STUDY ON THE OPPORTUNITIES AND BENEFITS OF THE GRAINS AND COCOA MASS ALKALIZING OPERATIONS

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Abstract
The study refers to the possibilities and advantages of the alkalizing operation of the cocoa groats (roasted cocoa beans, crushed and peeled) and of the cocoa mass, mandatory operation in the cocoa powder technology and for the higher quality of chocolate.
We presented the advantages and disadvantages of alkaline cocoa groats and cocoa mass, using data from the literature.We analyzed all of the cocoa groats alkalinity with the following alkali: potassium carbonate, concentrated ammonia and ammonium bicarbonate in different amounts.We determined that the decrease of the total acidity and volatile acidity compared to the control sample, indicating the alkaline substance with the most pronounced neutralizing effect.
The same samples were determined using cocoa mass instead of cocoa groats and compared the results.It should be noted that by alkalizing we weren't expecting a complete neutralization of acids or acidic substances (as proof there are the residual acidity small values) because cocoa powder must present a slightly acid reaction (pH 6.97 to 6.98).
If it is determined that the cocoa mass has final alkaline reaction, small amounts of citric acid or tartaric acid can be added, because the alkaline reaction impregnates an unpleasant leaching cocoa taste.
The color of the cocoa powder is affected by three main factors, namely: the alkalinity, the fat content and the degree of tempering the powder during processing. Tempering the powder during processing can lead to a well expressed reddish brown, but can just as well lead to a pale pink and sometimes white or gray. If the tempering was done correctly during processing, it was found that the color of the powder depends on the fat content and the degree of alkylation. If the cocoa powder is more alkaline it is has a reddish hue and can even go to magenta. Magenta corresponds to the pH transition to alkaline environment, this change is accompanied by an unpleasant flavor. A moderate alkylation generally produce a pleasant and well expressed aroma, whereas excessive alkalinity can destroy almost completely the specific flavor. In practice, the basification must be controlled and driven in such a way as to achieve a favorable balance between the color and flavor.

Keywords: cocoa groats, cocoa mass, alkylation, volatile acidity

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1. INTRODUCTION

In the cocoa beans composition we have identified: free organic acid like dextrogic tartaric acid (0.54%), acetic acid (0.90%), combinations of tannic acid (5.97%), cocoa red organic dye (2.90%) and theobromine (1.66%) which is a stimulant of the cardiovascular system [6,9]. These proportions are higher or lower depending on the variety of cocoa beans and impregnates a sour astringent taste.
The traditional chocolate manufacturing technology does not give a deletion or total transformation of these substances, in the cocoa powder manufacturing technology a new operation occurs, the treatment of cocoa groats with an alkaline solution (alkalization), in order to obtain an improved cocoa taste.
The alkylation process is a solely operation in the manufacture of cocoa powder, it can be applied in the process for the manufacture of high-quality chocolate.
Even though for chocolate manufacture, the alkalinity is more or less voluntary, applying especially when working with low-quality cocoa beans, when producing cocoa powder the operation is mandatory because the taste of the cocoa drink is astringent and stronger than chocolate.
Regarding how to perform this operation, experts opinions are divided, regarding the technological phase in which the cocoa beans

are alkalized and regarding the alkali that are used.
The most common method is to treat the cocoa beans with alkaline solutions after crushing and milling, that is treating the crushed cocoa core particles.
In some plants, cocoa beans are roasted, crushed, decorticated, and the core is treated and dried in special installations.
In other plants, the cocoa beans are dried as necessary in order to be crushed and peeled, the core is treated with alkaline solutions and then deep roasted.
It is also customary to treat raw cocoa beans (unroasted) with shell and after treatment to be roasted.
Sometimes cocoa powder is treated directly [2]
Another method is to treat the cacao mass with alkaline solutions or with anhydrous alkaline solutions. This method is effective because the contact area between the cocoa particles and the alkaline solutions is larger, but it presents some difficulty for the removal of water that was introduced mixed with the cocoa mass, operation that requires a rather long time. [1]
Alkali and acids act both with the tanning substances
The catechin is oxidized easily under the action of the atmospheric oxygen, forming soluble tannins that causes sour astringent taste.
Also, the cocoa red along with catechin and catechol tanning substances, by air oxidation, slowly turns to cocoa brown thereby improving the astringent taste of the cocoa product.
By alkalizing both cocoa red and the catechins tanning substances they transform completely to cocoa brown, resulting in the color stabilization.
Tanning substances behave as polyvalent phenols and has acidic character.
Their sodium salts are generally readily soluble and their potassium salts are soluble only in hot water.
The potassium salts of the tanning substances have the best properties, therefore, usually the alkalinization is made with potassium salt solutions.
The tanning properties of the acid substances and the posibility to form salts can explain the change of color and the tanning substances flavor from the cocoa.
The transformation of these substances in salts leads to changes in pH, color change and taste improvement of cocoa products [4, 5].
It should be noted, however, that the alkalization is not intended to complete the neutralization of the acids or of the acidic substances, as cocoa powder should have a slightly acidic reaction (pH = 6.97 to 6.98), and if there the cocoa mass has an alkaline reaction a small amount of citric or tartaric acid is added, because the alkaline reaction imprints an unpleasant leaching cocoa taste.

After various investigations that are not yet finalized it seems that in the cocoa beans there are catechin tannins.
The tanning substances have a number of properties which are of great importance in the manufacture of chocolate and cocoa powder, as follows:
- in acidic environment and especially when the pH is below 6, they have a light color, and when the pH rises above this value, they begin to darken; also, in the acidic environment their astringent property is emphasized;
- oxidizes easily, passing through colored combinations like reddish-brown-gray, called flobafene, whose presence imprints to some extent the characteristic color of cocoa beans and products.
Research shows that cocoa beans contain between 3 and 6% tannins and during roasting this content falls between 2 and 3.5%.
Besides the fact that they decrease in terms of quantity during roasting, the tanning substances become less astringent due to the fact that some of the volatile acids are eliminated.
This reduction of acidity, also has the effect of darkening the tanning substances [4, 5]
Catechine - catechins are hydro derivatives of flavon, which under the influence of acids becomes catechin tannins.
They are formed in plants through a process of condensation between multiple carbon molecules, that are initially colorless and soluble in water, but as the condensation progresses, they turn red, turning into flobafene.

In these reactions, the molecules of catechins and tannins are joined to one another by C-C bonds, which may be removed by hydrolysis.
Following acid hydrolysis of tannins, results gallic acid and ellagic acid.
The importance of plant physiology is the formation of ellagic acid in alkaline medium under the influence of air [3]
If the cocoa powder is more alkaline its hue more reddish and can even go to magenta. Magenta corresponds to the transition in the alkaline pH, this change being accompanied by an unpleasant flavor [7]
A moderate alkylation generally produces a pleasant and well expressed aroma, whereas excessive alkalinity can destroy almost completely the specific flavor.
In practice, the alkylation must be controlled and directed so as to achieve a favorable balance between color and flavor.
By alkalizing both cocoa red and catechin tanning substances turn completely to cocoa brown, resulting in color stabilization [8.9]

2. MATERIALS AND METHODES

Two samples were used for the analysis, namely:
- 1st sample: roasted and grounded cocoa beans, respectively cocoa grouts;
- 2nd sample: cocoa mass.
The total and volatile acidity was initialy determined and the total and volatile acidity after the alkali treatment and calculated as a percentage the value decrease of this acidity to the control sample.
Determining the total acidity of the cocoa groats was made using the Schulered modified method (used for current measurements).
Determining the total acidity of the cocoa mass was done by the titrimetric method.
Determining volatile acidity for the cocoa groats and the cocoa mass has been achieved by steam entrainment method of volatile acids after a prior acidification of the sample with tartaric acid followed by titration of the distillate obtained with sodium hydroxide in the presence of phenolphthalein as an indicator.

3. RESULTS AND DISCUSSION

The results are presented in Table no 1, on reducing acidity of the cocoa groats and cocoa mass using different alkalis.
- alkalizing cocoa groats
The ammonium bicarbonate express a high affinity to both the volatile acids which neutralize and also non-volatile acids.
It is noted that the highest dose of ammonium bicarbonate, 1.7 kg per 100 kg of groats, decrease the total acidity to 68.05% and the volatile acidity to 26.08%.
The potassium carbonate neutralizes the cocoa groats as follows: at a concentration of 1.5% the decrease of total acidity is 86.11%, while at a concentration of 2%, the decrease is 88.88%, and for the volatile acidity, the concentration of 1.5% the decrease of the volatile acidity is 39.13%, while at a concentration of 2% it is 45%.
The treatment of cocoa grouts with *ammonia* show a pronounced decrease in volatile acidity to the treatment with potassium carbonate, and ammonium bicarbonate, while the decrease of the total acidity is between the values obtained from the samples treated with ammonium bicarbonate and potassium carbonate.
- alkalizing cocoa mass
All samples record values of the decrease in total and volatile acidity, lower than their counterparts on the cocoa groats samples, except the sample with ammonia that imprints a 50% reduction of the volatile acidity, similar to the decrease of 52.17% from the same sample but with cocoa groats.
By alkalizing the cocoa mass not only it neutralizes the volatile and non-volatile acids, but at the same time eliminates the acidic character of the tanning substances, forming neutral salts of them.

Table 1. The reducing acidity of the cocoa groats and cocoa mass using different alkalis

No. of samples	Name and quantity of the material to be neutralized	Alkali used: potassium carbonate (kg)	Alkali used: concentra-ted ammonia (kg)	Alkali used: ammonium bicarbonate (kg)	Total acidity (degrees)	Volatile acidity (acetic acid grams)	Decrease of acidity: total acidity %	Decrease of acidity: volatile acidity %
1	100 kg grinded cocoa beans - control sample	-	-	-	7,2	0,46	-	-
2	100 kg grinded cocoa beans			1	3,6	0,40	50	15
3	100 kg grinded cocoa beans			1,3	3	0,37	58,33	20
4	100 kg grinded cocoa beans			1,7	2,3	0,34	68,05	26,08
5	100 kg grinded cocoa beans	1,5			1	0,28	86,11	39,13
6	100 kg grinded cocoa beans	2			0,8	0,26	88,88	45
7	100 kg grinded cocoa beans		3,8		3	0,22	58,33	52,17
8	100 kg cocoa mass – control sample	-	-	-	5	0,64	-	-
9	100 kg cocoa mass			1,7	3,9	0,51	22	20,31
10	100 kg cocoa mass	2			3,9	0,40	22	37,5
11	100 kg cocoa mass		3,8		3,4	0,32	32	50

This neutralization occurs very rapidly and is accompanied by the instantaneous color change (darkening it) and probably with the air oxygen is forming new flavor and aroma substances whose intensity also depends on the compliance parameters to the preparing operation of the chocolate mass.
There must be a temperature of 40-55° C, 20-30 minutes, in order not to liquefy the cocoa butter and to depreciate it qualitatively by loosing the specific aroma if the temperature would be higher.

4. CONCLUSIONS

The data obtained from the analysis performed on the alkalized cocoa grouts and cocoa mass samples, the following conclusions can be drawn:

- Alkalization of cocoa groats with potassium carbonate at a concentration of 2% recorded a great decrease of the total acidity, in the amount of 88.88%, while the decrease is 45% of the volatile acidity;
- Alkalization of cocoa groats with concentrated ammonia solution at a concentration of 3.8% registered the biggest decrease in volatile acidity of 52.17%, while the decrease in the total acidity is 58.33% more than that in the sample with potassium carbonate.

Hence it is concluded that neutralization with aqueous neutralizing substances
(ammonia solution), is much safer and with better results, but the disadvantage is that the operation of pre-drying for the water removal requires additional energy.

- Alkalization of cocoa mass with concentrated ammonia solution at a concentration of 3.8% recorded the highest decrease of the total acidity (32%) and the volatile acidity content (50%) compared to the samples treated with 1.7% ammonium bicarbonate and 2% potassium carbonate.

This study recommends that alkalinization of both cocoa groats and cocoa mass to be done with concentrated ammonia solution 3.8%, where they recorded the best results in lowering the total and volatile acidity.
Moreover, the literature shows that the formation of new substances with taste and aroma due to neutralization of acidic tanning substances which, in addition to intensifying the color, and also the taste and aroma by neutralizing the unpleasant astringent taste.
The intensity of this process depends on the alkalinity, fineness of grinding the cocoa groats and the pronounced alkaline character of the neutralizing substances used.

5. REFERENCES

Books:
[1] Banu Constantin – Manualul Inginerului în Industria Alimentară, Editura Tehnică, Bucureşti, 1999
[2] Bratu Magda Gabriela – Tehnologia produselor zaharoase, Editura Printech, Bucuresti, 2005
[3] Neniţescu C.D. – Tratat elementar de chimie organică, vol.II, Editura Tehnică, Bucureşti, 1958
Site:
[4] http://www.livestrong.com/article/363625-polyphenols-in-chocolate/
[5] www.superalimente.ro/cacao-boabe-organic-583756
[6] www.sănătate.bzi.ro/beneficiile-boabelor-de-cacao-5587
[7] www.icco.org/61-physical-and-chemical-information-on-cocoa-/106.html
[8] www.sciencedirect.com/cocoa beens-version
[9] info.sciencedirect.com/search/node/cocoa beens