The Chemistry of Chocolate:

Fermentations to Crystallization Kinetics in the creation of a Cherry Cordial

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Presentation Outline

Reactions Covered
• Fermentation
• Maillard Reaction
• Crystallization Kinetics
• Enzymatic Hydrolysis

Process Steps
• Cocoa Bean Growth, Harvest and Drying
• Roasting of the Cocoa Beans and Producing Chocolate
• Tempering of Chocolate
• Preparation of the Cherry Cordial Filling
COCOA BEAN GROWTH, HARVEST AND DRYING

The Fermentation Step
The cocoa tree
The cocoa tree

- **Theobroma cacao**
  - Height of the tree: 10 to 26 ft.
  - Diameter of the trunk: 8 to 10 in.
  - Oblong leaves: 8 to 12 in.

- The cocoa tree bears buds, flowers and fruits at the same time.

- The pods are harvested over a period of several months.
  - In West Africa there are 2 crops, the main crop extends from October to January and the mid crop from May to July.

- Tree growing area
  - 20° latitude north and South.
  - Requires a hot and humid climate
  - Low altitude (2300 ft. max.).
The cocoa tree - 3 species

• **FORASTERO**
  - Originally from the Amazon.
  - Production: more than 70% of world production.
  - West Africa: Ghana, Ivory Coast, Brazil
  - Good quality beans, less chocolate flavor than the Criollo and Trinitario

• **CRIOLLO**
  - Originally from Central America and some areas of Asia.
  - Production: 5 to 8% of world production.
  - Fine chocolate flavor often described as mild nutty, full chocolate.

• **TRINITARIO** (Hybrids between Criollo and Forastero).
  - Origin: Trinidad and Grenada.
  - Production: +/- 20%.
  - Some part of Venezuela and Colombia, Papua N.G., Madagascar.
  - Fine chocolate flavor often described as mild nutty, full chocolate, fruitiness.
Harvesting cocoa pods

Cocoa pods are grown on the trunk and main branches of the tree *Theobroma cacao*. 
The cocoa pod

1) COUPE LONGITUDINALE
2) COUPE TRANSVERSALE
Different Shapes of Pods
De-Podding

De-podding consists of breaking the pods with a piece of wood or a «machette», remove beans and the adhering pulp. Beans with pulp are then ready for fermentation.
Fermentation

• Fermentation and drying of cocoa is of vital importance.
  – Must start no later than 24 hours after de-podding.

• Objectives:
  – Prevent germination of the bean.
  – Separate the grain from the pulp.
  – Initiate chemical and enzymatic reactions inside the beans.
  – Develop flavor and color precursor.
  – Lower astringency and bitterness

• Fermentation last two to seven days
Drying

• After fermentation the beans are placed in trays or on the ground to dry.

• Sun drying is usually adequate. Bananas leaves are used for covering during rainstorms or at night.

• Drying reduces the water content, from 60 % to 7 %.
The fermentation process begins with the growth of micro-organisms. In particular, yeasts grow on the pulp surrounding the beans. Insects, such as the Drosophila melanogaster or vinegar-fly, are probably responsible for the transfer of micro-organisms to the heaps of beans.

The yeasts convert the sugars in the pulp surrounding the beans to ethanol. Bacteria then start to oxidize the ethanol to acetic acid and then to carbon dioxide and water, producing more heat and raising the temperature. The pulp starts to break down and drain away during the second day.

Lactic acid, which converts the alcohol to lactic acid in anaerobic conditions, is produced but, as the acetic acid more actively oxidizes the alcohol to acetic acid, conditions become more aerobic and halt the activity of lactic acid.
The temperature is raised to 40°C to 45°C during the first 48 hours of fermentation. In the remaining days, bacterial activity continues under increasing aeration conditions as the pulp drains away and the temperature is maintained. The process of turning or mixing the beans increases aeration and, consequently, bacterial activity.

The acetic acid and high temperatures kill the cocoa bean by the second day. The death of the bean causes cell walls to break down and previously segregated substances to mix. This allows complex chemical changes to take place in the bean such as enzyme activity, oxidation and the breakdown of proteins into amino acids. These chemical reactions cause the chocolate flavor and color to develop.

The length of fermentation varies depending on the bean type. Forastero beans require about 5 days and Criollo beans 2-3 days. Following fermentation the beans are dried. The oxidation reactions begun through fermentation continue during drying.
ROASTING OF THE COCOA BEANS AND PRODUCING CHOCOLATE

The Maillard Reaction
Chocolate process overview

- Harvesting Cocoa Pods / Twice a year
- Fermenting & Drying Beans
- Cleaning & Winnowing
- Roasting & Grinding Nibs
- Preparing Paste: Roller Refining
- Conching

Cocoa butter

Cocoa Mass

COCOA POWDER

Molding

Bulk Liquid Delivery

Packaging & Shipping
Cleaning and Winnowing

- Cleaning: sieved, de-dusted, de-stoned, metal removed.
- Winnowing: beans are winnowed to remove the shells.
Roasting and Grinding

- Roasting:
  - Critical to determine aroma and flavor.

Nibs are freed of bacteria

Nibs are ground

Cocoa liquor

Cocoa powder

Cocoa butter
Preparing the paste: roller refining

Sugar
Cocoa liquor
Cocoa butter
Milk Powder
Minor Ingredients

Mixer

Refiner
MAIN POINTS

1. Manual liquid addition
2. Automatic liquid addition
3. Bulk
4. Tipping station
5. Manual addition
6. Mixer: to make the mixes
7. Five roll refiner: refining
8. Conches: Conching
9. Magnet
10. Hammer mill
11. Sieve
12. (horizontal) finishing tank
13. (vertical) stock tank
MAIN POINTS

1. Addition of liquid and solid ingredients
2. overpressure outlet (sugar grinding)
3. lid for manual additions
4. Steering equipment
5. Load cell
6. Lock
7. Dosing screw
8. Conveyor belt
9. Liquid additions
10. Water jacket
The main countries:
- Africa (60% world production)
  - Ivory Coast
  - Ghana
- South America (15% world production)
  - Brazil
  - Ecuador
- Asia and Oceania (25% world production)
  - Indonesia
  - Malaysia

Cocoa is produced in tropical regions.
Cleaning of the particles
Destoner
Magnet
Roasting
Debacterisation
Breaker
Winnowing

grinding stages (from small pieces till fluid)

Stones
Metal
Heath

Raw cocoa beans

Particles

Moisture

Output of the shells

Cocoa-liquor tank
CM

Magnet

Cocoa-liquor tank
CM

Output of the shells

Particles

Grinding

Cocoa press

Cake

Cocoa butter CB

Cocoa powder CP

(*) Alkalified cocoa powder

(**) deodorised cocoa butter

Chocolate production

(**) decolorize / deodorizing

(*) Alkalify: process to change the color and the taste.

(**) positive release

(***)

GODIVA
Chocolatier

BARRY CALLEBAUT
**DRYING PROCESS**

- **COLD AIR**
- **WARM AIR**
- **HOT DRY AIR**
- **FULL-CREAMED MILK**
- **CONCENTRATED**
- **SKIMMED MILK**

- **SPRAY**

**ROLLER**

- **HOT CONCENTRATED FULL-CREAM MILK**
- **STEAM**
- **FAT**

- **FULL-CREAMED MILK**
- **CONCENTRATED**
- **SKIMMED MILK**

- **DRYING PROCESS**
HOMOGENOUS MIX WITH A GIVEN CONSISTENCY
Particles surrounded with fat
= Paste

A lot of little particles which are only partly surrounded with fat
= Powder

After the refining extra friction surface is created for which no fat is available.
1 kg solid mass
1 kg fat

- Size of the particles
- Surface to be covered

**FLUID**
- Big particles till 1 mm
- Small surface

**PASTE**
- Medium-sized particles till 200 µm
- Big surface

**POWDER**
- Small particles till 40 µm
- Very big surface
A specific time is necessary to reduce the thickness.

When the thickness is reduced to the half, the length of the film will be redoubled. Of course, the necessary time will be redoubled too.

When the thickness is again reduced to the half, the length of the film will be redoubled again. So again, the necessary time will be redoubled too ...
ROLLED 
NUMBER

<table>
<thead>
<tr>
<th>ROLL NUMBER</th>
<th>ROTATIONAL SPEED (tr/min)</th>
<th>TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>FAST 350</td>
<td>FINE 30</td>
</tr>
<tr>
<td>4</td>
<td>250</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>1</td>
<td>25 SLOWLY</td>
<td>30</td>
</tr>
</tbody>
</table>

FINE

COARSE

FINENESS

FLOW KG/HOUR

GAP

PRESSION

REFINED POWDER WITH FINAL FINENESS
THE RIGHT CONSISTENCY OF A MIX DEPENDS ON THE RECIPE AND THE REQUIRED FINENESS

- **‘DRIER’ MIX**
  - Maximum flow
  - Bigger particles
  - Short refining time

- **GOOD CONSISTENCY**
  - Good flow
  - Good rolling time

- **‘MORE LIQUID’ MIX**
  - Minimum flow
  - Small particles
  - Too long refining time

- The mix is taken easily by the rolls
- The rolls are pushed open rather easily

- Not enough resistance to push open the rolls
- The mix is not taken easily by the rolls
The final fineness of the whole conche will be wrong: Consequence: problems with rheology and taste.
POWDER

- The respective ingredients are mixed according to the recipe
- And then refined to the desired particle size (i.e. fineness)

CONCHING

LIQUID

➔ The desired flavor
➔ Comes close to the desired liquidity (ready for sampling)
- Flavor
- Moisture content
- Fluid rheology (flow behaviour of the product)
FINE POWDER

COCOA BUTTER (FAT) EMULSIFIER

OPEN

PUMP OUT

CONCHING

FILLING

CONCH 1

RECIPE X

CONCH 2

RECIPE Y

CONCH 3

RECIPE Z

CAN BE IDENTICAL OR DIFFERENT

COCOA BUTTER - FATS - AROMATICS... ARE ADDED

25 t

35 t

STORAGE OF LIQUID CHOCOLATE OR MOLDING

RECIPE X

RECIPE Y

RECIPE Z

CAN BE IDENTICAL OR DIFFERENT
- Lecithin
- Cocoa butter
- Fats

Fats, Milk

Lecithin added automatically

Flavor added by hand
MAIN POINTS

1. Conches
2. Magnetic filter
3. Hammer mill
4. Sieve
5. 6/10 tons balancing tank
6. 20/25 tons balancing tank
7. Vertical storage tank
8. Liquid loading
Too little self-friction present in the product in order to heat up the conch. Hot water helps to heat up the product.

The conch heats up significantly due to the self-friction of the product.

Cold water ensures that the product temperature never goes beyond the target value.

The conch is completely liquid now. Pumping-over commences.

Liquifying starts: lecithin/cocoa butter are added.

The conch is empty. A new cycle may start.

Conch filling starts eg: 4 mixtures at 1 mixture / hour.

End of conch filling.

Chocolate

Water
Lecithin is an emulsifier. In some cases, other emulsifiers could be used, e.g. PGPR (polyglycerol polyricinoleate), ammonium phosphatide, ...

Friction (viscosity) arises between the solid particles in the chocolate mass.

Lecithin reduces the friction, thereby improving the liquidity.

The mechanism at work here is as follows: a lecithin molecule has two ends:

1. Polar: this bonds with the solid particles.
2. Non-polar: this bonds with fat by enveloping the solid particles (with the lecithin), a “lubricated” friction is obtained.
TEMPERING OF CHOCOLATE

Crystallization Kinetics
→ Dark chocolate:
   Cocoa and sugar particles dispersed in a continuous phase of fat crystals and liquid fat
Chocolate microstructure

Image: courtesy of FTE (Ghent University)
Chocolate microstructure

Melting of about 16% of triglycerides above 23°C

<table>
<thead>
<tr>
<th>Triglyceride</th>
<th>Melting point</th>
<th>Triglyceride fraction (%) in cocoa butter</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOS</td>
<td>42°C</td>
<td>27%</td>
</tr>
<tr>
<td>POS</td>
<td>38°C</td>
<td>37%</td>
</tr>
<tr>
<td>POP</td>
<td>35°C</td>
<td>17%</td>
</tr>
<tr>
<td>SOO</td>
<td>23°C</td>
<td>13%</td>
</tr>
<tr>
<td>POO</td>
<td>16°C</td>
<td>3%</td>
</tr>
</tbody>
</table>

Liquid fraction ≈ 20% at 20°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid fat content</td>
<td>79 %</td>
<td>74 %</td>
<td>52 %</td>
<td>1 %</td>
</tr>
</tbody>
</table>
Chocolate microstructure ~ tempering

→ Why tempering chocolate (cocoa butter)?

Liquid cocoa butter

T, time, shear

Nucleation
Crystal growth
Cluster formation
Interconnected 3D crystal network

crystallization

Homogeneous or heterogeneous semicrystalline matrix (~ microstructure)

3 min 5 min 10 min 55 min
Chocolate microstructure ~ tempering

→ Why tempering chocolate (cocoa butter)?

cocoa butter polymorphs

melting T range:

- 33.5 - 37°C
- 29.5 - 33.5°C
- 27 - 29.5°C
- 22.5 - 27°C
- 18 - 22.5°C
- 13 - 18°C

Windhab (2011)
Chocolate microstructure ~ tempering

→ Why tempering chocolate (cocoa butter)?
⇒ producing stable crystals ($\beta_V$, $\beta_{VI}$)
⇒ controlled solidification and contraction of chocolate in cooling tunnel
⇒ fat bloom stability, good snap, good melting behaviour, good texture

Chocolate tempering Fry & sons (1847)

Seed tempering

Addition of:
- tempered chocolate (calllets)
- or
cocoa butter seeds (e.g., Mycryo® powder)
PREPARATION OF THE CHERRY CORDIAL FILLING

Enzymatic Hydrolysis
Enzymatic Hydrolysis to Create a Cherry Cordial

• Creation of the classic cherry cordial involves the inversion of sugar to provide the liquid filling that we all know and love

• Product consists of:
  – Classic chocolate shell, tempered as discussed in the previous section
  – Filling formulated to
    • Deposit with a high viscosity
    • Liquefy over two weeks time
Enzymatic Hydrolysis Overview

- Hydrolysis is the break-up of sucrose through the addition of the water to Glucose and Fructose
  - Via the addition of acid (acid hydrolysis)
  - Via the addition of enzymes (enzymatic hydrolysis)

- Common Reaction used to make Invert Sugar Syrups
Invertase Activity is Effected by pH and Temperature

- Product is formulated to optimize the activity of the Invertase from a pH standpoint
- Post production aging conditions (time and temperature) are set based on the Temperature Activity
# Cherry Cordial Recipe

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fondant</td>
<td>90%</td>
<td>Body of filling</td>
</tr>
<tr>
<td>Corn (Glucose) Syrup</td>
<td>7.5%</td>
<td>Viscosity control</td>
</tr>
<tr>
<td>Flavors and Acids</td>
<td>1.5%</td>
<td>Flavor</td>
</tr>
<tr>
<td>Invertase</td>
<td>0.5%</td>
<td>Enzymatic Hydrolysis</td>
</tr>
<tr>
<td>Preservative</td>
<td>0.5%</td>
<td>Control Microbial Growth</td>
</tr>
</tbody>
</table>

Plus 1 Maraschino Cherry

- Ingredients are mixed and heated to 32-35°C
- Filling is temperature is monitored to keep from melting the fat crystals in the chocolate shell
- Final product is cooled and stored for 2 weeks
Effect of time on viscosity of fillings using Invertase

Over time, the Invertase breaks down the sucrose molecules, causing the viscosity of the filling to reduce, behaving more like a liquid.
Finished Product
Thank You