Alkalizing Cocoa and Chocolate

Matching the proper alkalized cocoa or liquor to the proper application is the key to a successful product.

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Blommer Chocolate Co.

Throughout history no time period has had a greater impact than the 19th century on shaping the chocolate products of today. Rudolph Lindt developed the first conche in 1879, which led to flavor improvement of chocolate. Daniel Peter was the first person to successfully incorporate milk into chocolate in 1876 after many others had tried and failed. In 1847, Joseph Fry added additional cocoa butter into chocolate, giving us the ability to form the chocolate bars of today. In order for Joseph Fry to have access to cocoa butter, Casparus Van Houten developed and patented the cocoa press in 1828.

Van Houten owned a factory in Netherlands which was producing cocoa drinks from ground cocoa beans. His chemist son, Coenraad, recognized that further improvements could be made to the cocoa. In 1828 he combined alkaline salts with cocoa powder, which resulted in reduction of acidity (natural cocoa is typically 5.0–6.0 pH). This reduced bitterness and sourness, making the drink more palatable. It also improved the dispersibility of cocoa powder in liquid. While the cocoa butter content was significantly reduced from the natural cocoa through pressing, its ability to be incorporated into a drink still could be improved, and was, through neutralization. Color enhancement occurred as well. Coenraad recognized the darkening of the color, giving it the appearance of a more intense flavor. In general, the flavor was enhanced through the smoothing out of the sour and bitter flavor undertones, creating the precursor for cocoa drinks today.

Coenraad Van Houten patented his cocoa-alkalizing discovery in Netherlands in 1828, hence the phrases *dutched cocoa* or *alkalized cocoa* are now used synonymously in today's chocolate industry. Van Houten's patent ran out after 10 years and now the cocoa and chocolate dutching method is used extensively in the food industry. Alkalized cocoa or chocolate can be found in drinks, ice cream and frozen treats, baked goods, pastry and compound coatings, as well as alkalized or dutched chocolates.

Van Houten's discovery is the basis for this paper. Topics for discussion include alkalizing cocoa and chocolate today, alkalized chocolate and compound, as well as the application impact of alkalized cocoa.

THE ALKALIZING PROCESS

The process of alkalization can be broken down into three main categories: nib alkalization, cocoa cake alkalization and chocolate liquor alkalization. Each process has distinct advantages and disadvantages.

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Nib Alkalization

Nib alkalization (Figure 1) is the prevalent alkalization method across the United States and Europe because it offers advantages in coloring and flavoring not present in the other methods. Deeper and more intense reds are possible while offering a clean flavor.

The first step of nib alkalization is carried out by fracturing raw cocoa beans then removing the shell or skin. The remaining product is the cocoa nib or meat of the cocoa bean. The nibs are then soaked in an alkali solution with additional moisture added, possibly as high as 50 percent. The strength of the solution is predetermined by the desired pH and color of the end product as well as the starting pH of the cocoa beans used. This alkali solution is given time to penetrate and react with the cocoa nib. During this process, time and temperature are controlled because longer time, higher temperature and basic pH conditions favor formation of more intensified color due to sugar degradation, Maillard reaction and anthocyanin polymerization.

Aeration can be performed to further enhance red notes through intensified oxidation of anthocyanins and other polyphenolic substances, either while under pressure or at normal atmosphere. Steam or air pressure could be added to hasten the darkening or browning effects depending on system capabilities or desired outcome. Vacuum is also an atmospheric mechanism used to manipulate color and enhance moisture reduction.

Following the alkali reaction, roasting is required. Depending on the roasting system and moisture content of the nib alkali mix, some drying may be required before entering the roaster. Roasting will complete the drying process while enhancing chocolate flavor. The time and temperature of the roast will impact the final color and flavor in addition to the alkali reaction time.

When the alkali reaction and roasting are complete, the nibs are ground into chocolate liquor. The particle size is reduced (using a ball mill or stone mill), the liquor is pressed into cocoa cake and cocoa butter fractions, then the cocoa cake is milled into a fine powder. The red or dark powder is now complete. It is also possible to eliminate the pressing step and use the alkalized liquor directly in chocolate.

While flavor and color are positive attributes of nib alkalization, there are also some negative aspects. Alkalizing the cocoa nibs also alkalizes the cocoa butter. Cocoa butter processed with alkali can have increased soaps, which if excessive, can soften the cocoa butter and impact the tempering if chocolate is its final use. The cocoa butter flavor can be altered and, depending on the degree of alkalization, the cocoa butter color can be impacted as well. This creates the need for pretreatment and deodorization of the cocoa butter, which results in yield loss. Because of this cocoa butter yield loss and expensive equipment required, nib-alkalized cocoa is typically more costly than liquor-alkalized cocoa or alkalized cocoa cake.

Nib Alkalization

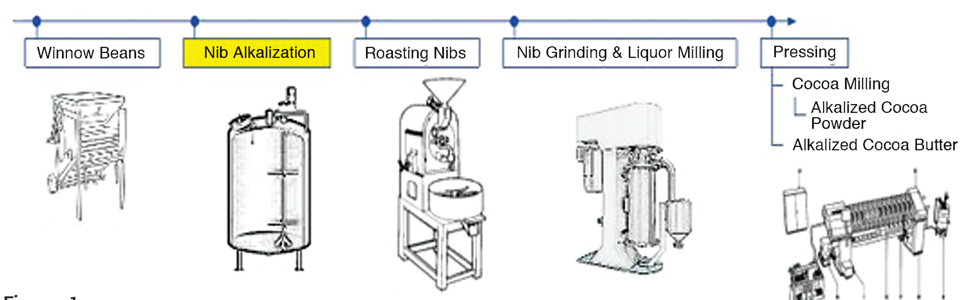

Figure 1

Cocoa Cake Alkalization

Cake alkalization (Figure 2) is performed with cocoa butter already pressed from the chocolate liquor, usually down to 10 to 12 percent fat content. The roasting, winnowing, nib grinding into chocolate liquor and pressing have already occurred when the cake alkalization takes place.

Cake alkalization is typically performed on kibble (gravel-sized pieces of cocoa ground from press cake) in a reaction vessel. Similar to nib-alkalized cocoa, the pH of the natural cocoa will impact the finished product. Also similar to nib alkalization, an alkali solution is added, time and temperature will continue to be factors, and pressure and vacuum are also being applied depending on the desired outcome. Aeration is applied as well in varying volumes to influence red notes in addition to being used as a drying mechanism. The alkalized kibble will be dried to 5 percent moisture or lower and then milled into a finished cocoa powder.

A positive factor of cocoa cake alkalization is that only the cocoa is alkalized and not the cocoa butter. Not having alkalized cocoa butter as a byproduct makes cake alkalization more economical and could lead to a lower price. It also gives nonbean roasters the opportunity to produce alkalized cocoa. Negative factors include limitations in color development and impact to flavor; flavors may be less pronounced or washed out as an already-roasted cocoa is being reprocessed. Additionally, because kibbled cocoa cake is inconsistent in size, penetration of solution to each particle will vary. Particle size reduction in cake alkalization is also a greater challenge than other alkalization methods. Through the wetting and then drying of the cocoa particles, agglomeration occurs, creating the need for higher energy requirements for cocoa particle grinding than nib or liquor alkalization.

Chocolate Liquor Alkalization

Chocolate liquor alkalization (Figure 3) is similar to cake-alkalized cocoa. It occurs after roasting, winnowing and grinding into chocolate liquor. As with other methods,

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Cocoa Cake Alkalization

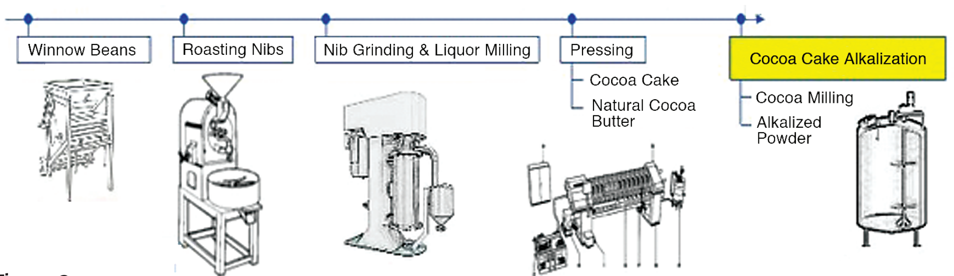

Figure 2

Chocolate Liquor Alkalization

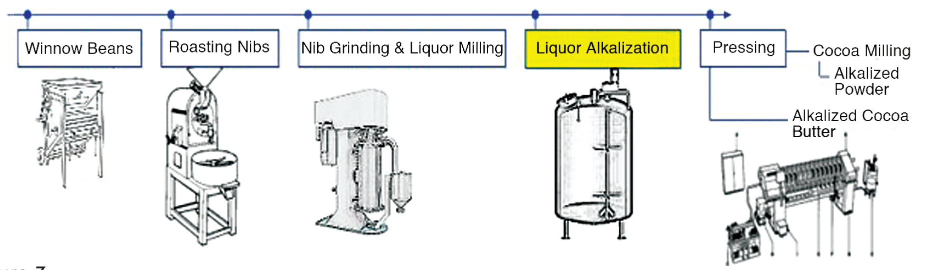

Figure 3

Good-flavor dutched cocoa or chocolate cannot be derived from poor-quality beans and could be a product's downfall before the process is started.

the starting pH is a factor and an alkali solution is required. Time and temperature as well as atmospheric influences affect the final product. There are limitations to moisture addition. Water addition to chocolate liquor makes it more viscous and difficult to work with. Also, due to the density of the mass, aeration influences are limited in their impact, creating less color change. After the alkali reaction, moisture removal is needed. This can be assisted with a thin film column evaporator and may further enhance flavor development. Pressing of the liquor (if being used for cocoa) and milling of the cocoa are needed to complete the alkalized cocoa powder.

A positive aspect of chocolate liquor alkalization is that noncocoa-bean processors are able to perform liquor alkalization and it can be performed with limited equipment. The negative is that the cocoa butter is alkalized, similar to nib alkalization, resulting in further processing of the cocoa butter and additional expense. There are color limitations as well. Because of the density, and inability to use moisture at high rates, deep reds are difficult to achieve and darker brown is usually the result.

Alkalizing Ingredients

The alkalizing ingredients shown in Figure 4 can be used in alkalizing cacao. The limiting quantity is for each 100 parts of cacao nibs; the total quantity of alkalizing ingredients used is not greater in neutralizing value than three parts by weight of potassium carbonate.

Varying rates of these alkali ingredients can be used to achieve the desired cocoa product. Each will result in different flavors and functional attributes. Cocoa beans, nibs, liquor or cocoa cake treated with these alkali ingredients will be accompanied by the statement *Processed with alkali* on an ingredient declaration label.

Alkalizing Ingredients Used in Alkalizing Cacao

CFR-Code of Federal Regulations Sec. 163.110-114

	Potassium	Sodium	Ammonium	Magnesium
Carbonate	K_2CO_3	Na_2CO_3	$(NH_4)_2CO_3$	$MgCO_3$
Bicarbonate	$KHCO_3$	$NaHCO_3$	NH_4CO_3	
Hydroxide	KOH	NaOH	NH_4OH	
Oxide				MgO

Figure 4

Processing Variables Impacting the Finished Product

There are multiple processing variables capable of influencing the finished product beyond the alkalizing agent used.

Cocoa bean origin The substrate of the alkalizing process has a major impact. Cocoa beans vary in flavor and color throughout the world and crop quality varies due to weather influences. Good flavor dutched cocoa or chocolate cannot be derived from poor quality beans and could be a product's downfall before the process is started. Color of the cocoa bean is important for powders. If a finished product of deep red cocoa is desired, it cannot be achieved unless some of the color is inherent in the bean.

pH The pH impacts flavor and color. This includes the starting pH of the beans (between 5.0 and 6.0) as well as the amount and type of alkali used. High pH is associated with darker colors.

Time/temperature Reaction temperatures for red cocoas will typically be in the 75° to 85°C range and browns and blacks will be in the 95° to 125°C range depending on desired color and equipment capabilities. Holding cocoa at high temperatures for extended periods of time will influence color and flavor and if held too long will eventually damage the flavor.

Moisture The amount of water used in the reaction can accelerate color formation and enhance red notes. Moisture between 20 to 50 percent can be used if the process equipment is capable and the moisture in the bean should be accounted for as well. High moisture will assist in achieving red ➤

notes but it should be noted that the water must be evaporated and may require extended drying or roasting time, affecting the flavor.

Oxidation Air quality and quantity will accelerate the alkalizing process. Aeration of the cocoa with high volumes of air for an extended period of time will enhance red notes.

Atmosphere Air pressure or steam pressure will accelerate the browning of the cocoa and assists when producing black cocoa. Steam pressure can also be used to accelerate nib penetration with the alkali solution. It should be noted that excessive pressure or agitation may cause the cocoa butter to diffuse to the surface of the nibs, causing flowability and manufacturing issues. Vacuum can be used as a tool as well but is typically used in the drying process.

ALKALIZED CHOCOLATE AND COCOA COMPOUND

According to Mintel Group there have been more than 100 new launches of chocolate and compound products containing alkalized liquor or cocoa over the last three years. This is in addition to many of the fine alkalized chocolate products already on the market.

Adding alkalized liquor into chocolate can have positive influences on the finished product. Nonalkalized chocolate liquor will be more acidic and bitter while a dutched liquor or cocoa properly alkalized to a neutral pH will have a less astringent taste profile. This gives a producer an opportunity to produce more than one flavor from the same bean type. The dutched flavor may pair more favorably with a shell-moulded or enrobed center, providing a superior flavor experience. Alkalized liquor or cocoa as an ingredient in chocolate may also present the producer with the opportunity to reduce conching time because many of the volatiles have already been removed.

Color of an alkalized chocolate is darker when compared to an identical nonalkalized formula. This presents some opportunities. Boxed chocolates tend to display multiple, noticeably different dark chocolates in the same box, differentiating each piece. The darker color may be a perfect application for the finished good. While it is less prevalent, alkalized liquor or cocoa can be used in milk chocolate as well.

The liquor percentage of the chocolate recipe can be completely alkalized or added as a blend of alkalized and nonalkalized chocolate liquor depending on the flavor desired. Additionally, alkalized cocoa can be added as an ingredient in chocolate to supply the dutched flavor.

Alkalized Cocoa in Compound Coating

Cocoa compound coating is an alternative to milk or dark chocolate and the added cocoa powder is the main flavor-driving ingredient. Compound offers the advantage of a coating with multiple meltpoints which can offer new product possibilities as well as the ability to supply products in warmer climates. The chocolate flavor is driven by the type and quantity of the alkalized and nonalkalized cocoa powder.

Cocoa powder is the main color driver as well. If strong cocoa flavor is not a requirement for the finished product, there may be opportunities to use darker alkalized powder in a lower dosage to produce the same color. This can present a quality improvement and possible cost savings. While the cocoa butter has been pressed from the liquor, 10 to 12 percent cocoa butter still remains in the cocoa. Cocoa butter in high-enough quantities paired with the added lauric fat in compound will create a eutectic effect. This is good for softening a chocolate center but is damaging to the shine and shelf life of a coating. Alkalized liquor is a possible ingredient for a filling or center but is not an ingredient for a compound coating for this reason. ➤

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APPLICATION IMPACT OF ALKALIZED COCOA POWDER

FDA description of cocoa powder is:

> the food prepared by pulverizing the remaining material after part of the cacao fat has been removed from ground cacao nibs. Optional alkali ingredients also specified and limited in CFR 163.110 (b) (1) may be used in preparation of cocoa. Cocoa powder will be less than 24 percent fat, falling under the designations high-fat (breakfast cocoa), medium-fat (10 – 22%) or low-fat cocoa (<10%) whether alkalized or non-alkalized.

Evaluating the ideal cocoa powder can be a difficult task as the final result is not always predictable. To evaluate cocoa impact properly, putting the cocoa in an application is always necessary to examine the cocoa's true intrinsic color. Early indicators such as extrinsic color can be misleading. For instance, 22 to 24 percent fat cocoa powder (breakfast cocoa) and a 10 to 12 percent fat cocoa powder alkalized to the same pH under the same parameters will appear different. The 22 to 24 percent powder will appear darker in color, giving the impression of stronger flavor and greater coloring impact. This will not be the case due to the fact that the 10 to 12 percent powder will have more cocoa solids and greater flavoring and coloring capability when used at the same rate. Other parameters such as moisture content and cocoa temperature can be misleading in extrinsic observation.

Cocoa Drinks

Cocoa drinks, whether hot or cold, often contain a lightly alkalized cocoa powder. The smoother taste with lowered bitter notes appears to appeal to the masses. Besides flavor and an attractive reddish-brown color, an alkalized cocoa offers greater dispersibility over a nonalkalized cocoa. However, while cocoa dispersion is greater in the dutched cocoa, it is not completely soluble. The cocoa will be initially dispersed in a milk or water drink but will allow for sediment to collect on the bottom of the container over time. The fat content is also a hindering factor in blending cocoa into a water-based drink. Emulsifiers such as lecithin are needed to reduce the surface tension between the fat-loving and water-loving molecules. Thickeners, such as carrageenan, are used to help keep the cocoa solids in suspension longer.

Desserts

Final impact prediction of alkalized cocoa powder on a dessert can be difficult as well. Type of dutched cocoa and the dosage used are obvious factors influencing the final flavor and color of the dessert. But, the other ingredients play a role as well. For instance, the addition of a nonfat milk powder may have a lightening effect on the final product color as well as muting some cocoa notes. Conversely, the addition of more fat to the recipe in the form of butter and margarine could have a darkening effect. If heat treatment of the dessert is required, color and flavor will be impacted as well. Air content plays a role in the color and flavor of a whipped or foam-forming dessert. Greater air content will lighten color and reduce flavor impact. A greater dosage of cocoa may be required to deliver the chocolate impact desired.

Ice cream is an ideal application for alkalized cocoa and, behind vanilla, chocolate ice cream is the second-most popular flavor. Similar to whipped desserts, the incorporation of air affects color and flavor impact. Chocolate ice cream with high overrun will appear lighter compared to the same recipe with reduced overrun. An increased dosage or a darker cocoa may be required if high overrun is a requirement to meet color standards. High overrun reduces cocoa flavor as well as the fact that ice cream is a frozen treat. Low temperatures desensitize the taste buds, creating a need for higher flavor impact delivered by a larger alkalized-cocoa dosage. ➤

Nothing can be more disappointing than looking at a rich-appearing chocolate treat, biting into it and finding out that it doesn't deliver the expected flavor.

Baked Goods

Chocolate cake and pastry are consumed and enjoyed worldwide. Cocoa powder is typically the flavor and color driver and, like whipped and cooked desserts, color and flavor of the final product are difficult to predict. Experimentation on type of cocoa and dosage used will be required when developing a new product to achieve the ideal visual and sensory experience. Any type and color of cocoa can be added but close attention should be paid to the pH of the cocoa used as well as the leavening agent. Natural cocoa is typically a 5.6 pH but can range as low as 5.0 pH. Alkalized red cocoas are typically in the 6.8 to 7.8 pH range, while black cocoa ranges from 7.8 to 8.6 pH. A cake recipe with natural cocoa powder and possibly other acidic ingredients, such as Greek yogurt, buttermilk or sour cream, will require baking soda as the leavening agent since the baking soda is acid activated. An alkalized cocoa with a pH greater than 7.0 will require baking powder for leavening since there is not sufficient acid to activate baking soda. Proper experimentation with new recipes should be performed as too little or too much leavening agent will have negative implications on leavening (rise) or flavor (metallic or bitter).

Flavanol Impact

It would be remiss not to discuss polyphenol and flavanol impact in this day and age since the cocoa and chocolate industry is receiving a substantial amount of positive press for high polyphenol and flavanol content. Polyphenols and one of its subgroups, flavanols, are known for antioxidant activity and many health benefits including improved cardiovascular health, reduced oxidative effects of LDL cholesterol, reduced blood pressure and many other potential improvements.

Polyphenols refer to a broad class of compounds found in all plants. The polyphenol category contains many subgroups including flavonoids, which break down into many other subgroups including flavanols, which in turn have subgroups of their own. For the purpose of this paper, the concentration will be on flavanols.

It is widely suspected that alkalizing of cocoa and chocolate will have negative effects on flavanol content. As discussed previously, there are many components to alkalization, including the extent to which the cocoa or chocolate is alkalized. The Hershey Center for Health and Nutrition performed a flavanol-content study on 20 commercial cocoa powders from seven different companies. The cocoa powders varied in range from nonalkalized to moderately alkalized with the gauge being the extractable pH. The pH range was pH 5.39 for the most acidic to pH 8.06 for the most alkaline. The 20 commercial cocoas were arranged into four categories: nonalkalized, pH 5.39 to 5.76; lightly alkalized, pH 6.77 to 7.13; moderately alkalized, pH 7.21 to 7.52; and heavily alkalized, pH 7.69 to 8.06. The fat was extracted and testing was performed to establish total flavanol content.

Total Flavanols versus pH

As indicated by the chart in Figure 5, the total flavanol content had an inverse relationship with the pH value. When the pH increased, the flavanol content decreased. In the case of the heavily alkalized cocoa, it decreased substantially, but still had flavanol content remaining. Even though there were losses, the average flavanol content of the lightly alkalized cocoa 13.8 (mg/g) and the medium-alkalized cocoa 7.8 (mg/g) would still remain in the top 10 percent of measured foods with detectable flavanols in the USDA database. Alkalization appears to have a neg- ➤

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Alkalization appears to have a negative effect on flavanols but cocoa health benefits are still significant.

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While this was a comprehensive study of the relationship of pH and flavanols, many questions remain unanswered. Not mentioned in the study were alkalizing agent used, type of alkalization process (nib, cake, liquor), roasting times, bean origin, fermentation levels, flavanol load prior to alkalization, etc. These and many other factors affect flavanol content in cocoa and chocolate beyond the alkalization process.

CONCLUSION

Alkalizing cocoa and chocolate has been applied and enjoyed for the past 187 years. Through the process, consumers have been able to enjoy dutched chocolates with their reduced bitter flavor and intensified color. Alkalized cocoa powders are now enjoyed in many colors, with distinctly improved flavors and in some cases used where a natural cocoa just wouldn't be a good application. Compound coatings have been possible since the invention of the cocoa press, but the ability to use alkalized cocoa greatly expands the color and flavor possibilities.

Alkalized cocoa and chocolate liquor is typically produced through three different methods: nib alkalization, cocoa cake alkalization and liquor alkalization. They have advantages and disadvantages for the suppliers and the users of these products. Nib alkalization offers the greatest range of color and usually the finest flavor, but it comes at a higher cost of production and higher cost to the consumer. Cake alkalization is usually less complicated to produce and has no impact on the cocoa butter, but it has color limitations as well as reduced flavor. Chocolate liquor alkalization requires less equipment to produce but has color limitations and can negatively affect the cocoa butter. Matching the proper alkalized cocoa or liquor to the proper application is the key to a successful product. □

Total Flavanols versus pH

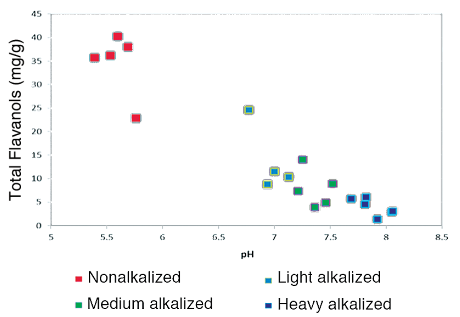

Figure 5 *Hershey Center for Health and Nutrition*

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