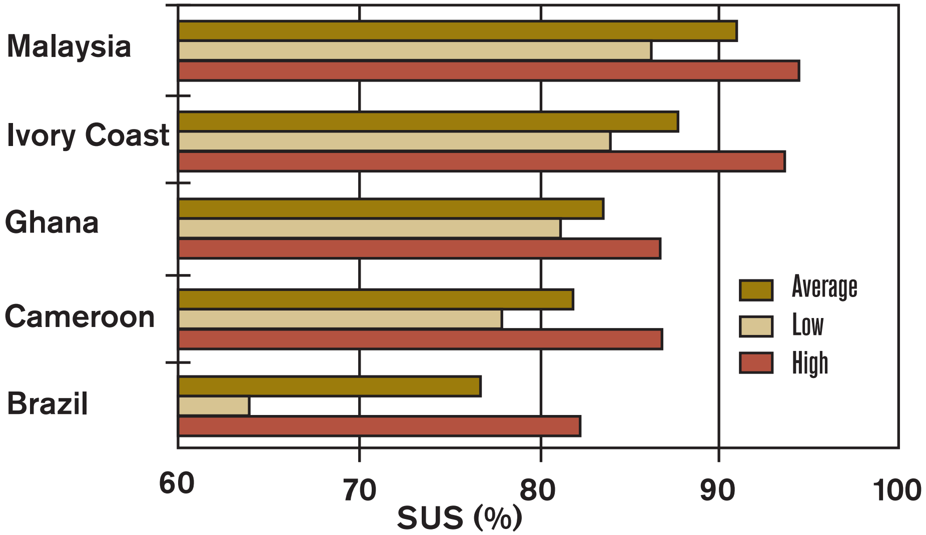
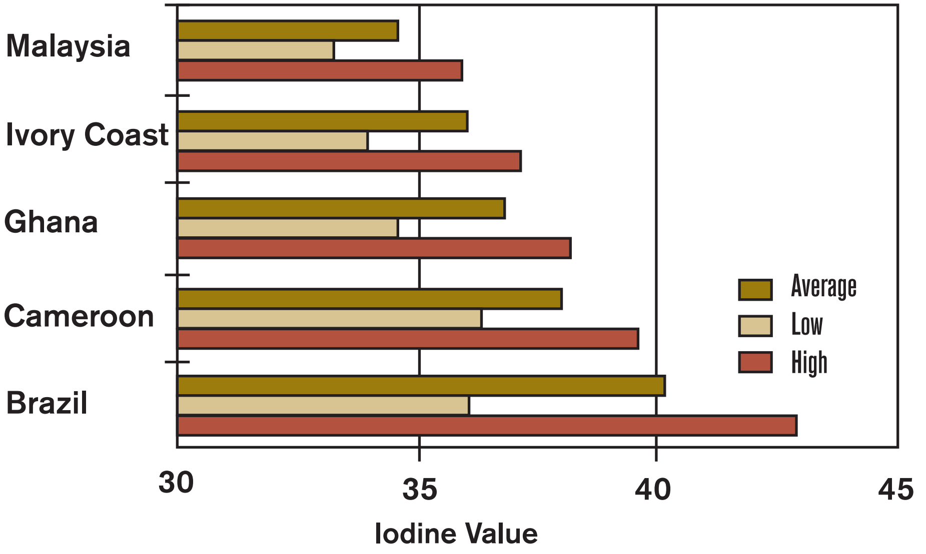


Table 4

Origin Cocoa Butter and Iodine Value



made from Malaysian beans is much harder than cocoa butter made from Brazilian beans, for example. The variations that can be observed for Brazilian beans are mainly due to the significant fluctuations in temperature between the summer and winter seasons in this region.

Unsaturated fatty acids in fats can be determined by means of the Iodine Value. (See Module 3, Methods of Analysis.) In Table 4, the variation in iodine values between the various cocoa bean origins is indicated. This indirect method, defining the Iodine Value, proves to be an effective yardstick for the hardness of cocoa butter.

A more direct method for determining the hardness is to determine the amount of solid fats present in the cocoa butter. Table 5 shows the differences and variations in amounts (content) of solid fats (SFC) found in cocoa butters from the same bean origin, measured at 30° C (86° F). From these data, it can be concluded that butter from Malaysian beans is harder than butter from Brazil and that butter from West African beans is somewhere in between these two. Penetration and snap tests on chocolate confirm these differences between the various origins.

From the aforementioned chemical (triacylglycerol) differences, the physical differences in the hardness of cocoa butter have been explained. However, cocoa butter with a low Iodine Value does not necessarily lead to a harder chocolate, compared to butter with a medium Iodine Value. There are two important reasons for this:

- It is essential that the cocoa butter is brought into the correct and stable crystal structure. (See page 107 under "Solidification behavior.") An example of the effects of the various tempering methods on the hardness of chocolate is given in Table 6.

TABLE 5

ORIGIN COCOA BUTTER AND SOLID FAT CONTENT

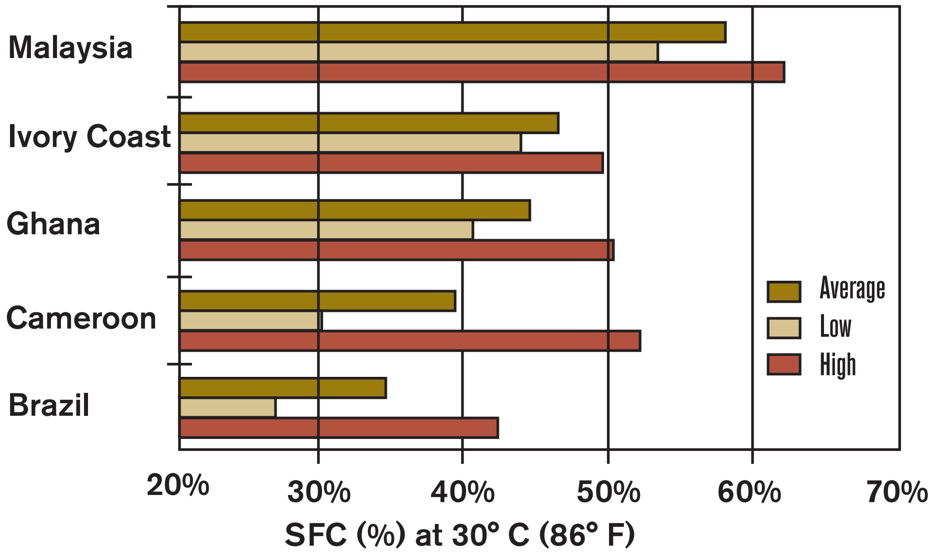
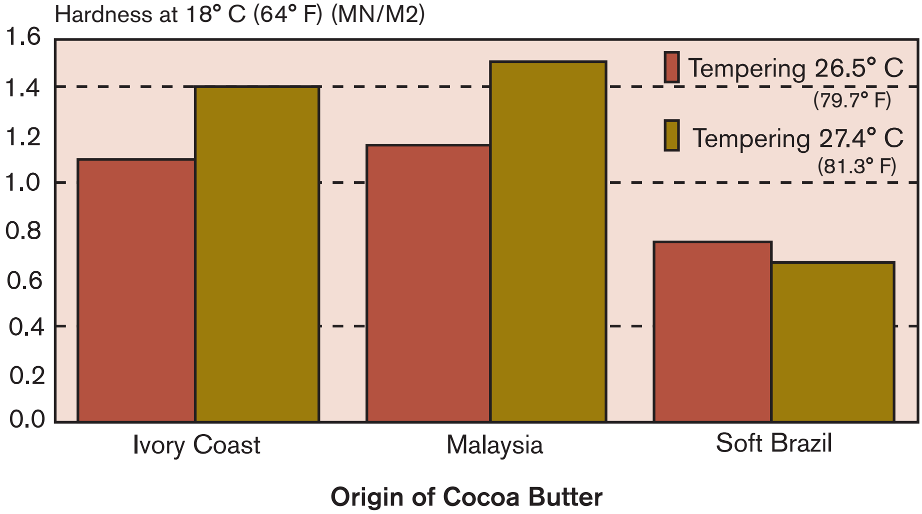


Table 6
Hardness of Milk Chocolate
Effect of Cocoa Butter and Tempering



- In chocolate recipes, fats other than cocoa butter, like dairy fat and possibly oils from added hazelnuts or almonds, are often introduced. These can have a major influence on the ultimate hardness of the chocolate. Through eutectics, differences in various cocoa butters can manifest themselves quite differently than what a mathematical calculation would lead one to expect.

Tempering—measured by means of a tempermeter

The tempering process is one of the most important steps in the manufacturing of chocolate. The degree of tempering, indicating the quantity of stable crystals that have been formed, can be measured by means of a tempermeter. With this method, a certain amount of liquid chocolate is cooled under specific conditions, and the temperature of the chocolate is registered with a temperature sensor. Initially, the temperature will drop linearly. When the temperature is low enough, the chocolate starts to solidify. Due to the crystallization heat, the temperature of the chocolate will change.

Optimal tempering
When chocolate is tempered properly, its temperature will remain more or less constant for some time during cooling. The released crystallization heat is then balanced by an equal amount of cooling energy. Only when the liquid cocoa butter is transformed into solid crystals will the temperature of the chocolate drop further.

Under tempering
If the chocolate is insufficiently tempered or not tempered at all, thus making fewer stable seeding crystals available, more crystallization heat will develop during cooling, as more liquid fat has to be transformed into the solid form. A distinct increase in temperature can be observed at the beginning of the crystallization. It will decline again after reaching a maximum.

Table 7: Polymorphy of Crystals of Cocoa Butter				
Form	X-Ray Pattern	Heat of Fusion	Melting Point	Chain Packing
		KJ/mol	iC (iF)	
I	K	unknown	17.3 (63.1)	double
II	Θ	85.5	23.3 (73.9)	double
III	P	113.0	25.5 (77.9)	double
IV	P	118.0	27.5 (81.5)	double
V	P	137.3	33.9 (93.0)	triple
VI	P	148.7	36.3 (97.3)	triple

This phenomenon is called under-tempered chocolate, and it often leads to demoulding and fat bloom problems because insufficient stable crystals were present during the cooling of the end-product.

Over tempering

Chocolate can also contain too many stable seeding crystals. This will be perceptible in the rheology of the chocolate. Because a significant part of the liquid fat has been withdrawn from the continuous phase of the chocolate and is now transformed to the solid form, less liquid fat is available for pumping the product. This type of chocolate will release little crystallization heat during cooling, rendering a rather flat cooling curve. As a substantial part of the phase transition (from liquid to solid) has taken place before the chocolate reaches the mould, less contraction will occur in the mould, leading to demoulding problems at the end of the process.

Crystallization is a process whereby time and temperature are important factors. They are determinants with regard to the speed of crystallization. The higher the re-crystallization speed, the smaller the crystals will become, and more crystals will be formed. The number of crystals is, in turn, important for the speed with which the chocolate will solidify, whereas the size of the crystals influences the final gloss and hardness of the end-product. Small crystals are preferred.

Solidification behavior

For the application of cocoa butter in chocolate, the solidification behavior of cocoa butter is its most important functional property. The conversion from liquid into solid form is a critical step in the chocolate production process that not only determines the quality and the shelf life of the end-product but also requires capital investments in tempering and cooling equipment.

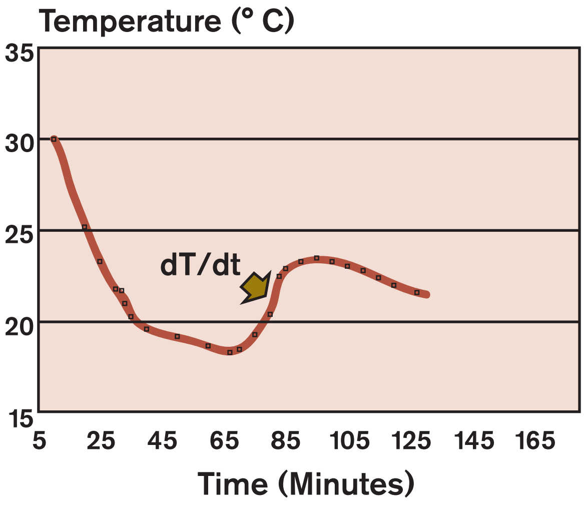
A number of factors have to be taken into account with regard to the solidification behavior of cocoa butter:

- the polymorphic crystallization properties
- influence of the cocoa bean origin
- influence of alkalization
- influence of deodorization

Polymorphic crystallization properties

A fat can solidify in various crystal forms that will then show different melting points. This is referred to as polymorphism. The density in which the fat crystals are packed and the ultimate crystallization form vary by crystal type. In their least-stable form, the triacylglycerols can freely rotate around their axis, resulting in poor packing of the crystals. Very little heat is required to bring them back to their liquid form.

Figure 1
Shukoff Cooling Curve of Cocoa Butter



In the case of cocoa butter, at least six crystal forms (I-VI) can be distinguished. The most stable form is the one where the fat molecules are most densely packed and structured in such a way that the least space exists between them. This form requires the most heat to convert from the solid to the liquid form and is indicated for cocoa butter as forms V and VI. Between the forms I + II and V + VI lie the meta-stable forms III and IV. In Table 7, the six forms, on the basis of the characterization of Wille and Luton, are given.

All cocoa butters, regardless of origin, demonstrate this polymorphic behavior. To be able to make stable end-products, the cocoa butter must assume the crystalline form V. This can be achieved by a process called tempering. The completely liquefied chocolate is cooled, usually by means of a scraped surface heat exchanger, so that part of the fat crystallizes into unstable crystals. Subsequently, the temperature is raised, so that most of these crystals will liquefy again, but a part will re-crystallize into the stable form.

By maintaining the temperature below the melting point of the stable crystal form, the product (chocolate) is being seeded with stable crystals. These are the basis of the crystal structure that will be formed during subsequent cooling.

Influence of the cocoa bean origin

Cocoa butters made from different bean origins can show different crystallization patterns. The explanation for these differences can be found in the different chemical composition of their triacylglycerol. (See page 103 under "Hardness.") Comparing the solidification characteristics of cocoa butters from various origins provides an indication of what these differences are. The Shukoff test is commonly used to determine the solidification characteristics of cocoa butter.

In Figure 1, the curve clearly demonstrates when the cocoa butter begins to crystallize. When the line deviates from the cooling line at a temperature of about

TABLE 8
ORIGIN COCOA BUTTER AND SHUKOFF COOLING CURVE

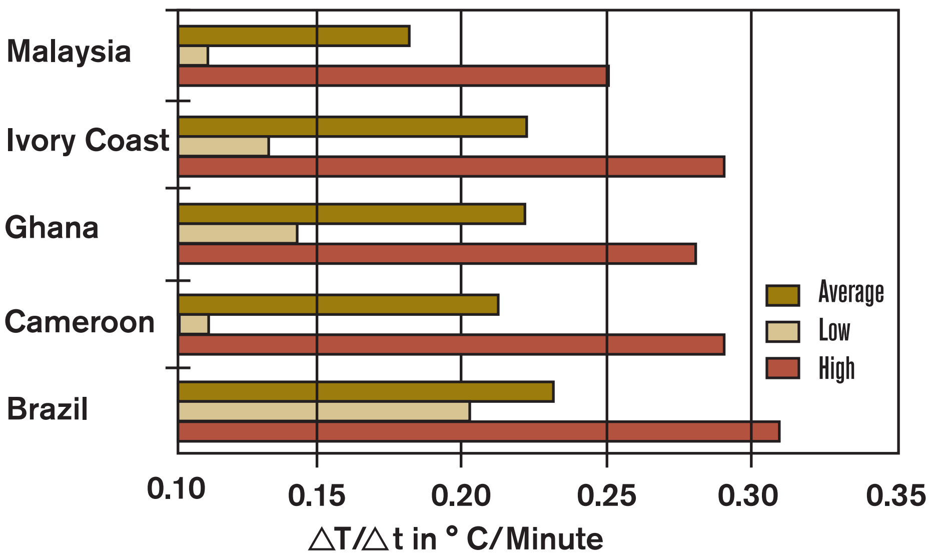


TABLE 9
ORIGIN COCOA BUTTER AND VISCOSIMETRIC COOLING CURVE

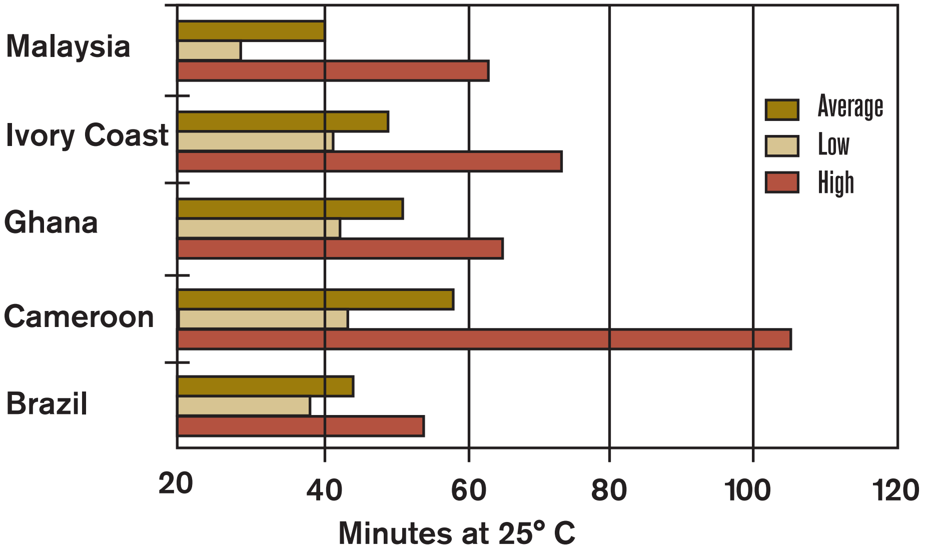
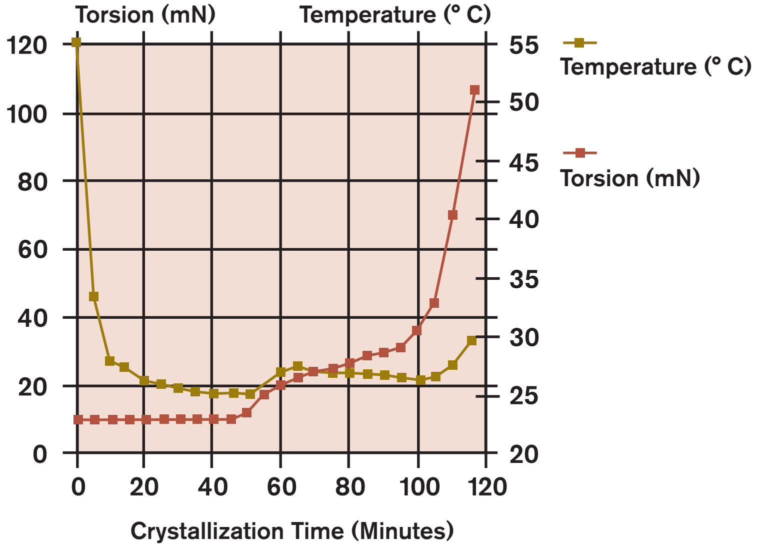


Figure 2:
Thermorheographic Cooling Curve of Cocoa Butter and Temperature During Measurement



20° C (68° F), the α-crystals start to form. When the line reaches its minimum, the Θ-crystals re-crystallize into the more stable P[1]-modifications. At this stage a lot of crystallization heat is generated. Due to the released crystallization heat, the temperature increases to a maximum, whereby re-crystallization occurs into the more stable crystal modifications. The increase in temperature between the minimum and the maximum temperature in degrees Celsius, divided by the time in minutes between both points (T/ t), allows such a curve to be expressed in a number. Table 8 on page 109 shows that these curves can differ substantially by origin.

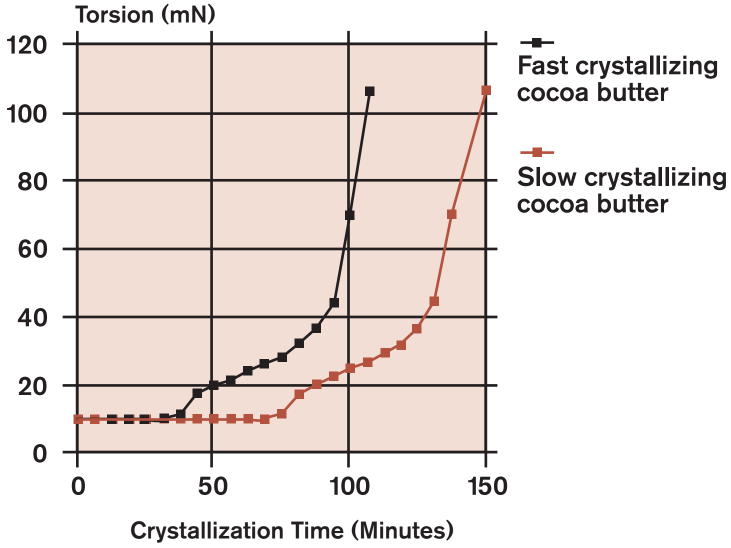
Brazilian butter appears to score better than Malaysian. However, it must be taken into account that the Shukoff curve only records the formation of the Θ-form and the transition to the meta-stable P[1]-form, whereas in practice, the transition to the stable P-crystals is of importance.

Other methods, like the viscosimetric cooling curve, can give a good indication of that transition. Cocoa butter is cooled to 25° C (77° F), and subsequently the increase in viscosity in the fat over time is followed at that temperature. The required time to reach a certain viscosity is a good indication for the crystallization behavior, which is shown in Table 9 on page 109.

The thermorheographic (TRG) method developed by Baenitz is another way to determine the crystallization behavior of cocoa butter during the tempering process. In a temperature controlled Z-kneader, cocoa butter is cooled to 24° C (75.2° F). In Figure 2, a typical TRG curve is illustrated.

Two phases can be distinguished from the curve. In the initial phase, the material is seeded with crystals, but as can be read from the force, the cocoa butter is still liquid. This point is indicated as t_1. The increase in temperature reveals that crystallization heat is released. α-crystals cannot occur at these temperatures. Conse-

Figure 3:
Thermorheographic Cooling Curves Comparison Different Types of Cocoa Butter



quently, the crystals formed are mostly of the P¹-form.

In the second phase, a marked increase in force is seen, indicating that a transition from the liquid into the solid form is occurring. This point is indicated as t_{total}. The slight increase in temperature means that re-crystallization from P¹- to P-crystals is occurring. In the figure, the typical differences in TRG behavior of a number of cocoa butters from various origins is illustrated. In this way, TRG can help obtain valuable additional information on the crystallization behavior of cocoa butter.

In general, the harder the cocoa butter, the more crystallization heat is released during the transition from the liquid to the solid form. This means that softer butter will solidify faster compared to harder butter and that milk chocolate solidifies faster than dark chocolate. The cooling temperature profile during the chocolate production process has to be adapted to this.

Influence of alkalization

Alkalization of cocoa is an important step in influencing both flavor and color of the solid parts of the cocoa bean: cocoa powder. The impact of alkalization on cocoa butter has been demonstrated in a study in which raw, roasted, and roasted/alkalized cocoa have been compared. In Table 10 on page 112, the analytical results are given, comparing cocoa butters from a single bean origin.

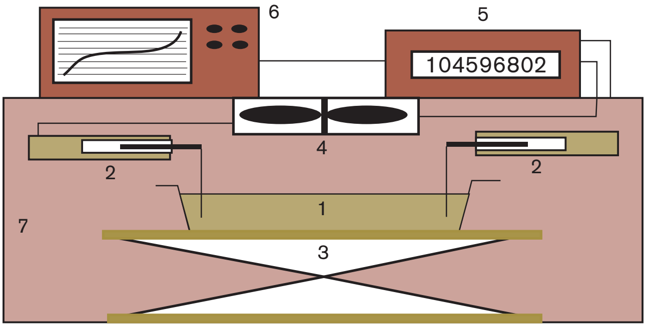
Though slight differences can be noticed in the analytical data, these differences appear to be of minor influence. In general, it can therefore be said that the alkalization process, if properly carried out, has no negative impact on the properties and characteristics of the cocoa butter.

Table 10: Cocoa Butters - Effect of Alkalization and Roasting			
	Raw Beans	Roasted Beans	Alkalized and Roasted
% ffa	1.28	1.29	1.12
% Diglycerides	0.95	0.98	1.03
% Sat. Fatty Acids 2 pos.	1.60	1.60	1.90
Oxyd. Stab. (hrs. at 120° C/248° F)	40.0	41.0	41.0
Cooling Curves			
Shukoff T/ t	0.21	0.20	0.18
Viscosimetric (min.)	39.0	40.0	51.0
Melting Curve			
% SFC (pNMR) 30° C (86° F)	39.0	39.7	39.6

Influence of deodorization
The effect of deodorization on the flavor of cocoa butter has already been discussed. It was also mentioned that a possible negative influence could be expected due to interesterification. If the symmetric molecule triacylglycerol is transformed into an asymmetric molecule with the unsaturated fatty acid on the 1- or 3- position, the hardness and the crystallization

Table 11: Cocoa Butters - Effect of Deodorization		
	Before	After
% ffa	1.23	1.18
% Diglycerides	0.95	0.93
% Sat. Fatty Acids 2 pos.	1.6	1.7
Oxyd. Stab. (hrs. at 120° C/248° F)	39.0	41.0
Cooling Curves		
Shukoff T/ t	0.18	0.19
Viscosimetric (min.)	39.0	43.0
Melting curve		
% SFC (pNMR) 30°C (86° F)	39.0	39.8

Figure 4: Measuring Contraction of Chocolate During Moulding



1=Chocolate in mould
2=Magnetic displacement sensor
3=Moving table
4=Ventilator
5=Displacement registration unit
6=Recorder
7=Thermostated cooling cabinet

behavior of the cocoa butter can be significantly influenced.

The characteristics of cocoa butter before and after deodorizing have been investigated and are shown in Table 11.

A minimal decrease in ffa (free fatty acids) can be noticed. However, the crystallization behavior and the hardness of the cocoa butter have hardly changed. It can therefore safely be assumed that deodorization carried out under controlled conditions has no negative influence on the properties of cocoa butter, other than the flavor. However, when processing high-ffa cocoa beans, a stronger deodorization might be necessary, with potential impact on color and crystallization behavior.

Contraction

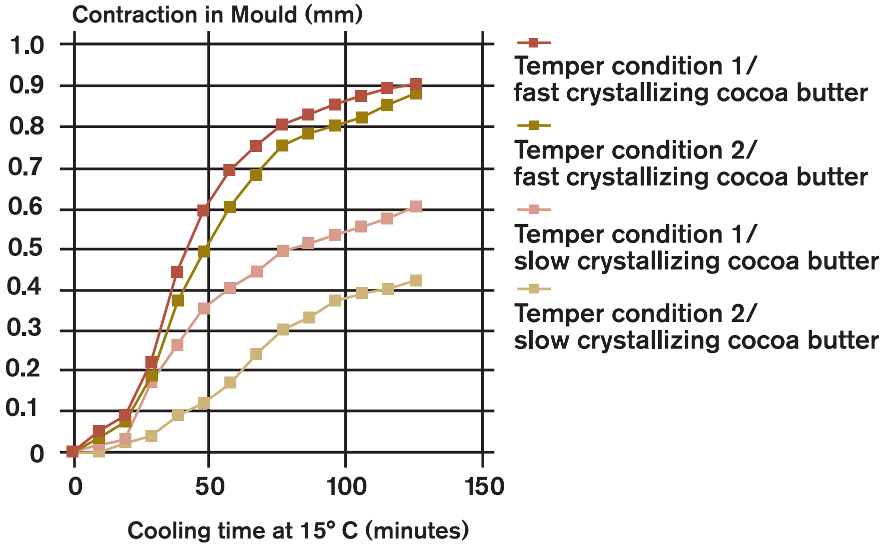
Contraction is an important parameter in the manufacture of chocolate, notably when demoulding the product. Its principle is based on the fact that liquefied fat has a higher volume compared to its solidified form. The crystal modification is also of importance: The stable P-crystal form in cocoa butter has 1.5 times more contraction property as compared to the Θ-form. This is due to the more dense molecular packing of the crystals.

When properly tempered, cocoa butter has a volume contraction of about 9%. For an average bitter chocolate recipe (33% fat), this means a volume contraction of about 3%, corresponding to a 1% linear contraction. In milk chocolate, the volume

Table 12: Cocoa Butters in Contraction Experiment

	CB1	CB2
Iodine Value	35.5	36.4
ffa	1.10	1.50
Diglycerides	1.50	1.90
Monoglycerides	0.20	0.20
Shukoff T/ t	0.19	0.14
% SFC (pNMR) 20°C (68° F)	75.0	71.0

Figure 5:
Contraction of Milk Chocolate
Effect of Cocoa Butter Type and Tempering Conditions



contraction is lower. Due to the eutectics caused by the milk fat in the cocoa butter, a significantly smaller part of the fat mixture will transform from liquid to solid form. However, normally the contraction will be quite adequate for demoulding.

As the proper crystal form is also an important factor for the degree of contraction, it is of great importance that adequate tempering has taken place. To demonstrate this, ADM Cocoa has developed a method to measure the contraction. In Figure 4 the required equipment is schematically illustrated.

A mould containing tempered chocolate is placed in the refrigerator. Before the cooling starts, a measuring device with two sensors is placed in the chocolate. As the chocolate solidifies, the sensors, due to contraction of the chocolate, will have moved accordingly. The movement of the sensors as a function of time is indicated by a recorder.

As an example, in Table 12 below and in the Figure 5 on page 114, two different types of cocoa butter (CB1 and CB2) are used in milk chocolate to demonstrate their different contracting properties.

Notably, the somewhat softer butter with a slightly elevated ffa appears to be more sensitive to differences in tempering, and the insufficient tempering leads to a much lower contraction compared to the product subjected to optimal tempering. Furthermore, it shows that the harder butter gives a better contraction than the softer butter.

In cases where the shrinkage may not be too strong, like in some enrobed products such as wafers and ice cream bars, several options are available:

- Use softer cocoa butter, like Brazilian butter
- Produce eutectic effects by adding milk fat
- Slightly overtemper the chocolate

Rheology

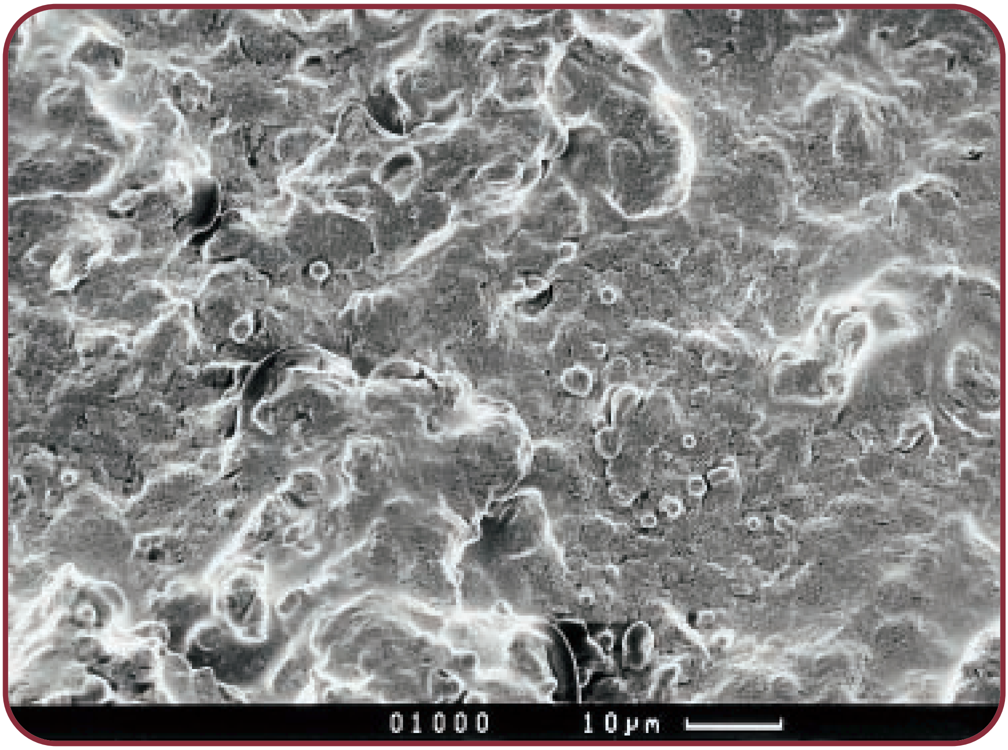
In the processing of chocolate, rheology plays an important role. Because fat is the continuous phase, the amount of fat available determines the ultimate rheology of the chocolate in liquid form. As cocoa butter is usually the most expensive ingredient in the chocolate recipe, the quantity of cocoa butter used is minimized and adapted to a required rheology.

The type of cocoa butter has no influence on the rheology. Cocoa butter, or any other fat in liquid form, behaves similarly, and butter from one particular origin is not better or worse than butter from another origin.

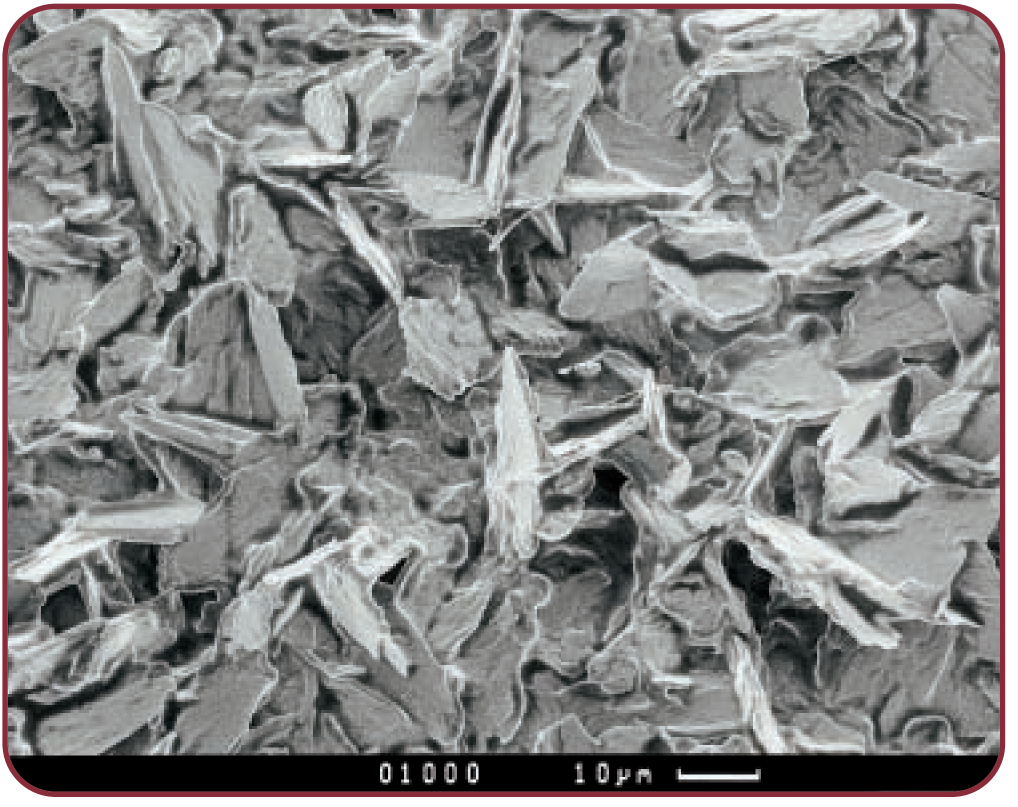
Gloss and shelf-life stability

Cocoa butter, or the fat phase in chocolate, is largely responsible for the gloss of the end-product. The dispersed dry matter in chocolate—sugar, dry fat-free cocoa constituents, and dry fat-free milk solids—do not contribute to the gloss. These cause the background color against which the gloss is visible. Gloss on white chocolate is therefore hardly noticeable, whereas the gloss on dark chocolate, because of the dark background, is very visible. Cocoa butter crystallizes into very small (1-2μ) crystals, resulting in a smooth surface. Light is then very well reflected. In addition, contact with the smooth surface of the mould enhances the gloss impression even more.

Gloss stability depends on the degree to which the fat crystals are stable. When fat crystals re-crystallize under uncontrolled conditions, which is usually a slow process, larger crystals will be formed. If these crystals are large enough that they can be seen with the naked eye, the phenomenon of fat bloom occurs. A picture of a bloomed chocolate surface is shown on



Electron scan microscopy of smooth chocolate



Electron scan microscopy of bloomed chocolate

page 116.

Fat bloom can be caused by:

- inadequate tempering, due to slow re-crystallization of still present Θ- and P'-crystals into large P-crystals
- melting of stable P-crystals followed by slow, uncontrolled re-crystallization
- fat migration due to other oils and fats, e.g. from nuts or from the enrobed center migrating to the surface of the chocolate

It is beyond the scope of this module to dwell extensively on this subject. It should be noted that certain forms of fat bloom seem to manifest themselves easier and faster in very hard fat systems as compared to softer fat systems.

Finally, not all bloom is fat bloom. When mistakes are made in moisture management, sugar bloom can occur: re-crystallization of sugar crystals at the surface of the chocolate. Obviously, cocoa butter has nothing to do with this.

When a chocolate product shows fat bloom, it is often thought that its quality has deteriorated due to mold growth, for example. The unattractive, grayish discoloration contributes to this perception. The occurrence of fat bloom, however, is likely due to the causes described. One well-known contributing factor is storage under fluctuating temperatures. Apart from the unattractive appearance, the quality of the product is not affected.

2. The application of cocoa butter

Chocolate production

There are two ways in which cocoa butter finds its way into chocolate: as a raw material and as part of the cocoa liquor. About half of the cocoa liquor consists of cocoa butter. This means that in dark chocolate, only a limited quantity of cocoa butter is added, whereas in milk chocolate, the added butter quantity forms the main part of the overall fat content.

The amount of butter used in the chocolate recipe depends on the sensory requirements, notably the fineness and the desired flavor, as well as on the rheology needed during processing of the chocolate. Particularly, the ultimate application of the chocolate itself dictates the rheological requirements. The lowest overall fat content is found in extruded and moulded chocolate. Typical fat contents for products like panning centers, chips, and chunks vary between 24 and 28% and for solid chocolate bars between 27 and 31%. Chocolate for shell products, enrobing, and panning has an intermediate fat content between 30 and 40%. For very thin enrobing purposes and coatings for dipping ice cream bars, fat contents of between 40 and 50% are used, and for spraying applications, even higher fat contents are required. It should be kept in mind that total fat contents are mentioned here; that is, the total of the added cocoa butter, the cocoa butter from the cocoa liquor, and in the case of milk and white chocolate, also the fat from the added milk constituents. In addition, the fat from nuts like hazelnuts or almonds should be taken into account.

Confectionery fillings

In the chocolate and confectionery industry, quite a tradition exists for high-quality fillings.

Usually, roasted nuts like almonds and hazelnuts are ground and blended with sugar and other ingredients, including cocoa and milk products. The oil from the nuts gives the filling a very soft, liquid texture that can easily migrate through the chocolate enrobing. By adding cocoa butter, the texture may be regulated from soft to cuttable or extrudable, and fat migration may be diminished. The advantage of cocoa butter is its complete compatibility with the chocolate that surrounds the filling, reducing eutectics and other problems to a minimum.

In the application of fillings, cocoa butter competes with other vegetable oils and fats that are usually lower priced. This limits the use of cocoa butter in this application to only products that are catered to the higher-priced market segment.

Other applications

Cocoa butter is defined in several pharmacopoeia under descriptions like cocoa butter (USP 1990, JAP 1991), *Cacao oleum* (DAB 10, 1992, PhNed 8), and Theobroma Oil (BRIT 1998).

For a long time, cocoa butter has been used in suppositories. Administering a medicine rectally provides an alternative to oral and intravenous options. Cocoa butter is very well suited for this purpose as it liquefies evenly and completely within 15 minutes at a body temperature of 37.6° C (99.7° F). Also its high oxidative stability makes the use of cocoa butter favorable.

Cocoa butter is a product of nature with its own unique properties, including unavoidable, natural fluctuations. Because the pharmaceutical industry requires different melting behavior, a range of crystallization times, and absorption of water-soluble medicines, the use of cocoa butter in suppositories has diminished. Today, more and more synthetic glycerides are used in this application.

The use of cocoa butter in skin creams, soap, and shampoo should largely be seen as a marketing tool, rather than an actual functional property. Usually, refined cocoa butter is used for these applications, and the quantities involved are limited.

3. Packaging, storage, and transportation

Cocoa butter is mostly stored in tanks and transported in special, properly insulated tank containers or tank cars in liquid form. Usually, the butter is loaded at temperatures from 60°-75° C (140°-167° F), depending on the destination and the transition time. During transport the temperature will drop about 2°-5° C (4°-9° F) per day depending on the outside temperature. At the point of discharge, the temperature should not have fallen below 40° C (104° F). This limits the transport time to about one week.

Tank cars should be operated under very strict conditions. They must only be used for food-grade products, and a certificate should indicate that the tanker has been cleaned and properly dried prior to loading.

If bulk shipping is not possible, the cocoa butter is packed in solid form, usually in cartons of 25kg (55 lbs.) that contain a polyethylene inner bag. The cartons are stacked on a pallet and shrink wrapped. During transportation, it is important that the product is not subjected to excessive heat.

Fats are known to quickly pick up volatile matters like odors from their surroundings. It is therefore very important that both during transport and subsequent storage cocoa butter does not come into contact with strong-smelling products. Paint; chemicals; cleaning agents; spices, herbs, and other flavoring substances should not be stored in the direct vicinity of cocoa butter.

If cocoa butter is stored under dry (RH 40-70%), cool (<20° C/<68° F), and dark conditions, the shelf life is at least 12 months.

When liquefying solid cocoa butter, high contact temperatures should be avoided. Stainless steel melting grids, heated by water up to 90° C (194° F), are recommended.

Liquid butter should be kept at temperatures of 40°-45° C (104°-113° F), preferably in a stainless steel or coated tank. The tank can best be heated by means of a warm water spiral or jacket. Steam heating is not to be advised because of its high contact temperature. Heating by means of hot air in the tank storage room is also an option, as are piping and an adequate thermostat tracing system.

Exposure to air or oxygen should be avoided as much as possible. Vertical storage tanks are therefore preferred over horizontal ones. Care should be taken that no air is trapped in the cocoa butter due to malfunctioning pumps, for example. The tanks can best be filled from underneath, rather than letting the butter fall from the top. Furthermore, air contact can be diminished by leaking an inert gas like nitrogen through the cocoa butter. This will drive out the oxygen, creating optimal storage conditions for cocoa butter. Even small amounts of oxygen can initiate the oxidation process. This is why it is important that, when blanketing, a first-grade inert gas free from oxygen is used.

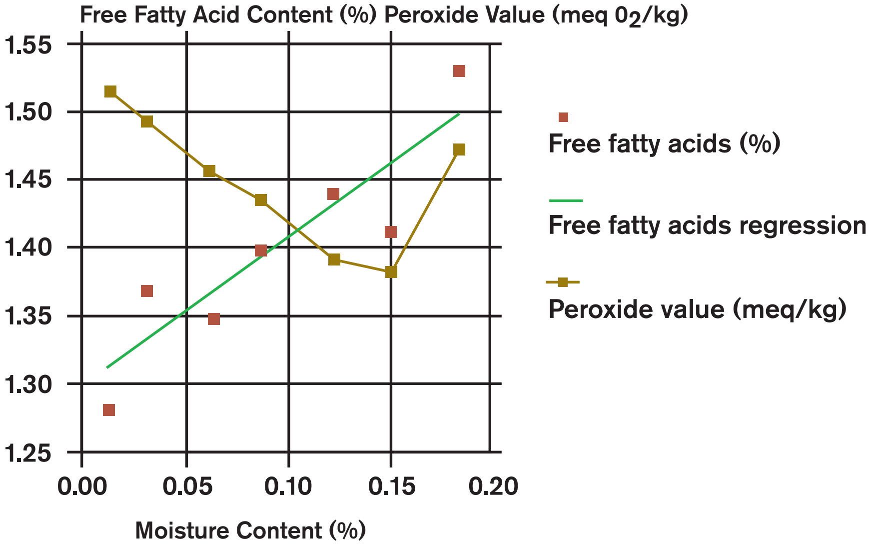
Metals and alloys like copper and bronze, which have a catalytic effect, must be excluded from the processing equipment (piping, pumps, seals, etc.).

Finally, care should be taken that fresh cocoa butter is not continuously being added to butter that has been stored for some time. If cocoa butter is kept in storage for too long, catalytic reactions can deteriorate the quality of the tank. Therefore, it is good practice to completely empty the tank on a regular basis.

Under optimal conditions as described above, liquid cocoa butter can withstand a storage time of two months without any problem.

The figure shows the results of an accelerated shelf life laboratory experiment. At

FIGURE 6: EFFECT OF MOISTURE ON COCOA BUTTER DURING STORAGE FREE FATTY ACID CONTENT AND PEROXIDE VALUE AFTER 42 DAYS AT 80° C



these extreme high temperatures, the ffa and the peroxide value run up so quickly that the maximum keeping time is reached after only three weeks. However, as mentioned, it concerns a laboratory experiment, whereby the ratio of contact surface and air versus the amount of fat is disproportionately unfavorable.

The effects of moisture on cocoa butter are shown in the pictures on pages 115 and 116. In this experiment, the moisture content varies between 0.01-0.18%. The cocoa butter was stored for 42 days at 80° C (176° F), after which the ffa and peroxide value were measured. With increasing moisture content, a linear, though modest, increase in ffa is noticeable. The peroxide value, on the other hand, reaches an optimum level at 0.15% moisture.

A possible explanation for this could be found in the hydration and sedimentation of the gums present in the cocoa butter. These bind the metal ions and are then removed from the fat into the sediment. In practical terms, this means that when cocoa butter is stored for a prolonged

SPECIFICATION OF TYPICAL DE ZAAN® PURE PRIME PRESSED COCOA BUTTER	
Acidity (%)	1.75 max.
Iodine Value	33-40
Refractive Index n_D(40° C/104° F)	1.456-1.458
Clear Point (°C/°F)	32-35/90-95
Blue Value	0.05 max
Unsaponifiables (%)	0.35 max.
Absorbance (270 nm), after washing with alkali	0.14 max.
Saponification Value	192-197
Peroxide Value	4 max.
Color (yellow + red)	min. 40 + 1.0/max. 40 + 2.0

Cocoa Powder 9

1. Functionality and attributes of cocoa powder

Introduction

The two most prominent attributes of cocoa powder are its abilities to give color and flavor to a wide variety of food products. In many instances, the consumer will directly associate brown color with chocolate flavor, and the darker the color, the stronger the flavor expectation will be.

These two attributes of cocoa powder in a food product formulation are only part of the story. Other aspects such as fineness, fat content, pH, and alkalinity may have an important functional impact on the end-product in which the powder is used.

Manufacturing parameters and other ingredients in the formula may distinctly influence the overall performance of cocoa powder in the final product as well. The structure of a cake, the smoothness of a pudding, the whipability of a cream, and the viscosity of a syrup may in part be determined by the type of cocoa powder used.

In addition, cocoa powder may function as an antioxidative agent in many product recipes, thereby having a positive effect on the shelf life of these products.

The advantage of cocoa powder as a flavoring and coloring agent is that many types are available, differing not only in color shades and flavor profiles, but also in other aspects that make them suitable for use in just about any food system, including foods with virtually no fat content.

So when choosing a cocoa powder for a specific product application, it is important to carefully determine which functionalities and attributes of the cocoa powder are to be priorities. A dark-colored, lightly flavored chocolate pudding is bound to disappoint the consumer, as will a homemade brownie that does not have the right texture or a chocolate milk beverage in which the cocoa powder has formed a difficult-to-disperse sediment on the bottom of the container.

In the next paragraphs a number of these functional aspects of cocoa powder will be discussed.

Standard of identity

Many countries have defined cocoa powder in their food laws. Depending on when these food laws were initiated and the prevailing chemical and physical analytical capabilities, as well as the process and technical advancements, these laws may differ on essential elements. In many instances, a differentiation exists between the product definition of cocoa powder and the legal specification of the product.

At the beginning of the 20th century, it was not technically possible to mechanically press the cocoa liquor into cocoa cake with a fat content below 20%. Hence, the standard of identity for cocoa powder in some countries indicates that the name "cocoa powder" is exclusively reserved for a product containing a minimum of 20% cocoa butter. Any powder with a lower fat content must be declared as low-fat cocoa, strongly reduced-fat cocoa, or a similar description. And some countries specify the fat content to be calculated on dry matter, whereas others require it to be calculated on the basis of a maximum moisture content.

Relevant Regulations				
Form	Low-fat cocoa powder	Reduced-fat cocoa powder	Cocoa	Breakfast cocoa
EU: Directive 2000/36/EC		< 20% fat	20% fat or more	
USA: 21 CFR 163	<10% fat		10-<22 % fat	22% fat or more
Codex Stan. 105-1981, Rev.1-2001	<10% fat	10-<20% fat	20% fat or more	

In this module we will use the descriptions "cocoa powder" as well as "high-fat" and "low-fat" for practical purposes only, disregarding whether or not these descriptions comply with the food laws of a particular country with respect to the fat content of the product.

The use of cocoa powder as an ingredient in a consumer product may also have an influence on how that product may or may not be labeled. Descriptions such as "chocolate" or "chocolate-flavored" are in many countries reserved for products that actually contain chocolate, whereas in others these terms are allowed to be used for products made with cocoa powder containing a certain minimum percentage of cocoa butter.

This illustrates the complexity of only one aspect of the standard of identity of cocoa powder: the matter of the fat content. Many more rules and regulations exist in different countries concerning the permitted production processes, the raw materials used, the product specifications and labeling requirements, extraneous matter, and even packaging.

It goes beyond the scope of this module to discuss the multitude of differences in the various existing food laws.

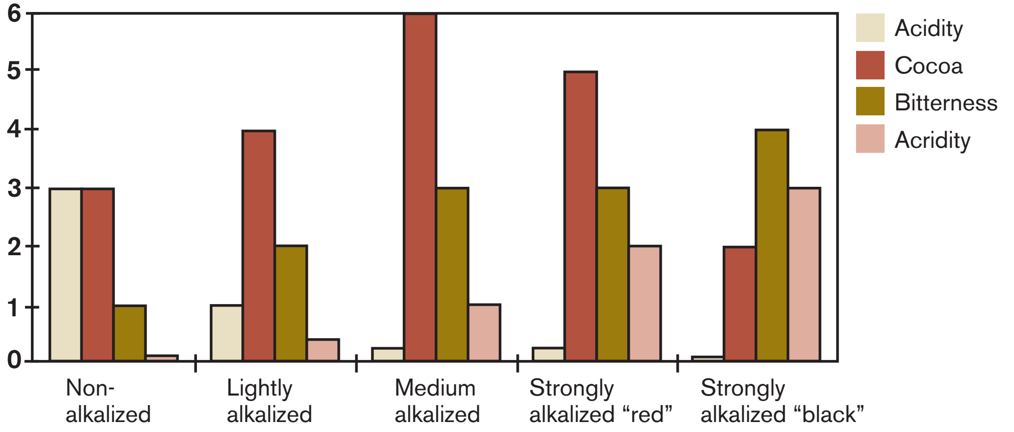
Flavor

Range of cocoa flavors

The range of De Zaan® cocoa powders available from ADM Cocoa can be divided into two basic types: non-alkalized or natural-process cocoa powders and alkalized, also called Dutch-process, powders. These two types have their own very specific flavor profiles. In Figure 1, the differences in flavor, expressed in acidity, cocoa, bitterness, and acridity, are indicated.

- Non-alkalized cocoa powders have an acidic, somewhat astringent flavor with a typical chocolate note. Many of the acids naturally present in the cocoa bean are still present in the powder after processing. Roasting is the principle step in the production process that can influence the development of the final flavor.
- In alkalized cocoa powders, alkalization partially neutralizes the acids present in cocoa and reduces the astringency. It is a precisely defined treatment of the cocoa solids with an alkaline solution such as potassium carbonate. Alkalization, in combination with the roasting process, allows the cocoa manufacturer to directly influence both the flavor and the color of the final product. Depending on the degree of alkalization, the flavor profile can be described as ranging

Figure 1: Flavor Profiles Cocoa Powders with Different Alkalization Degrees



from mild chocolate-like to a very pronounced, strong cocoa flavor.

Flavor is a characteristic that is very difficult to describe. The descriptions used in this book can best be read when comparing and contrasting them with each other. (See Module 4, Flavor and Flavor Development.)

Flavor and consistency

Because the consumer expects a specific product with consistent flavor characteristics, the raw materials supplier seeks to deliver ingredients that are able to provide this to the manufacturer. In this respect, consistency in flavor is one of the most important aspects. Here, the sensory evaluation process plays a key role.

Today's consumer is probably more responsive to the flavor of food than ever before. The food manufacturer has therefore never been more dependent on the consumer's flavor preference. As the flavor of cocoa powder is one of the primary reasons for its use in confectionery and other food products and is judged and defined by a person's capacity for sensing flavors, the sensory evaluation process plays a critical role in today's food manufacturing.

Guidance on tasting

When testing cocoa powders for a new product or reformulating an existing product, the following should be kept in mind.

Because the medium in which a cocoa powder is tasted has a substantial effect on the final flavor, it is wise to carry out comparative sensory tests on the effects of a powder on a newly formulated food product itself. For example:

- The temperature at which a final product is consumed affects its flavor. Testing should always be carried out at the eating temperature of the product. In other words, a cocoa powder meant for ice cream should be tested in ice cream.
- Cocoa powders meant for cakes should be tested in cakes because other ingredients can interact with the cocoa powder. Also, texture affects the taste perception.
- When cocoa powders in chocolate milk drinks are compared, the drinks should have equal viscosity, as a drink's viscosity has great influence on the taste perception.

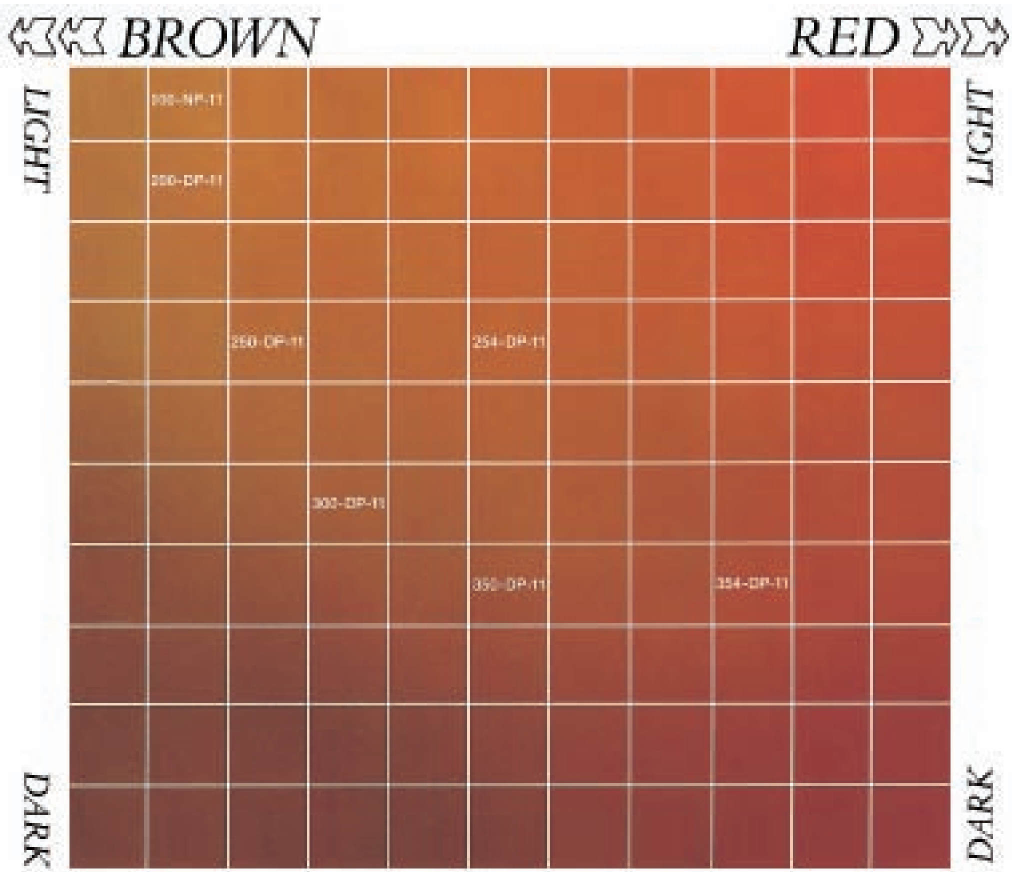
The circumstances in which sensory evaluation should be carried out can be compared with those for a musical instrument: Just like an instrument can only function at its best when the circumstances are also at their best, a human being can only participate in sensory evaluation adequately when the circumstances are right. This means allowing for complete concentration by the sensory evaluation participants without risks of distraction or external influences.

The flavor of cocoa powder is the primary reason the product is used in confectionery and foodstuffs. Cocoa is a product of nature, and fluctuations in flavor are, therefore, unavoidable. However, ADM Cocoa has developed the technology and has the expertise to limit such variations. The development of cocoa flavor is dealt with in Module 4, Flavor and Flavor Development.

Color

The color essential

The color of food products is a factor of critical importance to consumers and thus to food manufacturers. Color is one of the first messages the brain receives in making a sensory judgment on a consumer product. It carries a whole range of conscious and subconscious associations that affect sensory perception and thus appreciation. Because most consumers can detect very slight differences in color in the red-brown sector of the visible



Color Matrix

The sample on the left contains 11% less fat as compared to the sample of the same powder type on the right.

spectrum, differences in the color of cocoa-flavored and chocolate products can be easily detected.

The consistency of a product's color is also important to a food manufacturer, because it reinforces the image of constant product quality. Color variation between batches may create the impression of inconsistent production and quality control.

The color of a product containing cocoa has always been an indicator of taste due to the relationship between color, the quantity of cocoa, the degree of alkalization, and the consequent flavor modifications. Dark colors suggest a strong flavor. Light colors suggest a mellow or bland flavor. Cocoa powder is one of the primary colorants used in the food industry today.

Appearance

Cocoa powder contains naturally occurring colorants, most of which have been influenced in the alkalizing and roasting stages of the production process. Precise control of alkalizing and roasting allows optimum hue and color intensity of the powder to be obtained after grinding the nib and pressing.

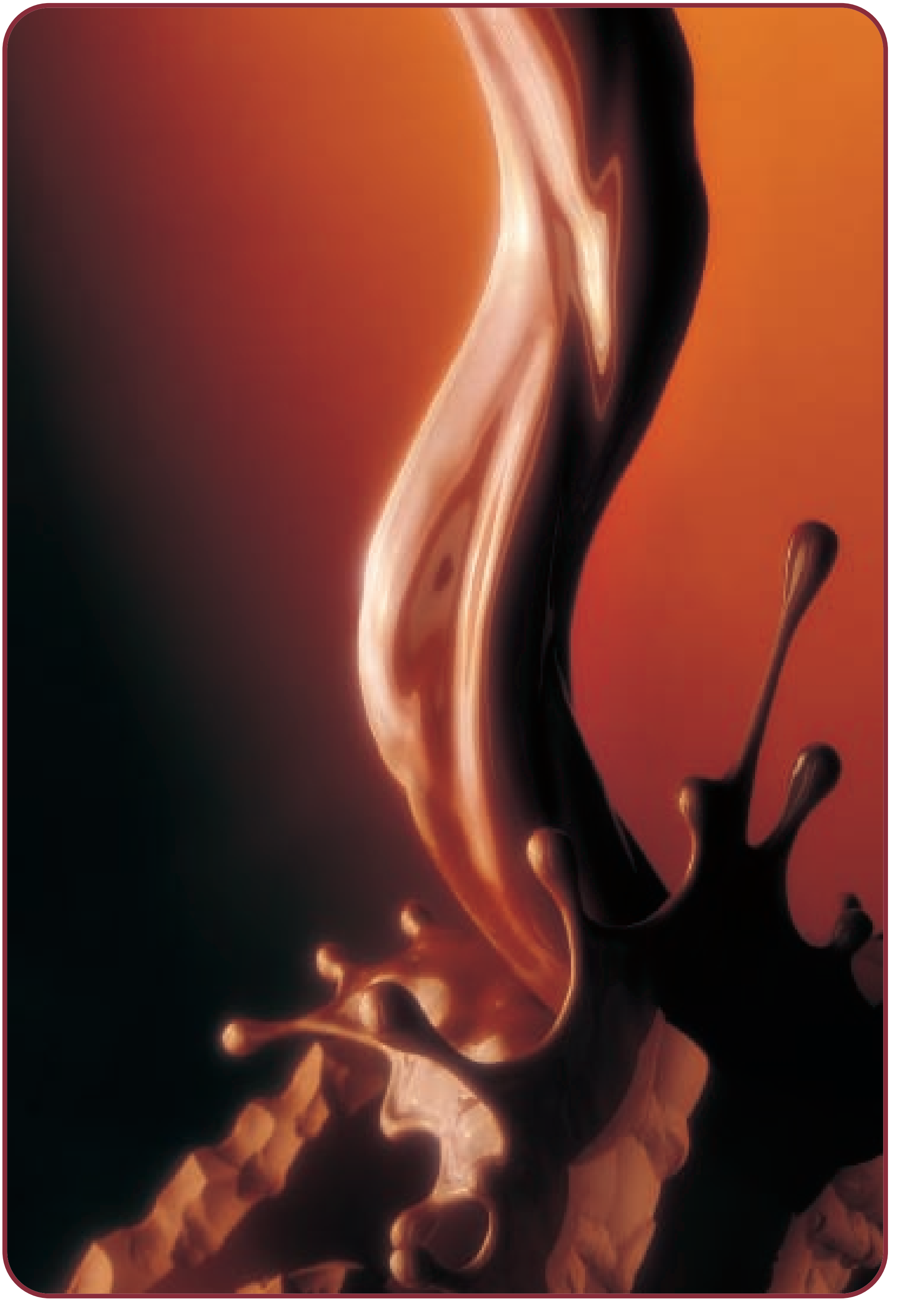
Non-alkalized cocoa powders usually have a light brown color, whereas alkalized powders may vary from light reddish-brown to very dark red-brown. (See Color Matrix.)

However, cocoa powder also contains a certain amount of cocoa butter, which, while intrinsically almost colorless, nevertheless affects the color of the powder. When evaluating the color of cocoa powder it is therefore important to distinguish the two ways in which color manifests itself: external color and intrinsic color.

External ("dry") color

The color of cocoa powder as such is the so-called external or dry color. This is strongly influenced by an optical effect in which the fat on the solid particles affects the light absorption. The higher the fat content of the powder, the darker the external color will appear to be.

The crystallization form of the cocoa butter in the solid particles determines the strength of this optical effect. When cocoa powder is subjected to temperature fluctuations, discoloration will occur due to a change in the crystalline form of the cocoa butter. The crystals should be small and in the stable form. This can be



achieved by rapid cooling and tempering. Slow cooling or rapid cooling without tem-
pering will result in larger crystals that impart a greyish hue to the cocoa powder. This discoloration, however, does not affect the quality of the product nor the intrinsic color in any way. Different pulverizing and tempering equipment and conditions (within or between locations) may also result in more external color variation.

Intrinsic color

The intrinsic color of cocoa powder is the color that the product made with the powder will ultimately have. In most finished products, the external color of cocoa powder no longer plays a role, and only the true color, the intrinsic color, is seen. The selection of a cocoa powder for its coloring capabilities should be based on evaluation of the color of the final product. This is the reason why De Zaan® cocoa powders are standardized on intrinsic color. As such, the external color of the powder is only of importance when the final product is used as powder, like in the case of truffles. For such cases, the dry color may also be specified.

Color matching

The production processes at ADM Cocoa are designed so that within the limits from light brown and red-brown to very dark brown, each required tint can be consistently produced. As a result of this great flexibility in the process, it is possible to perfectly match client color requirements.

The Color Matrix (see page 124) depicts only a limited number of cocoa powder types. They are part of the wide range of the De Zaan cocoa powders available from ADM Cocoa.

The cocoa powder Color Matrix gives an idea of the color range of powders available from ADM Cocoa. The matrix only includes types with a fat content of 10-12% and is based on the colors of the powders in dry form. The horizontal axis depicts the actual color changes from red to brown, while the vertical axis represents the lightness or intensity of the colors. It is not possible to reproduce in print the true brilliance of cocoa powders. Therefore, the color range of the matrix is only indicative.

Influence of cocoa color on the final product

The De Zaan powders cover a range of colors from red-brown to yellow-brown, to light and dark brown to almost black. A powder is selected by formulators and recipe experts according to the application requirements and naturally, the desired final color of the food product. Their decision is also a function of the other qualities they wish to impart to a product, such as flavor or texture.

The color of the food product depends not only on the type of cocoa powder used, but also on certain other factors:

- The other ingredients that are present in addition to cocoa powder also influence the color. For example, milk powder tends to "dilute" a brown cocoa color. A product that contains cocoa together with milk powder has a lighter color than the same product without milk powder. Another phenomenon: Chocolate milk made with skim milk has a darker color than with whole milk. The color of chocolate milk is clearly influenced by the presence of milk fat.
- The higher the concentration of cocoa powder, the more intense the color of the final product will be. Obviously, products with a low concentration of cocoa powder are lighter in color. Utilizing powders as color boosters, a light cocoa powder can be replaced by a darker powder without increasing its concentration. In some circumstances, a darker cocoa can be used to change or intensify the flavor as well.

- There are also technical reasons that might favor low concentrations of cocoa powder. Coatings based on lauric fats, for instance, should contain only a limited concentration of cocoa butter in order to prevent fat bloom. A very dark lauric coating could be made with a high percentage of light cocoa powder but with the risk of fat bloom. An alternative would be to use a darker cocoa powder at a lower concentration.
- The structure of the product. A cocoa-containing product that has been whipped so that it contains trapped air has a lighter color than a product that has not been aerated. Examples include ice cream and mousse.

The above applies to all products in which the intrinsic color of cocoa is important, and also in part to powder products in which the dry color of the cocoa powder is evident. The importance of the fat content of cocoa powder with regard to its dry color has already been mentioned. However, there are other factors that are important for defining color in dry products.

For dry products, both the colors of the other ingredients and the concentration of the cocoa powder determine the color of the final product. Factors that have an influence on such products include:

- The particle size of the other ingredients. A product in which cocoa powder has been mixed with a finely ground ingredient made of small particles will have a different coloration from one containing a more coarsely ground ingredient.
- The surface structure of a component such as sugar. Crystal sugar has a different surface structure than finely ground sugar. The latter, therefore, appears whiter than the former. This has an obvious effect on processed sugar products.

Indicative Composition of Cocoa Powder

	High fat (22-24%)	
Cocoa butter	23%	11%
Fat-free dry cocoa	72%	84%
Moisture	5%	5%

- The method and extent of agglomeration. There are various systems available to agglomerate cocoa-containing powders. Partly dissolved sugars as well as emulsifiers can play an important role in the agglomeration process. Both affect the surface of the dry matter in particular, causing the external color to be darker.

Fat content

Cocoa butter constitutes about half the weight of the cocoa nib. This fat is partially removed from the cocoa liquor by means of mechanical pressure as high as 450 kg/cm^2. Depending on the pressing time and the setting of the press, the resulting cocoa cake may have a fat content varying between 8 and 24%. It is technically not possible to press exactly to a specific percentage of cocoa butter; therefore some tolerance is necessary. However, this should be as narrow as possible and it is generally specified with a margin of ±1.0%. Most commercially available cocoa powders contain 10-24% fat, while the 10-12% fat range is the most widely used.

Although cocoa butter has hardly any flavor of itself, it does contain specific flavor ingredients, as cocoa powder does. It contributes to an overall rich mouthfeel in a number of products such as mousse and ice cream, while in white chocolate and milk chocolate, the flavor of cocoa butter can have a significant effect. Fat also masks both the bitter element of cocoa as well as the sour element, rendering a more chocolate-like, softer flavor.

The indicative composition that high-fat cocoa powder contains fewer coloring and flavoring constituents on an equal-weight basis. On the other hand, the dry, external color of high-fat powder is substantially darker and more brilliant compared to low-fat cocoa powders. (See page 124 under "Color.") This can be of particular interest for applications such as truffles and dry mixes in which the dry color is of importance.

When low-fat and high-fat powders are exchanged in a formula, a correction should be made for the difference in fat-free dry cocoa matter between the two, if the color and flavor intensity of the end product should remain the same.

Low-fat powders are recommended for use in compound coatings that contain lauric fats, as a higher cocoa butter content has a negative influence on the gloss retention of these coatings.

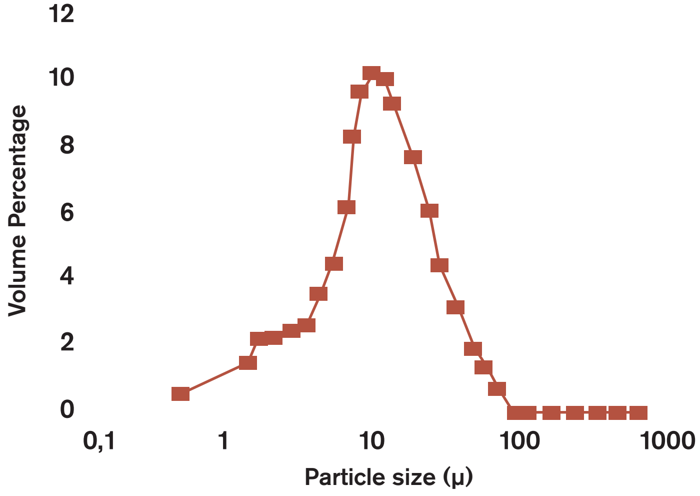
Due to the lower fat content, the 10-12% fat powders are less susceptible to lumping and are more free flowing. These powders are therefore better suited for products like vending mixes.

In some product formulas it is desirable to keep the fat content as low as possible. This goes, of course, for low calorie diet products, but also for products in which the presence of fat should be avoided for technical reasons, such as aerated products like a meringue or an angel food cake.

pH and alkalinity

The pH of non-alkalized cocoa powder is dependent on the acidic components of the cocoa beans from which the powder has been made. The variation in pH can be controlled to a certain extent by blending certain types of cocoa beans. In general the pH of non-alkalized cocoa powders ranges between 5.0 and 6.0, and it can be observed that this slight acidity contributes to the typical chocolate, some-

Figure 2:
Typical Particle Size Distribution
De Zaan® Cocoa Powders



what fruity flavor of these powders.

The pH of alkalized cocoa powders is largely determined by the amount and type of alkalis used during production. The added alkalis not only influence the pH of the cocoa powder but also raise its alkalinity and ash content. This may have an effect on the product in which the powder is used. This is particularly the case with bakery products (affects leavening) and dairy-based products (affects milk protein stability). In our technical information bulletins *Cocoa Powders in Bakery Applications; Chocolate Milk, a Complicated Product; and Chocolate Flavored Desserts* this matter is further discussed.

It can be said that the pH of cocoa powder usually has limited influence on the ultimate pH of the final product because the amounts of cocoa powder used in the product formulas are comparatively small. The products in which it is processed mostly have a buffering capacity. In some specific cases, however, a small change in pH can adversely affect the outcome of a product. The stability of foam, for instance, is higher at a low pH, which suggests the recommendation of low pH powders if foam development is an important feature of the final product such as in milk shakes. Higher pH levels may also decompose some vitamins.

Fineness

The fineness of cocoa powder is usually determined in the liquor grinding phase of the production process, but cake grinding can also have an effect. For many applications, proper tempering of the cocoa powder is an important processing step, both for the dry color and for avoiding lump formation. This holds true in particular for high-fat cocoa powders.

In most applications the fineness of cocoa powder is of major importance. The finer the powder, the smaller the individual particles and the greater the surface area of the powder will be. This can affect both flavor development and mouthfeel of a finished product. Also, very finely ground cocoa powder has a positive effect on the color intensity of the end-product, as well as on the viscosity of products such as syrups. Fine powders also show less tendency to settle out in liquid products.

Furthermore, the finer the powder, the more quickly its effect becomes evident in the mouth and the less the powder can be detected as an ingredient by itself. In chocolate milk or milk-based desserts, for instance, the presence of a small amount of coarse particles can easily be noticed. They can be seen against the white background of the milk as brown specks and can adversely affect the smooth mouthfeel of the product.

In biscuits, cookies, or cake mixes, the fineness is a less sensitive factor, as the particular character of the powder is lost in the overall flavor appreciation of the final product due to its texture. However, in bakery products, fineness of powder has an effect on the water absorption in the dough phase and thus on formulation and handling characteristics.

When considering the fineness of a cocoa powder, a distinction has to be made between the average fineness and the particle size distribution. Figure 2 illustrates the typical particle size distribution of selected De Zaan® cocoa powders. The tails of the curve do not influence the average fineness of the powder. However, it is the percentage of the coarse particles in the right tail, their nature, and their size that may have an effect on the end-product.

Shell content

Shell does not contribute to cocoa flavor and cocoa color and has to be removed from the cocoa nibs as required by standards. With removal of most of the shell, the microbiological status is improved. In addition, wear and tear on equipment such as roller refiners and homogenizers by the hard cocoa shell particles is reduced.

Determining the shell content of cocoa powder is not a simple matter. Many of the methods of analysis used for this purpose are unsatisfactory. In the U.S., the FDA requires the shell content to be analyzed with AOAC method 970.23 (1990).

Rheology and water absorption

Cocoa powder has an important effect on rheology and water absorption in many of the products in which it is used. A distinction can be made in food systems where water is the continuous phase (dough for bakery products, desserts, toppings, and chocolate beverages) or in products where fat forms the continuous phase (compound coatings, chocolate, and fillings on fat basis).

Whenever moisture is available, cocoa powder will compete with other ingredients to absorb it. It can take in moisture up to 100% of its own weight. In comparison, flour can absorb moisture up to 60% of its own weight.

This means that in dry mixes, a balance in water activity will be established between the various ingredients. The water activity of cocoa powder is low: With a moisture content of 5%, the water activity amounts to about 0.3. Flour has a much higher water activity, namely 0.55, and a moisture content of 14%. In bakery mixes, a balance will therefore be established between all the ingredients.

As a consequence of the strong water absorbing capacity of cocoa powder in bakery mixes, stiffer dough and dryer bakery products with more breakage will occur if no moisture correction is made when flour is partially replaced by cocoa powder. To avoid this, the moisture content in cocoa powder-containing dough must be adjusted. As a guideline, it can be said that 40% of the weight of the cocoa powder has to be added as extra moisture in order to obtain an optimal result. In ADM Cocoa's technical information bulletin *Cocoa Powders in Bakery Applications* this subject is extensively discussed.

In food products containing a high

quantity of moisture, cocoa powder also has an effect on the rheology of the ultimate product. For example, in chocolate milk, cocoa powder forms a network with the stabilizer and the milk proteins, that to a large extent, avoids settling of the cocoa particles. When this network is disturbed by shearing forces, the product loses its initial viscosity and will quickly become thin fluid.

After it has come to rest again, the network will recover itself, but not entirely. This phenomenon is called hysteresis. It is a good indication of the degree to which the product is sensitive to settling of the non-soluble cocoa particles.

The fat content of cocoa powder influences the rheology as well. In water-based systems, the cocoa butter, like oil in a water emulsion, is distributed in small fat globules. The more fat available, the richer and more viscous the end-product will be. Therefore, high fat cocoa powder gives chocolate milk not only a richer flavor, but it also makes the product more viscous. These subjects are further discussed in ADM Cocoa's technical information bulletin *Chocolate Milk, a Complicated Product*.

In syrups and other sugar-rich products such as toppings, the rheology of the end product is not stable during storage. Aggregation and sedimentation of solid particles and sugar crystallization lead to undesirable after-thickening effects.

This is caused by an interaction between cocoa particles and the sugar in the syrup. In the toppings, it is triggered by a slow crystallization of the sugar.

A three-dimensional network is developed that results in a higher viscosity. Alkalized cocoa powders have a positive effect on retarding after-thickening during storage and are therefore recommended for these applications.

Cocoa powder in almost moisture-free systems like chocolate and compound coatings manifests itself as a dispersion in the fat or oil present in the product. Here, the fat is the continuous and the powder the discontinuous phase.

Cocoa powder is very finely ground, giving it a very large specific surface. At first, the powder will show a distinct fat-absorbing tendency, but as a result of shearing forces during processing, a substantial part of the fat is freed up for the continuous phase, and then the viscosity drops sharply.

Another phenomenon in compounds is the effect of moisture in the sugar-rich environment. At very low concentrations (1% and higher), an important increase in the liquid chocolate or compound coating can be observed. Cocoa powder, with its maximum of 5% moisture, is an important source of moisture in the recipe. The development of shearing forces and the evaporation of moisture take place during the conching. This processing step is therefore of great importance for the rheology of the end product.

This subject is further dealt with in ADM Cocoa's technical information bulletin *Cocoa Powder and Compound Coatings*.

Wettability and dispersibility

One of the problems confronting a user of cocoa powder is slow dispersibility in an aqueous system. Manufacturers of instant products especially have to address this phenomenon. In fact the problem refers not just to solubility (about 30% for cocoa powder), but rather to the whole complex of wettability and dispersibility of cocoa powder as such.

When cocoa powder is added to cold water or cold milk, the powder tends to float on the surface because of its poor wettability. When one tries to disperse the cocoa powder in a liquid by stirring, the still insufficiently wetted powder particles will partially remain in and on the surface of the liquid as small lumps.

By its nature, cocoa powder is not inclined to disperse but to float on the surface of a liquid. This is primarily due to the cocoa butter present in the powder, which repels water and prevents the wetting of the powder particles.

Wettability and dispersibility can be significantly improved by blending the cocoa powder with lecithin. As an emulsifying agent, lecithin is a mixture of phosphatides that is surface active. The lipophilic (fat-affinity) part of the molecule attaches to the cocoa butter present in the cocoa powder, and the hydrophilic (water-affinity) part of the molecule attracts the water in the solution. It is recommended to use lecithinated cocoa powders rather than adding the lecithin separately during the agglomeration process of products such as two- and three-component instant cocoa beverages. (See also ADM Cocoa's brochure *Sol Lecithinated Cocoa Powders*.)

Notwithstanding the fact that cocoa powder has poor wettability, it is very hygroscopic. When exposed to a humid environment, it will immediately attract moisture, which may lead to bacteriological spoilage due to mold growth. Cocoa powder should preferably be stored under cool (15°-20° C/59°-68° F), dark, and dry (RH <50%) conditions, in its original protective packaging. (See also "Packaging, storage, and transportation" later in this module.)

2. The application of cocoa powder

Introduction

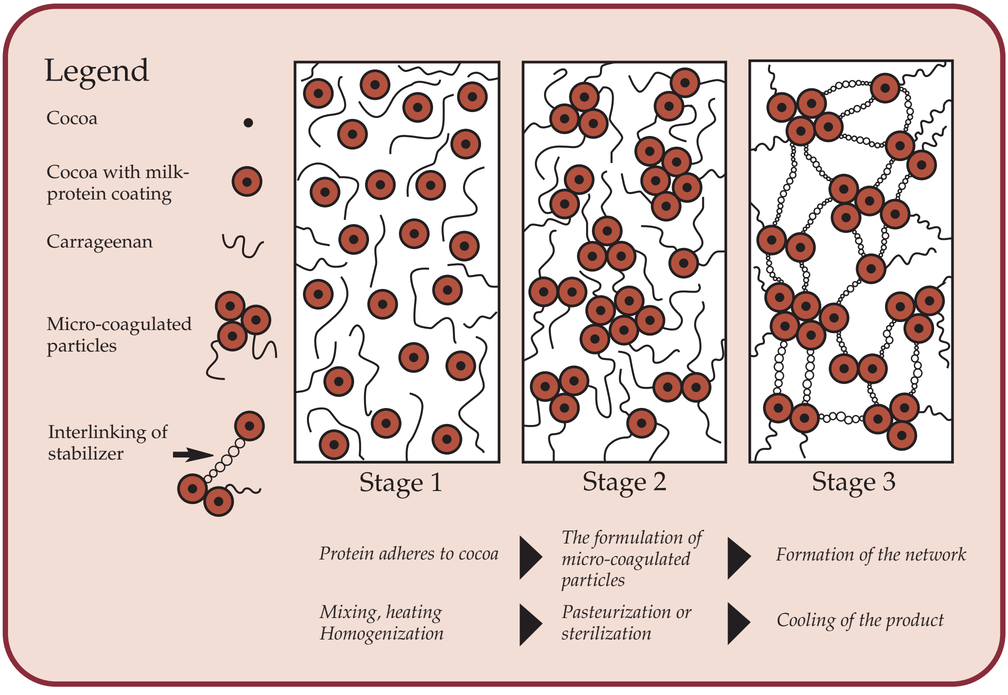
As far as is known, cocoa powder is consumed in every country of the world. While almost any cocoa powder can be used in any food product, considerations of taste, color, performance, legislation, and cost mean that certain cocoa powders are more effective than others, sometimes significantly. ADM Cocoa recognizes that it is important to optimally advise the users of cocoa powder in their product formulations. It is often the combination of the type of cocoa powder, the appropriate amount in the formula, and the manufacturing parameters that determine the desired results.

In this section, consideration is given to the most common applications of cocoa powder. It does not, however, go into the same detail as the numerous technical information bulletins issued by ADM Cocoa. It is these that represent the key and comprehensive information source for the cocoa powder user in a particular area.

ADM Cocoa has listed cocoa powder applications by industrial food product segment. Of course, this can only be done on an arbitrary basis and is not exhaustive. The listing should therefore be regarded as informative only.

The industrial product applications can be grouped as follows:

Dairy products
- chocolate milk
- milk shakes
- custard
- mousse
- whipped toppings
- pudding
- fermented dairy products
- dairy premixes



A simplified model of network formation in chocolate milk

Ice cream and frozen desserts
- ice cream
- frozen yogurt
- novelties
- ice cream premixes

Bakery products
- cakes
- pastries
- brownies
- doughnuts
- pies
- cookies
- wafers
- biscuits
- biscuit and wafer fillings
- frozen bakery products
- breakfast cereals
- bakery premixes

Confectionery, coatings, and cocoa products
- fudge
- frostings and icings
- fillings
- confectionery coatings
- ice cream coatings
- vermicelli/flakes
- spreads
- toppings
- syrups
- extracts
- coated cereals
- breakfast cocoa powder

Instant products and premixes
- dry 2/3 component drinking mixes
- vending mixes
- dairy premixes
- bakery premixes
- ice cream premixes

Dairy products

Dairy products are those made primarily from liquid milk. As there is a significant risk of microbiological deterioration, they must be pasteurized or sterilized. An enormous variety of cocoa-flavored milk-based products is available to the consumer.

Chocolate milk, for example, is a very effective way of imparting the cocoa flavor, as the liquid character means almost instant exposure of the flavor components. The challenges of chocolate milk lie in the stabilization of what is inherently an unstable system. Only part of the cocoa powder will dissolve in the milk, whereas the majority of the particles will settle out as sediment over a period of time. In order to hold cocoa powder particles in suspension, a relatively high viscosity is required. This can be achieved by using a stabilizer such as κ-carrageenan that will react with milk proteins and cocoa particles to form a three-dimensional network holding these particles in suspension. The various stabilization systems and production methods of chocolate milk are discussed in ADM Cocoa's technical information bulletin *Chocolate Milk, a Complicated Product*.

Puddings, mousses, and custards are usually milk based. The addition of stabilizers, sugar, emulsifiers, color, and flavor ingredients leads to products with a specific flavor, color, viscosity, and texture. Stabilizers and emulsifiers are of critical importance for mouthfeel, whereas flavor and color determine whether a dessert is delicious and attractive to look at.

It is difficult to predict which cocoa powder will give the optimal color and flavor to a particular milk-based dessert. Product formula and heat treatment are just two of the factors that play a major role. On the basis of defined criteria for what the end product must comply with powder types for a specific formulation can be preselected. The ultimate choice, however, will more often than not be the result of practical and taste panel experience.

The desired texture and air content of a dessert are significant in determining the type and dosing of the cocoa powder to be used. The lighter the texture and the higher the air content, the more concentrated the color and the flavor of the cocoa powder should be.

The technical information bulletin *Chocolate Flavored Desserts* gives extensive details on the application of De Zaan® cocoa powders from ADM Cocoa in a variety of popular desserts, including a number of product recipes with processing recommendations.

Ice cream and frozen desserts

The color and flavor of chocolate-flavored ice cream come mainly from cocoa solids, which can be introduced as a constituent to the ice cream, a chocolate or compound coating, or in a combination thereof. Ice cream and desserts are made of similar ingredients. The main component is water, which serves as a solvent and will form ice crystals. Sugars affect flavor and structure. Non-fat milk solids impart the milk flavor, and fats impart the structure and creamy effect so characteristic of ice cream. Stabilizers increase the viscosity, create a gel, stabilize the system, and prevent the ice cream from melting too easily. Emulsifiers reduce the surface tension between the fat and water phases and have the effect of arranging the fat globules around the air bubbles to form a homogeneous structure. All of these factors affect the eating properties of the product, including the mouthfeel, and can be influenced by adjusting the product formulation and the processing conditions.

ADM Cocoa's technical information bulletin *Cocoa Powders and Ice Cream* specifically deals with the effect that cocoa powder has on the manufacturing of ice cream and frozen desserts.

Bakery products

This large product category covers many types of cakes, biscuits, and cookies. These are essentially dry in the sense that most moisture has been removed in the baking process.

Alkalization influences the pH, alkalinity, ash content, flavor, and color of the cocoa powder. The alkalinity of the cocoa powder can affect baking properties in the same way as baking soda. To select a cocoa powder for a baking application, it is therefore important to look not only at the flavor and the color but also how it will affect the baking process.

Cocoa powder readily absorbs moisture. If, for example, a cake is baked and part of the flour is replaced by cocoa powder, the baker must raise the amount of water and make a correction in the amount of baking soda, as otherwise the cake would have a volume too low and a texture too dry.

Medium to strongly alkalized cocoa powders are generally used in bakery products. As mentioned, the alkalinity of the cocoa powder may have a significant effect on the color of baked products such as cakes and cookies. Excessive baking soda (pH >8) will change the color of the end product from yellowish-brown to reddish-brown.

More so than in some other product categories, the recipe instructions and procedures for baked products containing cocoa powders can be critically important for achieving a satisfactory product. ADM Cocoa has compiled a comprehensive technical information bulletin, *Cocoa Powders in Bakery Applications*. This publication deals with the effects of cocoa powder in relation to other ingredients and the technology in a number of bakery applications, including a number of product formulas and recommended processing methods.

Confectionery, coatings, and cocoa products

This product category comprises applications based on fat-sugar, water-sugar, and water-fat-sugar systems.

Fat-sugar systems are those in which the main ingredients are fat, sugar, and cocoa powder, such as compound coatings and fillings. Depending on the amount and type of fat, a product will be soft or hard at room temperature. For compound coatings made from different vegetable fats, both alkalized and non-alkalized cocoa powder can be used. This is a matter of flavor and color appreciation and of costs: The flavor/color impact of a lower level of alkalized cocoa powder may be stronger than that of a higher level of natural cocoa powder.

Non-alkalized cocoa powders are lighter in color than alkalized powders. If milk solids are added or incorporated, the difference in color between alkalized and non-alkalized powders will become more evident. The whitish milk powder functions as a background that will emphasize the color and its brilliance.

Cocoa powders with higher cocoa butter contents can have an adverse effect on the gloss stability of compound coatings made with lauric fats.

For ice cream coatings, alkalized cocoa powders are often used. The reason for this is that the detection of the chocolate flavor is dulled by the low temperature of ice cream. The stronger flavor and darker color of the alkalized powders render their full impact in this application.

In the technical information bulletin *Cocoa Powder and Compound Coatings* a detailed description is given as to the behavior of cocoa powder in different fat systems and the composition and manufacturing methods of a number of coatings.

Water-sugar and water-fat-sugar systems include products such as syrups, fudges, toppings, and frostings, where water forms the continuous phase. This has the effect of altering the rheology and mouthfeel of the product to respond to the specific demands of the application. Improved preservation is partially obtained by the addition of sugar and other preservative ingredients. This means that the quantity of sugar in these products is often higher than in products of fat systems.

In these applications, in addition to non-alkalized cocoa powders, strongly alkalized powders are often used. This is balanced by the high sugar content present and its ability to mellow the sometimes-pronounced flavor of the strongly alkalized cocoa powders.

When using water in relatively high viscosity products, consideration must be given to the total carbohydrate percentage of the cocoa components. The starches, sugar, and dietary fiber establish a bond with the water, as a result of which a thickening effect may occur over time, such as in syrups.

It is important that with sugar syrups, the correct proportions of the various types of sugar are chosen. An incorrect choice of sugars may lead to crystallization, which in turn produces a change in viscosity. In many cases, the cocoa powder is seen as the cause of this, while it is more often caused by problems in the area of the sugars used.

Instant products and premixes

Instant cocoa products are mixes that are added generally to cold milk or water. Just adding a regular cocoa powder to cold milk and stirring will not create an attractive looking product. The reasons for this are:

- Cocoa powder contains cocoa butter, which behaves hydrophobically in

cold milk.
- Cocoa powder is a fine powder and contains starch, which, by nature, favors the creation of lumps of cocoa in cold milk.

To prevent this, it is better to mix cocoa powder with sugar first and then add cold milk gradually while stirring. By making a high-viscosity paste, the lumps of cocoa are easily eliminated.

However, most consumers find it less convenient to make chocolate milk in this way. A ready-to-use mix to be added to warm or cold milk or water naturally has preference. For this reason, the so-called instant products have been developed. An instant product is generally a two- or three-component mix:
- Two-component mixes are mainly made of crystal sugar and cocoa powder.
- Three-component mixes are mainly made of cocoa powder, crystal sugar, and milk powder.

Because milk consists largely of water, it is important to change the hydrophobic cocoa powder into a hydrophilic powder. The cocoa manufacturer does this by coating the cocoa powder particles with an emulsifier such as lecithin. The lecithin molecule is made up of hydrophobic and hydrophilic parts. The hydrophobic part anchors itself to the cocoa butter on the cocoa solid particle. The hydrophilic part of the lecithin molecule is directed to the outside of the cocoa particle. In this way, a cocoa particle is created with an outer surface that has a hydrophilic character. When this lecithinated cocoa particle is added to cold milk or water, it is easily dispersed.

However, if a dry mixture of sugar crystals and lecithinated cocoa powder is added to cold water, the sugar crystals immediately fall to the bottom of the glass, followed much more slowly by lecithinated cocoa particles. This results in non-optimal dispersion. To improve the dispersion, the heavier sugar crystals are attached to the cocoa powder by agglomeration. The sugar crystals are moistened with water/steam. The lecithinated cocoa particles adhere to the wet sugar crystals, and the agglomerated particles are then dried. This creates sugar cocoa agglomerates that are easily dispersed in cold milk.

Lightly alkalized lecithinated cocoa powders are generally used in instant products.

In vending machines, hot water is added to a mix of cocoa powder, sugar, and milk powder to produce hot chocolate. Because the cocoa butter melts in the hot water, the hydrophobic character of the cocoa powder plays a less important role. As a result, it is not recommended to use lecithinated cocoa powder in vending mixes. The mix, however, should be agglomerated to ensure good mixing with the hot water.

In ADM Cocoa's technical information bulletin *Cocoa Powder and Dry Mixes*, extensive information is made available on this particular application of cocoa powder.

3. Packaging, storage, and transportation

Packaging

Cocoa powder is a complex and vulnerable product. It is not only very hygroscopic; it also tends to quickly pick up foreign odors from its surroundings. Therefore, the product should be properly packed and stored. The packaging itself must be able to endure transportation over long distances and varying handling conditions and should be able to stand up to a prolonged storage period. The powder itself is a product that enjoys a long shelf life, provided that packaging and storage conditions are adequate.

Cocoa powder storage under optimal conditions

Depending on the geographical destination, the cocoa powder is usually packed in paper bags of either 25 kg or 50 lbs. These bags are made of multi-layer kraft paper and a polyethylene moisture barrier. The bags are stacked 30 (750 kg) or 40 (2,000 lbs.) to a wooden pallet. A cardboard anti-slip sheet is placed on the pallet to protect the bags at the bottom. A plastic foil and wrapping is fitted around and over the pallet to protect the bags from dirt, pests, humidity, and damage (instability) during handling and transportation. The pallets can be lifted from four sides and are single, one-way (non-returnable) transport units.

Coding

Each individual packaging unit of cocoa

products carries the identification of the manufacturer and country of origin, the product type, the product description, the lot identification number, the net weight, and a unique production code for verification and identification (traceability). Pertinent information in this code includes the date of manufacture, the pallet number, and the filling line/machine. Typically, each packaging unit also includes transport and storage instructions, e.g. keep cool and dry.

For microbiological sampling and analysis, a different lot definition is used: a quantity of product produced and handled under uniform conditions. (See Microorganisms in Foods 2, I.C.M.S.F. (1986), page 22.) Often, such a microbiological lot consists of the product bagged or filled from a single line within a limited period, e.g. six-24 hours.

Transport and storage

Under incorrect transport and storage conditions, certain changes in cocoa powder's physical characteristics can occur. For instance, if cocoa powder is compressed beyond a certain level, agglomeration or lumping of the cocoa particles occurs. Stacking beyond a certain height will give rise to this pressure and must therefore be avoided. It is not recommended to stack more than 20 bags or two pallets high.

The air surrounding the pallets of cocoa powder should preferably have an RH <50%. This level of humidity is the upper limit to hold cocoa powder in a microbiologically stable state. But even with an RH <50%, care must be taken that no sudden temperature changes of the surrounding air occur. Even under favorable conditions, this can cause condensation on the inside of the packaging that may lead to possible growth of mold.

Also the cocoa butter present in the cocoa powder is sensitive to temperature changes. If it is subjected to a temperature too high, it will melt. When the temperature drops again, the cocoa butter will re-crystallize, giving the cocoa powder a gray discoloration. It will also cause the particles to stick together.

Although these factors do not have an influence on the intrinsic quality of the cocoa powder, lump formation can make the powder difficult to handle in further processing.

Protection of cocoa powder against rodents and insects is also essential. The greatest danger comes from damaged bags and unhygienic storage conditions. The product must be stored in a clean, regularly inspected area. Rodents and other pests can be controlled by traps or electric defense mechanisms.

The following recommendations are made for adequate transportation and storage conditions:

- Use only cool, dark, and dry food-grade storage areas in which the temperature is between 15°-20° C (55°-65° F) and the RH is <50%.
- Stack no higher than 20 bags or two pallets.
- Position the pallets with sufficient space between them and the wall to avoid local temperature variations and pest infestation.
- Keep the storage space clean and free of rodents, insects, birds, and other pollutants.
- As much as possible, prevent sudden temperature changes.
- Avoid exposing cocoa powder to direct sunlight, hot lamps, or other direct sources of heat.
- Ensure the absence of strong smelling products in the vicinity, such as coffee, tea, tobacco, spices, paints, chemicals, and cleaning substances.
- Even though the cocoa powder has a much longer shelf life, use up stocks

within 12 months.

Packaging reduction

ADM Cocoa's policy with regard to product packaging is first and foremost to properly protect the product so that the user receives it in an optimal condition. Beyond this, the issue of packaging and its effects on the environment must be addressed. In response to worldwide public concern over protection of resources and biodegradability of packaging materials, many countries are reacting by taking action to reduce packaging. We are
seeking to:

- minimize the size and quantity of packaging materials used
- make it reusable, if packaging is unavoidable
- make it recyclable, if it can't be made reusable

Bulk and semi-bulk packaging

Packaging materials and handling technology are developing very fast. New systems are constantly coming onto the market. However, transportation of cocoa powder in bulk, in whatever way, is ultimately going to be the only adequate solution to this problem. Tank cars have already made their entry, and the semi-bulk flexible intermediate containers are rapidly gaining in popularity. For users of large quantities of cocoa powder, this bulk packaging from ADM Cocoa reduces handling and logistics costs significantly while protecting the product's integrity. They carry between 800 and 1,000 kg (1,750 to 2,200 lbs.), depending on the type of powder. For more information on this type of packaging, please contact one of the sales offices of ADM Cocoa listed on page 151.

4. Specification of cocoa powder

Introduction

Specifications are important for the user of cocoa powder to formulate an end-product, set quality standards, and comply with food legislation. Specifications relate to consistency, quality, and safety and are only meaningful when the corresponding methods of analysis are indicated. These methods of analysis can be found in Module 3: Methods of Analysis.

Controllable and non-controllable factors

Defining specifications is particularly challenging for products made from raw materials with a natural origin. In the manufacturing process of cocoa powder, there are important production steps where quality aspects can be influenced and controlled. These are:

- Alkalizing: allows control of color, flavor, and pH
- Roasting: allows control of flavor and microbiology
- Pressing: allows control of fat content
- Grinding: allows control of fineness

However, some characteristics can be controlled only to a limited extent. These are the natural constituents of cocoa, for example: the content of starch, protein, and theobromine or the cocoa butter composition. The pH of the non-alkalized cocoa powder is determined by the acidic components of the beans used and can only be controlled by the selection of the beans.

Many users of cocoa powder require nutritional information on the product for the calculation and declaration of the nutritional value on their consumer packages. For different types of cocoa powders, this nutritional information is given in Module 6: Health and Nutritional

Aspects. Because cocoa beans naturally vary with origin, season, and differences in processing, this information is indicative only and is not a part of our standard specifications.

Food safety aspects

ADM Cocoa is certainly aware of the essential character of safety in food products. A working and certified HACCP ensures that food safety hazards are continuously monitored and controlled. Many factors can influence cocoa product food safety. A brief summary is given below.

Impurities

Impurities are defined as everything present in cocoa powder that theoretically should not be there. They can be subdivided into two categories:

- Foreign matter relates to all items that are not intrinsic to the product and that may have been introduced during harvesting, transportation, and processing of the raw material. These non-indigenous materials, such as pieces of wood, metal fragments, and sand, must be removed and carefully controlled.
- Extraneous matter can be defined as material that is intrinsic to the processed product and includes insect fragments and cocoa shell. Its presence is unavoidable but can be controlled by applying Good Manufacturing Practices (GMP) and adequate processing. Tolerable levels of extraneous matter are set in the Defect Action Levels by the Food and Drug Administration in the USA.

Metallic iron

The presence of metallic iron is inherent to cocoa given growing, postharvest, and manufacturing conditions. Good manufacturing practices and the use of powerful magnets help control the levels of these very fine particles.

Pesticides

Cocoa trees and their fruit are prone to attack by microorganisms and insects. To fight these pests, fungicides, insecticides, and pesticides may be applied but mostly on the cocoa pod and not on the beans themselves.

Heavy metals

As is true with most agricultural crops, trace levels of heavy metals often found in the soil may be found in cocoa. Because cocoa beans from origin countries commonly come into contact with soil, shell removal to the levels specified under regulatory standards is known to help limit the levels of these naturally occurring metals.

Mycotoxins

Mold growth on cocoa beans occurs on occasion. Some of these molds can produce mycotoxins. This may occur at the farms during harvesting, ripening, fermentation, and drying. It is thus possible that mycotoxins like aflatoxins and ochratoxine A are present on cocoa beans. It is impossible to remove every impurity from cocoa powder during manufacturing. Regulatory authorities have recognized this. However, careful selection and handling of raw materials and good manufacturing practices help control the levels of such impurities.

Specification components

It is important to note regarding the components of typical De Zaan® cocoa powder specifications that ADM Cocoa operates a number of cocoa processing plants around the globe. The raw materials supplied and the nature of processing may vary from one plant and/or region to another. As a result, the specific attributes and values in specifications may differ simply due to the raw materials in use and the specific

nature of the processing employed.
The final application for a specific cocoa powder is best used as a guide to determine which component values, methods of analysis, and other product features are most important to that application.

Flavor and color
No matter how important various features may be, cocoa powder is ultimately used in the finished product for its flavor and color. The food industry has every interest in using cocoa powders with features that are as optimal and consistent as possible. That is why reliable methods are important to determining whether a delivery conforms to a reference sample in color and flavor. These methods are outlined in Module 3: Methods of Analysis. Further information regarding sensory evaluation can be found in Module 4: Flavor and Flavor Development. Reference samples are available from ADM Cocoa. With these, customers can carry out their own checks.

Fat content
The food legislation of many countries has divided cocoa powders into different categories based on their fat contents. Within the regulations in effect, industrial customers select the fat content that is optimal for their products. It is not technically possible to press to an exact fat percentage; some tolerance is necessary. However, this specification should be as narrow as possible. ADM Cocoa specifies the fat content within a 2% range.

pH
The alkalization process increases the pH value of the natural, lightly acidic cocoa. The degree of alkalinity is determined by the extent of alkalization and the acidity of the cocoa beans. Controlled processing results in definable pH ranges. Non-alkalized (natural) cocoa powders may have wider pH ranges caused by the natural variation in the acidity of the cocoa beans.

Fineness
A clear distinction must be made between fineness determined by sieving of the dry cocoa powder versus sieving the cocoa powder in a water suspension. The fineness of powder as such is not relevant in most applications. Cocoa particles are partly agglomerated and do not disintegrate completely with dry sieving. However, agglomerates will immediately disintegrate when the powder is brought into suspension or when heat is applied. The wet sieve test with warm water is, therefore, the best determination of fineness. (See Module 3: Methods of Analysis.)

Fineness is a characteristic for which different applications have various demands. Manufacturers of chocolate milk will immediately notice the presence of a slight amount of coarse cocoa particles in their products and may experience problems with their homogenizers.

An easy test for coarse particles is to put cocoa powder in milk. The particles can be easily seen when they are placed against the light background of the milk.

Moisture content
Some food laws allow a moisture content of max. 9% for cocoa powder. In practice, this percentage appears to be too high. With rapid decreases in temperature during storage or transport, condensation inside the packaging can occur. With such a high moisture content, mold can grow in the product. Our experiences show that a moisture content of a max. of 5% is best.

Microbiological characteristics
It is important that limits be placed on the microbiological quality of cocoa powder, especially as related to specific applications. The reasons for this are:

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THE ADM COCOA ORGANIZATION

ADM Cocoa operates 13 industrial chocolate and cocoa ingredients factories in eight countries on four continents. It allows us to integrate and implement technologies and expertise from all of these units, and so to benefit fully from the acknowledged operational and organizational know-how of our parent company, Archer Daniels Midland Company, one of the world's leading food processing companies.

ADM Cocoa is structured effectively to help our customers worldwide to make the most of chocolate and cocoa ingredients.

If you would like to know more about ADM Cocoa, talk to your representative or contact us at one of the locations listed.

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