CHEMICAL AND PHYSICAL METHODS OF CHOCOLATE PROCESSING: ADMINISTRATION PROCESS

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Abstract. *From the harvesting of the cocoa beans to the formulation of the final chocolate product many complex changes occur. The properties and behavior of the fat and the dramatic change in flow characteristics are most notable. The purpose of the work is to clarify the relationship between the types, composition, methods of preparation and consumption of chocolate and its impact on human health. In order to achieve the goal, we set the following work tasks: to get acquainted with the history of the origin of chocolate; to investigate the indicators of chocolate quality; evaluate informational, quantitative characteristics of chocolate; to determine the effect of chocolate on the human body, to conduct qualitative reactions to individual chemical substances included in the composition of chocolate.These changes occur in part during the refining process which includes roasting, winnowing, grinding and conching. Most notable in influencing the product is conching which is the agitation of chocolate coupled with aeration and heat. This treatment is a time and energy consuming process but has a remarkable mellowing effect on the flavor and promotes a decrease in viscosity of the final product. The escape of undesirable volatiles derived from oxidative and carbonyl reactions catalyzed by heat and aeration have been implicated. Research methods: study of literary and electronic media, generalization of the material found, sociological survey, chemical experiment, analysis of the obtained results. The physical effects brought about during conching encompass more than a simple mixing. Included, in addition to the chemico-physical aspects of conching itself, are the aspects of the cocoa bean, fermentation and roasting which may influence the product The scientific novelty of the obtained results: qualitative reactions were carried out on individual chemical substances included in the composition of chocolate. The methodological basis of the research is fundamental principles of the system approach, relevant aspects of market and technical research and state regulation of chocolate products studied with application economic-statistical and physico-chemical methods. It is used in the work the following methods of the developed product: statistical, organoleptic, method determination of protein content in the finished product, method of determining the indicator glycemic The composition of chocolate was theoretically investigated. In the perspective of further research, we plan to expand the assortment of porous chocolate due to the creation of new flavors (Ex. porous chocolate with caramel flavor, fruit flavors based on white chocolate mass).*

Keywords: *cocoa beans, chocolate product, conching, chemico-physical aspects of conching itself, chocolate coupled with aeration and heat, simple mixing; administration process.*

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Introduction. The appeal of chocolate is at least half a millenium old. Early historical evidence reveals that the cocoa tree first thrived in the tropical parts of the Americas where it was grown by the Aztecs of Mexico and the Mayas in Central America. The Mexicans called the fruit of the tree "cacavacentli" and the drink prepared from it "chocolatl". As a drink, the fermented and sun-dried beans were first hand-husked, roasted, then ground and mixed with maize, annatto, vanilla, chili or some other spice. The resultant semi-liquid paste was formed into small cakes, dried, then broken, dissolved in hot or cold water and consumed.

In 1502, Christopher Columbus saw a cargo of beans in a trading ship off the Gulf of Honduras, and the first specimens to reach the Old World were those he took to Spain as a souvenir of his fourth voyage. The Spaniards thought the prized drink bitter, so they mixed it with sugar and in this form it became popular in Spain. The fame of chocolate gradually spread throughout Europe, reached America in the seventeenth century, and even though "chocolate houses" and drinking clubs no longer exist, the popularity of chocolate remains.

The per capita consumption of confections, in which the category of chocolate products is included, is still highest in the European countries even though each American consumes 7.0 kg of confections per year. Pennsylvania alone in 1972 was responsible for 42.2% and 13.2% of net United States sales of chocolate and confectionery items, respectively In another census report[4] total value of United States sales of chocolate candy in 1978 amounted to 2.2 billion dollars[2].

The earliest industrial attempts to produce cocoa mass took place during the seventeenth and eighteenth centuries. Cocoa beans were roasted in iron pots, the shells removed by hand sifters, and nibs ground to mass in a mortar or on a curved grinding stone. These instruments and others were the ancestors of modern chocolate technology tools.

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Fermentation begins when the pods are split and the acidic, sugar-containing pulp is inoculated with a wide range of microorganisms originating from fruit flies, farmers' hands and pod walls. Anaerobic yeasts begin to flourish and dominate the flora of the mass for approximately 2 days, and metabolic heat and pectin esterase activity eventually cause the pulp to break down and "sweat." The pH of the environment rises as the sweatings are drained and as citric acid is metabolized by the organisms. found certain lactic acid bacteria usually if not always present in the early stages of fermentation.

Whether acetic acid directly affects the flavor of chocolate is a matter of debate. When pulp was sterilized before fermentation and roasted in the normal manner, the resultant chocolate flavor was considered unchanged. He concluded that normal concentrations of acetic acid were necessary for normal chocolate flavor. Much more important than its direct, potential contribution to taste, however, was the influence of acetic acid on bean death. It is not until acetic acid penetrates the twenty or more bean shell layers (testa) and enters the cotyledons that the beans cease to respire. Bean death is characterized by a loss in cellular segregation, or an increase in cell wall permeability. It is only after bean death that critical enzymesubstrate reactions take place. These reactions are vital to the subsequent development of chocolate flavor.

A brief synopsis of these reactions is in order. Annikova found that proteolysis and sucrose hydrolysis are rapid after bean death, and moreover, the concentrations of both free amino acids and reducing sugars reached maximum values at about the same time during fermentation. These flavor precursors are extremely important during later processing steps. It is also recognized that some amino acids present due to proteolysis react and form complexes with oxidized polyphenols (quinones) and if allowed to remain uncombined, the inherent bitterness of some amino acids, peptides and polyphenolic compounds would affect chocolate flavor adversely.

The addition product is able to catalyze the oxidative deamination of amino acids without the intervention of polyphenol oxidase:

$$\tfrac{1}{2}\text{protein} \longrightarrow \text{proteaseamin oacids} + \tfrac{1}{2}O_2 \longrightarrow \text{�ketoacid} + NH_3 \qquad (1)$$

Annikova have confirmed the formation of peptide-polyphenol complexes in fermented beans by demonstrating the presence of substances which react like tannins as well as proteins.

The histology of the seed (bean) before, during and after fermentation has been well documented by light microscopy Borysenko. The fresh, unfermented cotyledon or nib is comprised of three types of cells, namely, the epidermal, pigment and storage cells. The epidermal cells are of a monocellular structure, elongated and brown, containing unidentified particles of 2–4 μm. Pigment cells are responsible for color since they contain anthocyanins, theobromine, caffeine and polyphenols. Their mass represents approximately 10% of the cotyledons. The storage or parenchyma cells, which contain cocoa butter, aleurone (protein) granules, enzymes and starch grains, are by far the most predominant cell type and comprise the balance of the seed mass[2].

During fermentation, the color of the cotyledon first changes from a speckled purple appearance to a more uniform purple color as a result of the diffusion of anthocyanins into cells which originally did not contain the pigments. Eventually the color fades as enzymes degrade the cyanidin glycosides under anaerobic conditions. When oxygen has gained access to the cells during the oxidation-condensation phase, the purple color changes to brown. The presence of purple pigment in dried, fermented beans indicates that fermentation was incomplete or imperfect. The shell or testa, although not used as a routine quality index of fermentation, also changes dramatically throughout the process. What was originally a white, closely fitting skin will become a pale brown, crisp, more readily removable shell. It was originally, and is still, believed by some that the sole object of fermentation was to free the beans from the pulp, prevent germination and facilitate shell removal. While this is largely true, it is essential to realize that fermentation is critical for flavor optimization as well[3].

Recent scanning electron microscopy (SEM) studies by Borysenko of raw, roasted, unfermented and fermented cocoa beans revealed differences in morphology as a result of bean treatment. A six-day microbial fermentation caused the testa to change from a leathery and continuous, closely adhering skin to a friable, more easily removable shell. Changes in the cotyledons were less obvious. When beans were roasted at 150° C for 20 min, the testa and endosperm became porous and brittle, and cellular contents of the germ and cotyledon became thermally coagulated. Also noted in the roasted shell were dissolution of the cutin layer accompanied by hairline fissures in the surface. Both these developments, as well as the increase in porosity, undoubtedly contribute to shell brittleness, and facilitate shell removal. Observations by SEM of the cocoa bean during various treatments may be considered useful in the future quality control evaluations. Certain plant structures, such as tracheary elements (spiral vessels) and bordered and simple pits are easily.

After fermentation, the beans are dried. Lopez and believe that proper drying is as important as proper fermentation, for without it beans grow moldy and off-flavors are produced. Moisture must be reduced to about 6% and the dehydration process must not be too rapid. It has been found that artificially dried cocoa beans contain higher concentrations of acetic acid than beans dried slowly in the sun, and that chocolate prepared from them possesses a distinct "fruity" flavor, presumably due to the formation of acetate esters. Kolomiets found propionic acid always eveloped during fermentation, and noted this acid and others of low molecular weight increased in absolute amounts during the transition from fermentation to drying. They attributed this behavior to changes in dominant microbial populations and not to unrepresentative sampling. A complete report on bean drying by natural and artificial means has been given by[4].

When fermented beans are between 6 and 7% moisture, they are bagged, transported to the manufacturing country and stored in a cool atmosphere of not more than 80% relative humidity. The chocolate manufacturer is at this time responsible for sampling and testing the incoming product. The cut test and flavor test are the two basic quality assurance measures of the plant. Unfortunately, these tests are not totally objective in nature, and as a result, reports vary depending on the grader.

Trends in recent years have brought about changes in the processing procedure of cocoa beans. More and more processed products, i.e., liquor and powder, are being imported into manufacturing countries. As developing countries industrialize the trend accelerates. Kolomiets has now nearly completed the switch to 100% liquor, and Brazil, in particular, is also gradually replacing more and more beans with liquor.

It is not difficult to see how this switch is associated with a loss of quality control by the manufacturer. Syrokhman states several criticisms concerning the imported liquor products (Fig. 1).

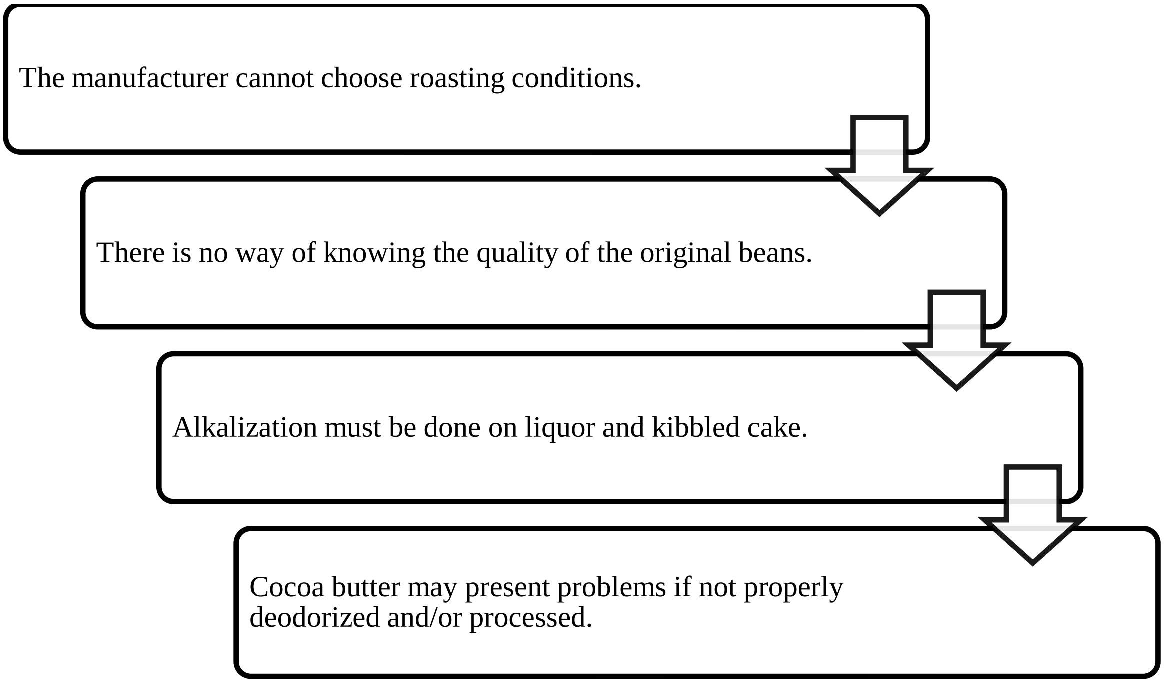

Figure 1. Basic comments on imported liquor and vodka products by Syrokhman

On the positive side are the savings to the manufacturer in cleaning, winnowing and grinding machinery. The cost to transport the bean shells also vanishes; this can amount to considerable cost savings since the shell comprises about 12% of total bean weight. Cooperation between the producing and manufacturing countries is continually improving, so that many of the earlier sanitation and production problems have been largely eliminated [5]

When beans are imported, they must be stored and/or cleaned, roasted, winnowed and refined. The roasting process has evolved throughout the years from the solid fuel or gas-heated rotary drum roaster to the hot air batch roaster to the continuous model whereby cascading beans meet a transverse flow of high-temperature air. Roasting is usually a “long time-low temperature” or “short time-high temperature” process, with temperatures up to 150° C and roasting times up to 40 min being common. Roasting conditions are dependent on the type of bean, when and where it was harvested, treatment received after harvesting and the type of flavor required in the finished product.For example, flavor beans such as Caracas and Maracaibos require a heat treatment in the range of 131–146°C, while other beans such as Ghanas may receive a heat treatment in the range of 146–184°C. Discharged beans must be rapidly cooled to prevent overroasting so that no sharp, disagreeable odor is imparted to the finished chocolate.

Conventional bean roasting is performed on the whole, dried, fermented bean. The roasting process causes additional moisture to be lost through the bean layers; the bean shrinks as the shell loosens, and as a result the shell is easily removed when the beans are cooled. The texture of the cotyledon also becomes friable during the heat process so that it can be ground more easily. Syrokhman illustrated by SEM the brittleness typically encountered as a result of roasting at high temperatures. First, hairline cracks or fissures appeared on the outer roasted seed coat surface. These were accompanied by melting or dissolution of the cutin layer. Second, holes or pores exposing parenchyma cells developed on the surface closest to the cotyledon. The unroasted undersurface, by contrast, was smooth and uninterrupted. These developments, together with cotyledon shrinkage upon cooling, quite likely were responsible for shell brittleness. As pointed out by the authors, in cases of questionable roasting procedures and temperatures of processed beans, SEM analysis could be used to provide qualitative indicators such as the relative extent or degree of roasting as evidenced by the appearance and size of surface cracks and the melting of surface cutin.

Chemically, the number and types of reactions occurring in the beans during roasting are of great magnitude. If beans are not roasted the resultant product will not have a characteristic chocolate flavor. On the other hand, roasting as a single process is insufficient to develop a full flavor. Typical chocolate flavor is dependent on the chemical precursors formed during fermentation coupled with the thermal reactions of compounds in the later stages of manufacture. Much work has been done to isolate and characterize the flavor compounds generated during roasting, and no one compound has been found to be responsible for typical, roasted chocolate flavor.

Probably the first chemical event to occur during roasting is the distillation of some undesirable low-boiling compounds. It is generally believed that many of these compounds are water-soluble, and therefore miscible with the water vapor phase. Stekolshchikov measured free and bound acetic acid in Nigerian cocoa beans before and after continuous roasting at 120°C for 20 min. They found a decrease in free acetic acid but an almost corresponding increase in acetic salts. The result was that total acidity remained the same. Stekolshchikov also noted very little loss of acetic and propionic acids from the shell during roasting.

Hundreds of other compounds have also been detected in headspace volatiles and in other fractions of roasted cocoa beans. Many of these compounds are aldehydes, ethers, phenols, nitriles, sulfur compounds, pyrazines, ketones, alcohols, furans and esters (Stoll *et al*., 1967; van Praag *et al*., 1968; van der Wal *et al*., 1971; Vitzthum *et al*., 1975). Analysis of the bean constituents before and after roasting shows that, of the major constituents, free amino acids, peptides and reducing sugars undergo the most change while alkaloids, polymeric phenols and lipids are practically unaffected (Diemair *et al*., 1959b; Kleinert, 1965; Zak and Keeney, 1976). This strongly suggests that non-enzymatic carbonylamine reactions play an important role in the chocolate flavor complex. have shown that the reducing sugars are essentially destroyed during roasting, and the amino acid fraction is partially degraded. They attributed this partial degradation to the relatively low content of reducing sugars and potential reducing sugars (sucrose) in the system. Stekolshchikov found that alkylpyrazine formation in Ghana cocoa beans was linear up to 30 min roasting time at 150°C. They also determined that the total alkylpyrazine content of typically well fermented bean varieties was approximately twice that of lightly or nonfermented varieties following an equivalent roast. Pyrazine concentrations in roasted beans were found to be primarily influenced by the level of ketoses resulting from fermentation. An excellent review on the non-enzymatic browning reactions which occur during cocoa bean roasting is given by Foster [8].

Ponomaryev have described chocolate as a favorite source for the isolation and identification of pyrazines. The basic fraction of cocoa compounds contains many pyrazines; however, the neutral fraction and headspace have a characteristic cocoa aroma which includes many other compounds. As many as twenty-two pyrazines were reported by van der and in a review of pyrazines thirty pyrazines were reported in cocoa products. In the review, pyrazines were noted as one of the few classes of compounds which are associated with desirable food flavor properties. The concentration of pyrazines may be dependent on the level of the roasted bean which varies with the variety [7].

Aims. The purpose of the work is to clarify the relationship between the types, composition, methods of preparation and consumption of chocolate and its impact on human health.

Methodology. Cocoa was one of the first products in which thiazoles were identified. At least two of the volatile compounds have been identified. In a review paper, Ponomaryev indicated that the formation of thiazoles appears to require carbonyls as well as amino acids. Therefore, the initial reactions involving reducing sugars and amino acids appear to be prerequisites for flavor development. Most pyrazine and thiazole identification has been conducted on washed cocoa beans and information is lacking in the final conched product. The unique flavor and aroma attributed to pyrazines and thiazoles therefore warrant further investigation.

The role of sulfur compounds as an important flavor constituent is well accepted. Their low flavor threshold enables these low molecular weight compounds to be detected at trace levels. Analysis of fermented and dried cocoa by Prytulska and Romanenko demonstrated that a methyl-S-methionine sul-phonium salt was present and it decomposes readily to dimethyl sulfide. This dimethyl sulfide has been isolated in cocoa aroma[6].

After roasting, beans are cooled, and the shells and dense germs are separated from the nibs. The principle of winnowing, in general, depends on the density of the shells and nibs which can be separated by a combination of grating and vibrating screens together with controlled air currents. More recently the rotary sieve air separator has been replaced by a bank of flat vibratory sieves; from the end of each of these sieves a separate air lift removes the lighter shells. Although complete separation is the aim of every manufacturer, this is never realized and, as a result, shell in clean nibs is allowed at 1.75% by weight under Food and Drug Administration regulations.

Alkalization is one of several routes which may be taken by the manufacturer to modify the final chocolate. As previously mentioned, van Houten in 1828 first soaked nibs in solutions of potassium carbonate prior to drying. Romanenko realized that improved wettability, or dispersibility, in addition to pleasant taste and darker color, was gained by this process. In the alkalization of nibs today, alkalies such as bicarbonate, carbonate, sodium, ammonium or potassium hydroxide, and magnesium oxide or carbonate can be used in dry form or in aqueous solution on nibs, liquor or cocoa. In the case of nibs, for each one hundred parts by weight used (as such or before shelling), the total quantities of such alkalies must not be greater in neutralizing value than the neutralizing value of three parts by weight of anhydrous potassium carbonate. Nibs are then subjected to a water-removal process after they have rested in the alkali for a length of time. Whether the water-removal treatment involves a simple drying or a full roast depends on the sample's history.

The chemistry of the alkali process is extremely complex. Among the more important changes are the increase in pH of the beans from 5.2 to 5.6, with the resultant liquors ranging in pH between 6.8 and 7.5. The initial and final pH will depend on such factors as the type of beans and their degree of fermentation, the type and amount of alkali used, the ratio of alkali to nib or liquor and other processing details. A darker color is another result of the alkali treatment. A darker color does not mean a stronger flavor, however. Alkali-treated chocolate and cocoa actually exhibit milder flavors than their untreated counterparts because the free acids generated during fermentation are neutralized. Prytulska Tannins in cocoa beans such as flavone and flavanol are responsible for the different color formations found in alkalized products.

The nibs, alkalized or not, are next ground by a series of grinding plates or stones. It is during this process that a phase inversion takes place. As the grinders shatter cellular structure, the fat globules release their fat. The frictional heat generated during this process causes the fat to melt and coat the nonfat particles in a more or less continuous phase. The resultant liquor is the base from which all chocolate is made.

Chocolate liquor blends, additional cocoa butter and sugar are mixed together, with or without milk solids, emulsifiers and flavors, and the mixture is further ground or refined. To refine the particles and to disperse them in the liquid cocoa butter, roll-refining is the most widely accepted method used today. The refining process establishes the particle size of the finished product. The lower limit of particle sizes which can be detected by the tongue is approximately 20–30 μm . Prytulska and Romanenko However, particles are never completely within this range, as no industrial process can totally eliminate coarser particles[6].

Results and discussion. The refining process is a disruptive one whereby the homogeneity of the chocolate suspension is impaired. Since the surface area of the nonfat particles is greatly increased, it becomes necessary to control the frictional heat generated so as not to scorch the chocolate, but more importantly, not to eliminate a large proportion of volatile compounds which otherwise might contribute favorably to chocolate flavor.

The first and most obvious requirement of the conching process is re-establishment of a homogeneous mix after the disruptive effect of refining. The chocolate from the refiners, in the form of flakes and crumbs, must be worked so that it is transformed to a fluid paste.

It is desirable to review several of the more common conche types before discussing the functions of the process. Romanenko was a sea shell-shaped stone trough whose granite roller constantly moved the chocolate back and forth. This longitudinal conche is the oldest type of conche in use today and most closely resembles the original. It is common practice to process chocolate for 2 to 3 days, even up to 5, in the longitudinal model.

As labor and material costs increased, it became necessary to economize the process. Designed for reducing the time of treatment, the rotary conche accomplished mixing by means of a rotary stirrer which caused movement in a horizontal as well as in a vertical plane. Another modern high speed conche was ruggedly designed to work chocolate in wet and dry states. This unit has three horizontal agitator shafts with blades designed to both lift and shear the mass, and is jacketed for precise temperature control[7]. Dry conching in specially designed rotary conches is another relatively new development which shortens the time requirement while still achieving satisfactory results. The principle utilized in this process is to work the dry powder from the refiners against itself, with little or no addition of cocoa butter during the working. Because of the greater surface area exposed by a powder (as opposed to a fluid), and the local generation of frictional heat Syrokhman, evaporative chemical processes are facilitated.

There is much speculation within the trade that many of the conventional techniques universally used in the production of chocolate will be replaced by completely new processing methods. One such emphasis is being placed on continuous processing techniques. In the conching cycle, liquor is continuously pumped and sheared into a thin turbulent film Zadorozhnyi. As this film falls, it meets air which is moving upward. The air picks up moisture and unwanted volatiles from the chocolate and discharges these volatiles. A variation of this technique has been studied by, Ponomaryev who found that degassing thin layers of unconched chocolate under reduced pressure reduced the amount of volatile constituents present in the chocolate.

Syrokhman claims that new units called flavor reactors will eventually replace traditional conching. In this equipment, individual compounds or mixtures of compounds are subjected to the treatment essential for odor and flavor formation. Fat, which normally impedes the removal of steam volatile components and the formation of new flavor compounds, is absent.

A majority of manufacturers, however, still rely on traditional batch-conching methods to enhance the flavor and texture of chocolate.

Even though benefits of conching were recognized, no one knew with certainty the causes of improvement. The functions attributed to the conche were: expulsion of the moisture still retained in the mass, loss of tannic acid and free acetic acid, and full development of aroma and homogenization of the processed mass to give the smooth texture. It was not until published results of his investigation of the process and suggested that the causes of improvement of the chocolate were the removal of air, a loss of moisture and volatile acids, and the smoothing of particles. Acetic acid was known to be liberated because its odor was very prominent in the air above a conche. Aasted also asserted that caramel would not form because the temperature was not high enough and the oxidases would not be effective due to their destruction during the roasting period. He also reported that the bitter-flavored theobromine and caffeine were not affected by conching[5]. However, he believed that oxalic acid was the most important of the acids in the cocoa beans as far as chemical changes were concerned. He stated that the oxalic acid increase during conching could be determined analytically. However, the total acid content was lower at the end, even when volatile acids were disregarded. Furthermore, he reported that the oxalic acid determination was not very reliable. To summarize Aasted's findings, one can say that conching has the following effects: reduction of acetic acid, total acid, tannins, water and proteins which get tanned and precipitate. As a result the pH increases from 4.9 to 5.7.

While Aasted measured different variables, Syrokhman, Zadorozhnyi, analyzed the factors controlling the development of a conched flavor. These factors are agitation, aeration, temperature and time. While a minimum agitation is required, violent mixing would only control the time required to accomplish the end result and to what extent forced aeration is required at a given temperature. The combinations of all these processing variables are infinite and when one considers the number of possible bean blends and conche designs it is easy to see how complex the analysis of conching can become[6].

Conclusions. The complexity of processing cocoa beans into chocolate is realized by the studies reviewed here. With the changing economic and marketing conditions of the bean-producing countries constantly before the chocolate processors, more detailed elaboration of the factors which control flavor and texture is extremely important[4,5].

Understanding the process of conching should lead to a more rational approach to conche design. This was the purpose of research conducted in Germany and reported by Ponomaryev. He placed emphasis on physical and physico-chemical processes of chocolate manufacture which he felt had been underrated for a long time. He emphasized that conching was a process where chemical changes are as important as the physical ones. There was little doubt in his mind that dispersion processes played a major part and that chemical changes occur not only in the volatile components but also in the non-volatile cocoa components such as polyphenols, carbohydrates and protein compounds. Unfortunately, he reported no data on these changes[7].

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