Crystallization of fat and oils

Dr. ir. Nathalie De Clercq
9th of September
Crystallization ➔ Melting behaviour ➔ demands for a good chocolate
Crystallization → Melting behaviour = demands for a good chocolate

- Enough solid fat at 20°C:
  → good ‘snap’ upon fracture
- Enough solid fat between 20-25°C:
  → preventing stickiness at consumption
- Sharp melting profile between 25-30°C:
  → mouthfeel, flavour release and cold sensation
- Melted at body temperature:
  → preventing ‘waxy feeling’
Outline

- Fats and oil: chemistry
- Importance of fat crystallization
- Structural levels in fat crystallization
  - Primary crystallization
    - Thermodynamic driving force, nucleation, crystal growth, polymorphism
  - Microstructural development
  - Macroscopic properties
- How to measure?
- Case study cocoa butter
Outline

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Fats and oils

- Oil/fat = mixture of triacylglycerols
- Animal or vegetable origin
- Triacylglycerols

\[
R'\text{C'O}CH_2\text{O}C\text{R}\xrightarrow{1) OH^-}CH_2\text{O}C\text{R''} \xrightarrow{2) H_3O^+} \text{CH}_2\text{OH} + \text{RCO}_2\text{H} + \text{R'CO}_2\text{H} + \text{R''CO}_2\text{H}
\]
Fatty acids

- Aliphatic carboxylic acids with 4 or more carbon atoms
- Even number of carbon atoms
- 3 different types of fatty acids

- Short (4 - 6 C-atoms), medium (8 - 14 C-atoms) and long chain (≥ 16 C-atoms) fatty acids
### Fatty acids

- **Systematic and trivial names of frequently occurring saturated and unsaturated fatty acids**

<table>
<thead>
<tr>
<th>Systematic name (acid)</th>
<th>Trivial name</th>
<th>Chain Length ($\omega$-notation)</th>
<th>m.p. (°C)</th>
</tr>
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<tbody>
<tr>
<td>Decanoic</td>
<td>Capric</td>
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<td>Dodecanoic</td>
<td>Lauric</td>
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<td>Myristic</td>
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<td>Palmitic</td>
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<td>Stearic</td>
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<td>Oleic</td>
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<td>9-trans-Octadecanoic</td>
<td>Elaidic</td>
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<td>13-Docosenoic</td>
<td>Erucic</td>
<td>22:1_9</td>
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<td>9,12-Octadecadienoic</td>
<td>Linoleic</td>
<td>18:2_6</td>
<td>-3.0</td>
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<tr>
<td>9,12,15-Octadecatrienoic</td>
<td>$\alpha$-Linolenic</td>
<td>18:3_3</td>
<td>-11.9</td>
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<td>Arachidonic</td>
<td>20:4_6</td>
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<td>Eicosatetraenoic</td>
<td>EPA</td>
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<td>5,8,11,14,17-</td>
<td>DHA</td>
<td>22:6_3</td>
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<tr>
<td>Eicosapentanoic</td>
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<tr>
<td>4,7,10,13,16,19-</td>
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<tr>
<td>Docosahexaenoic</td>
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</tr>
</tbody>
</table>
- *cis* isomer predominates in unsaturated fatty acids
- more unsaturation $\Rightarrow$ lower melting point

- **Stearic acid** (18:0)  
  - m.p. 70°C
- **Oleic acid** (9-18:1)  
  - an $\omega$-9 fatty acid  
  - m.p. 16°C
- **Linoleic acid** (9,12-18:2)  
  - an $\omega$-6 fatty acid  
  - m.p. -5°C
- **Linolenic acid** (9,12,15-18:3)  
  - an $\omega$-3 fatty acid  
  - m.p. -11°C
Minor components:
- free fatty acids, monoacylglycerols, diacylglycerols
- phospholipids
- unsaponifiable matter: sterols, tocopherols, wax esters, hydrocarbons, fat soluble vitamins
Cocoa butter = fat

Cocoa butter

(1) & (3) = Palmitic acid (P) (± 26%) and/or Stearic Acid (St) (± 36%)

(2) = Oleic acid (O) (± 33%)

Typical chemical composition = Unique physical properties

→ Depending on the origin

16.5%–19%  38.5%–40%  23%–26%

Fatty acid (1)
Fatty acid (2)
Fatty acid (3)
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**Importance of fat crystallization**

Many fat-rich products with a substantial amount present in the crystallized form

- Affects product structure and texture
- Determines product quality
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Structural levels in fat crystallization

- **Macroscopic properties**
  - Fat

- **Microstructural development**
  - Crystal Network
  - Crystal Clusters

- **Primary crystallization**
  - Crystals
  - Triacylglycerol Molecules

**Macroscopic World**
- >0.2mm

**Microstructure**
- 0.25-200μm

**Nanostructure**
- 0.4–250nm
Primary crystallization: driving force

- Driving force
  = difference in chemical potential $\Delta \mu$ between liquid and solid

1. Crystallization from solution
Supersaturation needed

- $= concentration C (m^{-3}) > concentration at saturation C_s (m^{-3})$

\[
\Delta \mu = R_g \times T_K \times \ln \left( \frac{C}{C_s} \right)
\]

- $R_g = universal gas constant (8.314 J mol^{-1} K^{-1})$
- $T_K = absolute temperature (K)$
- $(C/C_s) : supersaturation ratio = \sigma$ (·)
2. Crystallization from the melt:

Supercooling needed

\[ T_{km} - T_K = \Delta T = \text{supercooling (K)} \]

\[ \Delta H_m: \text{molar melting heat (J/mol)} \]

\[ (\Delta T/T_{km}) = \sigma_r (-): \text{relative supercooling} \]
Nucleation = generation of a crystal nucleus by assembling growth units

⇒ critical activation-energy needed!!!
1. Primary homogeneous nucleation
   • not catalyzed by foreign surfaces or existing fat crystals
   • Up to 30K supercooling needed
Homogeneous Nucleation

\[ T > T_{\text{melt}} \]

True melt

\[ T = T_{\text{melt}} \]

Crystal embryos

\[ T << T_{\text{melt}} \]

Crystal lattice
Primary crystallization: nucleation

1. Primary homogeneous nucleation
   • Not catalyzed by foreign surfaces or existing fat crystals
   • Up to 30K supercooling needed

2. Primary heterogeneous nucleation
   • Catalyzed by foreign surfaces (e.g. impurities, impeller blades etc.)
   • Most frequent in natural fats and oils, enough impurities present
Heterogeneous Nucleation

$T > T_{\text{melt}}$

True melt

$T = T_{\text{melt}}$

Nucleation

less supercooling

$T < T_{\text{melt}}$

Crystal lattice

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Primary crystallization: nucleation

1. Primary homogeneous nucleation
   • = not catalyzed by foreign surfaces or existing fat crystals
   • Up to 30K supercooling needed

2. Primary heterogeneous nucleation
   • = catalyzed by foreign surfaces (e.g. impurities, impeller blades etc.)
   • Most frequent in natural fats and oils, enough impurities present

3. Secondary nucleation
   • = catalyzed by crystals of the crystallizing material ⇒ secondary nuclei
   • Very frequent in crystallization from solution and in industrial crystallizers
• **Depends on**
  - **external factors:**
    - Supersaturation, supercooling, solvent, temperature, presence of impurities, ...
  - **internal factors:**
    - Structure, bonds, crystal defects, ...

**Mechanism** of crystal growth depends on the type of interface:
- flat (F), kinked (K), stepped (S)

Schematic representation of three types of growth sites. Each cube depicts a growth unit.
- Palm stearin crystallizing at 30°C after cooling down from 80°C at 10°C/min
- Real time duration of the movie: 5min, 2.5 min to volume filling
Polymorphism

- Polymorphism
  = the existence of several crystalline phases with the same chemical composition that have a different structure, but yield identical liquid phases upon melting.

- Polymorphic transition
  ⇒ less stable to more stable polymorphs
  ⇒ ‘solid-state’, ‘melt-mediated’ or ‘solvent mediated’

- Importance: obtaining and maintaining (during storage) of specific macroscopic properties
  o E.g. sandiness in margarine and fat bloom on chocolate are caused by a polymorphic transition
Polymorphism

- 3 basic polymorphs (α, β′, β), each with their specific properties

- Subcell packing of the hydrocarbon chains (cross section of the aliphatic chains): hexagonal (α), orthorombic (β′), triclinic (β)
- Different angle with respect to the end methyl group for the different polymorphs
- Zigzag form of one of the 3 chains perpendicular to the other 2 for the β′ form
- Zigzag structures of 3 fatty acid chains in the same plane for the β form
Polymorphism

- 3 basic polymorphs ($\alpha$, $\beta'$, $\beta$), each with their specific properties
  - Melting range, melting heat: $\alpha < \beta' < \beta$
  - Density: $\alpha < \beta' < \beta$
  - Stability: $\alpha < \beta' < \beta$
  - Activation-energy for nucleation: $\alpha < \beta' < \beta$
    - Onset of spontaneous nucleation: $\alpha > \beta' > \beta$
    - The least stable polymorph crystallizes first and will transform to a more stable polymorph as a function of time

- Different submodifications possible depending on the TAG composition

- At low temperatures: $\gamma$ polymorph = sub $\alpha$ polymorph
Polymorphism

- Identification of the different polymorphs
  ⇒ XRD diffraction lines: WAXD (wide angle X-ray diffraction) → short spacings
Organization of the TAG molecules

- The TAG molecules form layers in a specific stacking
- Layer thickness ~
  - Chain length
  - Tilt of the end methyl group
  - Type of packing
- Two types of longitudinal packing, resulting in pairs of 2 or 3 fatty acid chains long, 2L and 3L resp.
- Longitudinal packing ~ TAG composition
  - Many mono-unsaturated TAGs (unsaturation on 2-position)
    - preferentially 3L
    - fatty acids separated in saturated and unsaturated zone
- Determination by XRD diffraction pattern: SAXS (small angle X-ray scattering) → long spacings
Structural levels in fat crystallization

- Macroscopic properties
  - Rheology
    - Mechanical Strength
    - Sensor Impressions
  - Fat
- Microstructural development
  - Crystal Network
  - Crystal Clusters
  - Crystals
  - Triacylglycerol Molecules
- Primary crystallization
  - Macroscopic World
    - >0.2mm
  - Microstructure
    - 0.25-200μm
  - Nanostructure
    - 0.4–250nm

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Microstructural development

- Schematic presentation of the microstructural development:
  1. aggregation of crystals
  2. network formation
     - Continuous 3D network
     - Liquid fat trapped within the network
  3. sintering
Microstructural development

- Network properties depend on:
  - Number and size of the crystals
  - Interactions between the crystals
  - Presence of other components

- Influencing factors
  - Crystallization temperature
  - Cooling rate
  - Agitation
  - Storage time
Structural levels in fat crystallization

- **Macroscopic properties**
  - Fat

- **Microstructural development**
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  - Crystal Clusters
  - Crystals
  - Triacylglycerol Molecules

- **Macroscopic World**
  - >0.2mm

- **Microstructure**
  - 0.25-200µm

- **Nanostructure**
  - 0.4–250nm
Macroscopic properties

- How does the consumer experience the product?
  - Smell
  - Taste
  - Appearance e.g. Fat bloom
  - Mouth feel (cool sensation, no waxy taste)
  - Melting in the hand, sticking to fingers
  - Snap
  - ...

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- Case study cocoa butter
How to measure?

- DSC (Differential Scanning Calorimetry)
- pNMR (pulsed Nuclear Magnetic Resonance)
- XRD (X-ray Diffraction)
- Microscopy
- Rheology
- Texture analysis
- Sensorial analysis
Primary crystallization: How to measure?

- DSC
DSC (Differential Scanning Calorimetry)

- Measures the difference in heat flow between the sample (=fat) and the reference (=air) while both are subjected to the same temperature-time protocol.
Primary crystallization: How to measure?

- **DSC (Differential Scanning Calorimetry)**
  - Provides information on processes that involve heat release (exothermic processes, e.g. crystallization) or heat absorption (endothermic processes, e.g. melting)

- **Applications**
  - Monitoring kinetics of crystallization
  - Recording melting profile → melting point provides an indication of polymorphism

![Melting profile of chocolate](image)
Primary crystallization: How to measure?

- pNMR (pulsed Nuclear Magnetic Resonance)
  - Electromagnetic pulse absorbed by $^1$H-protons
  - Disturbance of the spin of the protons
  - Relaxation to the equilibrium
  - Fast for "solid" protons (crystals)
  - Slow for "liquid" protons
Primary crystallization: How to measure?

- pNMR (pulsed Nuclear Magnetic Resonance)
  - Solid fat content as a function of time (isothermal) or temperature (non-isothermal)
  - SFC as a function of temperature:
    - Equilibrium situation at each T, no information on kinetics

**Isothermal at 15°C**

**Non-isothermal**

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SFC of different palm oil fractions as a function of temperature

- palm oil
- stearine
- oleine
- vhst
- PMF
- super oleine

%SFC vs. T(°C)
Primary crystallization: How to measure?

- **XRD (X-ray Diffraction)**
  - 100% certainty on the polymorphic form

- Synchrotron radiation (ESRF (European Synchrotron Radiation Facility) in Grenoble)
  - More intense X-rays \(\Rightarrow\) recording time is limited to a few seconds
Microstructure: how to measure?

▪ Microscopy
  o Visual representation
    • Morphology, size, number of crystals
    • Aggregation and network formation
  o Several techniques
    • Polarized light microscopy
    • Confocal scanning laser microscopy
    • (Cryo-) Scanning electron microscopy
Microstructure: how to measure?

- Rheology

Crystallization of palm oil at 18°C

Primary crystallization

Microstructure

Step 1

Step 2

Phase angle [°]

Complex modulus [Pa]

Isothermal time [min]
Macroscopic properties: how to measure?

- Texture analysis
  - Puncture test
  - Breaking test
  - Texture profile analysis test
- Sensorial analysis
  - Taste panel
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Cocoa butter

- *Theobroma cacao*:
  - Up to 6 m tall
  - Cocoa fruit: 20 cm
  - Contains 30-40 seeds (65% moisture)
  - Originally from tropical Amazon forest
  - Cultivated by
    - Mayas from Yucatan, Guatemala
    - Aztecs from Mexico
Chemical composition

- Narrow triacylglycerol composition:
  - Mainly POP, POS & SOS
  - But also PLP, POO, PLS, SOO, SLS & SOA

- Variation in triacylglycerol composition depending on geographical origin

<table>
<thead>
<tr>
<th>Land</th>
<th>#stalen</th>
<th>PLP</th>
<th>POO</th>
<th>PLS</th>
<th>POP</th>
<th>SOO</th>
<th>SLS</th>
<th>POS</th>
<th>SOS</th>
<th>SOA</th>
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<td>1</td>
<td>1.1</td>
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<td>2.2</td>
<td>40.0</td>
<td>31.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Isothermal crystallization (20°C) of cocoa butters of various origins and CBS monitored by DSC
Polymorphism

- Narrow triacylglycerol composition
  - complex crystallization behavior/ polymorphism
- 3 basic polymorphs + # sub polymorphs
- 4 to 6 polymorphs recognized and named depending on the author

<table>
<thead>
<tr>
<th>Author</th>
<th>Polymorphic form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vaeck (1961)</td>
<td>γ</td>
</tr>
<tr>
<td>Larsson (1966)</td>
<td>β'₂</td>
</tr>
<tr>
<td>Wille &amp; Lutton (1966)</td>
<td>I</td>
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<tr>
<td>Van Malssen et al. (1999)</td>
<td>γ</td>
</tr>
<tr>
<td>Systematic nomenclature</td>
<td>β'₃ (sub-α)</td>
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</table>
Polymorphism in cocoa butter

Possible phase transitions in cocoa butter (Van Malssen et al., 1999)

Desired polymorphic form: contraction, gloss, snap

Tempering of chocolate to the desired polymorphic form

Direct crystallization (during cooling)
Melting
Recrystallization via the solid phase
TEMPERING

- TEMPERING is a step in the production process during which seed crystals are formed in the molten chocolate.
- Important to obtain crystals in polymorph V as this results in the desired properties such as gloss, color, hardness, snap and shelflife.
- The seed crystals in polymorph V created during tempering will ensure that the rest of the chocolate also crystallizes in polymorph V.
TEMPERING

Several steps can be identified (see figure)

A: melting all the crystals present
B: removal of sensitive heat
C: formation of stable and unstable crystals
D: melting of unstable crystals, only the stable crystals remain
Importance of crystallization in chocolate production

- **COOLING**
  - Further crystallization based on seeds formed during tempering
  - Proper time-temperature program in cooling tunnel is important: gloss, sufficient hardening at the end of the cooling

- **STORAGE**
  - Ongoing crystallization (depending on the cooling): crystallization heat can get trapped in the wrapping
  - Amongst others, polymorphic transition to form VI
  - Fat bloom
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Tempering

- VIDEO!
Case study: Influence of refining on the cocoa butter properties
Cocoa butter refining

Conventional Cocoa Butter Refining

Crude Cocoa Butter

Polish Filtration

Deodorization
Steam stripping

Refined Cocoa Butter

- Good quality refined cocoa butter
  - < 1.75% free fatty acids
  - Free from foreign material
  - Molds
  - Rancidity
Cocoa butter refining

• High demand → more poor quality crude cocoa butter
  ▪ High FFA, high (non-hydratable) phosphatides, Fe
  ▪ High alkalinity, dark colour (difficult to bleach)
• Increasing demand for different types of cocoa butter
  ▪ Colour ranges
  ▪ Degree of neutral flavours
• Removal of alkaloids: theobromine and caffeine
  ▪ Deposit on the surface of vapour scrubbers → reduce the performance
• Steam refining should preserve unique crystallisation properties of cocoa butter

Improved refining process required
Cocoa butter refining

**Conventional Cocoa Butter Refining**

- Crude Cocoa Butter
  - Polish Filtration
  - Deodorization
    - Steam stripping
  - Refined Cocoa Butter

**Improved Cocoa Butter Refining**

- Crude Cocoa Butter
  - Silica Pretreatment
  - Bleaching
    - Bleaching earth (and activated carbon) 90°C/50 mbar
  - Deodorization
    - Packed column stripping or tray deodorization
      - short time/low pressure, adjustable temp.
  - Refined Cocoa Butter

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Research question

Cocoa butter refining conditions

? 

Milk chocolate quality

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Experimental design

Crude cocoa butter

Silica pretreatment

Packed Column Steam Refining
150°C – 175°C – 200°C – 225°C – 250°C

Milk chocolate production

**Evaluation:**
- FFA, trace elements, soaps, tocopherols, alkaloids
- Colour, oxidation parameters
- Crystallization properties

**Evaluation:**
- PSD, rheological properties, sensory properties

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### Influence of silica pretreatment

<table>
<thead>
<tr>
<th></th>
<th>Crude CB</th>
<th>Silica pretreatment</th>
<th>Observation</th>
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<tbody>
<tr>
<td>FFA (%)</td>
<td>2.14</td>
<td>2.28</td>
<td>≈</td>
</tr>
<tr>
<td><strong>Trace elements</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>P (ppm)</td>
<td>63.52</td>
<td>8.66</td>
<td>~90% Degumming</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>3.20</td>
<td>0.24</td>
<td>~90%</td>
</tr>
<tr>
<td>Tocopherols</td>
<td>264.64</td>
<td>246.55</td>
<td>≈</td>
</tr>
<tr>
<td><strong>Alkaloids</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Theobromin</td>
<td>75.71</td>
<td>35.17</td>
<td>~54%</td>
</tr>
<tr>
<td>Caffeine</td>
<td>437.96</td>
<td>331.36</td>
<td>~25%</td>
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<tr>
<td>Soaps (ppm sodium oleate)</td>
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<td>N.D.</td>
<td>Complete removal</td>
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<tr>
<td><strong>Colour</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$L^*$ $\geq$</td>
<td><em>37a</em> $\geq$ <em>3.8b</em> $\geq$ <em>59.2</em></td>
<td>$L^*$ $\geq$ <em>73a</em> $\geq$ <em>-4.83b</em> $\geq$ <em>100.5</em></td>
<td>$L^<em>$ $\uparrow$ Bleaching effect $b^</em>$ $\uparrow$ more yellow</td>
</tr>
<tr>
<td>OSI (hours)</td>
<td>32.43</td>
<td>61.30</td>
<td>~50%</td>
</tr>
</tbody>
</table>
Influence of temperature during packed column steam refining

**FFA removal as function of refining temperature: sigmoid decrease**

![Graph showing FFA removal as a function of refining temperature. The graph includes data points for CB and Sil CB with a sigmoid curve showing a decrease in FFA with increasing temperature. The 1.75% legal limit is also indicated.](image-url)
Temperature during packed column steam refining

- No influence
  - P and Fe
  - Acylglycerol composition
- Limited influence
  - T > 175°C: 30% reduction soaps
  - T > 175°C: limited reduction tocopherols
- Complete removal theobromine and caffeine at T ≥ 200°C
- Exponential decrease of b* as function of temperature: less yellow
Influence of temperature during packed column steam refining

**Oxidative properties:** $T \rightarrow$ primary oxidation products transform to secondary oxidation products

**Percyde**

<table>
<thead>
<tr>
<th>Packed Column Temperature (°C)</th>
<th>NA</th>
<th>150</th>
<th>175</th>
<th>200</th>
<th>225</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peroxide (meq O$_2$/kg oil)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CB</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>sil CB B</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

**p-Anisidine value**

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<th>NA</th>
<th>150</th>
<th>175</th>
<th>200</th>
<th>225</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Anisidine value</td>
<td>0</td>
<td>0.5</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td>CB</td>
<td>1</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>sil CB B</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

KOI: Cocoa processing and chocolate production - 2013
Influence of temperature during packed column steam refining

Oil stability index (OSI):
- Limited influence of temperature
- Si-pretreatment: less prone to oxidation
  → Removal of Fe

Packed Column Temperature (°C)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>OSI (hours)</th>
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<tr>
<td>250</td>
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</tr>
</tbody>
</table>

CB B
Sil CB B
Crystallization properties

SFC content in temperature range 20°C to 30°C (tempered IUPAC procedure: 40 hours at 26°C)
Isothermal crystallization at 20°C for 240 min
- Start with formation of α, followed by transition to the β'-polymorph
- Kinetics of the β' crystallization: Foubert Model parameters
  - \( t_{\text{ind}} \): time needed to achieve 1% crystallization: decrease as function of column temperature
  - \( K \): rate constant: increase as function of column temperature
  - \( a \): no clear effect

→ sooner and faster crystallization as \( T \) increases, so as function of FFA removal
Influence of refining on CB properties

- Read more
  - Ayala et al. 2007, JAOCs, 84, 1069-1077
  - De Clercq et al., 2012, Journal of Food Engineering, 111, 412-419
Case study: Influence of DAG on the crystallization of CB
(crude) cocoa butter

MODIFICATION

chocolate
**Innovation**

= Creation of new products, high added value
  • Nutritionally, taste, appearance, functionality
  • BUT with same quality level as the standard product

→ Modification of cocoa butter
  o Cocoa butter based diacylglycerols
  o DAG

  • Distinct physicochemical properties compared to TAG
  • More hydrophillic and water soluble
  • Nutritional benefits (mainly 1,3-DAG)
    – Different metabolic pathway
    – Lower body weight gain and body fat accumulation
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Production

CB Diacylglycerols

Characterization

Phase behaviour
0 – 100% CB – DAG

Isothermal crystallization
CB + max. 10% DAG

Dark chocolate Migration fat bloom

Fundamental

Applied
KOI: Cocoa processing and chocolate production - 2013

CB Diacylglycerols

Characterization

Phase behaviour
0 – 100 % CB – DAG

Isothermal crystallization
CB + max. 10% DAG

Dark chocolate
Migration fat bloom

Production
DAG production

- **Diacylglycerol (DAG)** is 2 fatty acids + glycerol

  - 1,3-DAG
  - 2,3-DAG
    - = 1,2-DAG
DAG production

Enzymatic glycerolysis

- 15% enzyme
- Substrate molar ratio: 1.12
- Reaction temperature: 70°C
- Reaction time: 6 hours

Cocoa butter TAG
DAG production

enzymatic glycerolysis

- 15% enzyme
- Substrate molar ratio: 1.12
- Reaction time: 6 hours
- Reaction temperature: 70°C

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20% TAG

30% MAG

50% DAG

Short path distillation:
4 steps, combination temperature and reduced pressure

KOE: Cocoa processing and chocolate production - 2013
Melting behaviour of CB vs CB DAG

Heat Flow (W/g) vs Temperature (°C)

-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
-40 -20 0 20 40 60 80

Cocoa butter

14°C
22°C
33°C
61°C

Cocoa butter DAG
Exo Up

KOI: Cocoa processing and chocolate production - 2013
Cocoa butter /diacylglycerol: 100/0; 90/10 ... 10/90; 0/100

![Graphs showing the effect of temperature on SFC for different cocoa butter/diacylglycerol compositions.](image-url)
KOI: Cocoa processing and chocolate production - 2013

Production -> CB Diacylglycerols

Characterization

Phase behaviour
0 – 100 % CB – DAG

Isothermal crystallization
CB + max. 10% DAG

Dark chocolate
Migration fat bloom
- Isothermal crystallization behaviour
  - Heating to melt all the crystals
  - Cooling at 10°C/min
  - Isothermal at 20°C for a defined time
- Different experimental techniques
- At 20°C: two step crystallization process: $\alpha$ to $\beta'$
KOI: Cocoa processing and chocolate production - 2013
SAXS diffraction patterns

Cocoa butter

2.5% DAG
SAXS diffraction patterns

Cocoa butter

10% DAG

SAXS diffraction patterns
KOI: Cocoa processing and chocolate production - 2013

Isothermal crystallization

Cocoa butter

1.25% DAG

2.5% DAG

5% DAG

10% DAG

WEEK 1

WEEK 3

Cocoa butter

1.25% DAG

2.5% DAG

5% DAG

10% DAG
Conclusion

- Crystallization mechanism is changed!
- Microstructure $\neq \rightarrow$ Macrostructure $\neq$
Crystallization of fat and oils

Dr. ir. Nathalie De Clercq
9th of September