Reinigung von Produkten aus nachwachsenden Rohstoffen mit fraktionierter Kristallisation

Manfred Stepanski, Sulzer Chemtech AG, Winterthur/CH
Matter of Biomass

- Carbohydrates (Glucose, Starch, Cellulose, etc.)
- Fats and Oils
- Lignin
- Proteins
- Enzymes
- Vitamines
- Pigments
- Flavour and Odourous Substances
Crystallization used for Biomass Products

- Purification of lactide for Polylactic Acid (PLA)
- Winterization of oils
- Fractionation of higher and lower melting fat fractions
- Separation of essential fatty acids
- Purification of fatty acids
- Purification of minor components of fats (Phytosterol)
Binary Phase Diagram

- **Crystal A**: Liquid A + B
- **Crystal B**: Liquid A + B
- **Solid A + B**: M
- **Liquid A + B**: L
- **Eutectic Point**: M
- **100% A**: $x_p$ to $x_F$
- **100% B**: $x_R$ to $x_E$
Principle of Crystallization

Mass and Energy Flow:

- Crystallization
- Phase Separation
- Melting

Cooling

Heating
Terms influencing the average composition of the solid state:

Adherence of liquid phase (adhere),

Inclusion of liquid phase inside the crystallites (inclusion I),

Inclusion of liquid phase between the crystallites (inclusion II),

Incorporation of other components in the crystal lattice (incorporation).

Source: König, University Erlangen
Features of Crystallization

- Low temperature level
- Good selectivity
- Low energy consumption
- With or without solvent
  - From solvent: Supersaturation (evaporation or cooling)
  - From melt: "Simple“ cooling
- Suspension or layer crystallization
Equipment for Suspension Crystallization

Equipment for crystallization – batch or continuous operation:

- Agitated vessels with internal or external cooling
- Vessels with forced circulation and external cooling
- Scraped-wall crystallizers

Equipment for separation – batch or continuous operation:

- Drum or belt filters
- Filter presses
- Centrifuges
- Wash columns
Layer Crystallization

Static crystallization

Falling film crystallization

Plate

Stagnant melt

Tube

Circulated melt, falling film
How does Fractional Crystallization work?

One Purification Stage

Phase 1: Crystallization
- Cooled Surface
- Crystals
- Melt
- Step 1: Layer growth

Step 2: Drain off residue

Phase 2: Partial Melting/Sweating

Phase 3: Total Melting

Cooling

Heating

Feed liquid

Product liquid

Residue liquid
Temperature Cycle

Temperature Cycle:

- Phase 1: Crystallization
- Phase 2: Draining
- Phase 3: Sweating, Melting

Temperature vs. Time
Mass Flow Diagram

- **Stripping Stage**
- **Feed Stage**
- **Rectification Stage**

Flow directions:
- **Feed**
- **Product**
- **Residue**
Static Crystallizer

- HTF in
- HTF out
- Melt inlet
- Cooling / heating plates
- Tank
- Liquid outlet
Falling Film Crystallizer, operation

- tubular crystallizer
- external heat transfer fluid, falling film
- internal melt circulation, falling film
- most efficient mass and heat transfer
Falling Film Crystallization

- Feed
- Buffer vessels
- Pure product
- Residue
- Crystallizer
- Falling film product
- Falling film heat transfer medium
- Collecting vessel
- Product pump
- Heat exchanger
- Heat transfer medium pump
Falling Film Crystallizer
Crystallization of Lactide for Poly Lactic Acid

High purity lactide from melt crystallization is the key for high quality PLA
Key drivers of PLA demand:
- Positive regulatory and policy framework (Green Dot in Germany; Japanese directives)
- Stimulation of regional agricultural economies
- Innovation in chemical and plastics industries
- Consumer acceptance of bio-based polymers
- Green image of retailers and brand-owners

World capacity bio-plastics
Poly Lactic Acid Production Steps

1. Sugars
2. Fermentation
3. Lactic acid
4. Lactide production
5. L-Lactide crystals
6. PLA
7. Ring opening polymerization
8. Lactide crystallization
Crystallization - Staging

Falling film crystallization

Crude lactide

L-Lactide ~90%
Meso-Lactide 2-5%

L-Lactide >99.9%

Pure Lactide

Phase diagram

Static crystallization

L-Lactide <55%

Recycle

T

A

x_R

x_F

x_P

B

Residue

Feed

Product
Natural esters (triglyceride)

Glycerol

Oleic acid

Linoleic acid
Fractionation of Fat Fractions

These bonds break to produce fatty acids and glycerol

Crystallization of
- Triglyceride or
- Fatty acids
## Fatty Acid Sources

### Typical Fatty Acid Composition of vegetable and animal fats and oil

<table>
<thead>
<tr>
<th>Oil or Fat</th>
<th>Unsat./Sat. ratio</th>
<th>Capric Acid (C10:0)</th>
<th>Lauric Acid (C12:0)</th>
<th>Myristic Acid (C14:0)</th>
<th>Palmitic Acid (C16:0)</th>
<th>Stearic Acid (C18:0)</th>
<th>Oleic Acid (C18:1)</th>
<th>Linoleic Acid (ω6) (C18:2)</th>
<th>Alpha Linolenic Acid (ω3) (C18:3)</th>
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<tr>
<td>Almond Oil</td>
<td>9.7</td>
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<td>-</td>
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<td>7</td>
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<td>Beef Tallow</td>
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<td>Butterfat (cow)</td>
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<td>3</td>
<td>11</td>
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<td>12</td>
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<td>Canola Oil</td>
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<td>Cocoa Butter</td>
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<tr>
<td>Cod Liver Oil</td>
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<td>Cottonseed Oil</td>
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<td>Flaxseed Oil</td>
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<tr>
<td>Grape seed Oil</td>
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<td>8</td>
<td>4</td>
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<tr>
<td>Lard (Pork fat)</td>
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<td>-</td>
<td>2</td>
<td>26</td>
<td>14</td>
<td>44</td>
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<td>Olive Oil</td>
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<td>Palm Oil</td>
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<td>Safflower Oil</td>
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<td>78</td>
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<tr>
<td>Sesame Oil</td>
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<td>-</td>
<td>-</td>
<td>9</td>
<td>4</td>
<td>41</td>
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<tr>
<td>Soybean Oil</td>
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<td>Sunflower Oil</td>
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<td>Walnut Oil</td>
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<td>11</td>
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<td>28</td>
<td>51</td>
<td>5</td>
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Melting Point of Fatty Acids

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Melting Point (°C)</th>
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<tbody>
<tr>
<td>Capric C10:0</td>
<td>31.3</td>
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<tr>
<td>Lauric C12:0</td>
<td>44.0</td>
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<tr>
<td>Myristic C14:0</td>
<td>54.4</td>
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<tr>
<td>Palmitic C16:0</td>
<td>62.9</td>
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<tr>
<td>Stearic C18:0</td>
<td>69.6</td>
</tr>
<tr>
<td>Oleic C18:1</td>
<td>16.3</td>
</tr>
<tr>
<td>Linoleic C18:2</td>
<td>-5.0</td>
</tr>
<tr>
<td>Linolenic C18:3</td>
<td>-11.0</td>
</tr>
</tbody>
</table>
How to obtain crystals of fat?

From solvent:
Supersaturation (evaporation or cooling)
Crystallization in the most stable polymorphic form,
Generally \( \beta \)

From melt:
Cooling
Cooling rate effect on the polymorphic forms: \( \alpha, \beta' \) or \( \beta \)
Parameters Fat Crystallization

**Fat**

**Melting**

**Crystallization**
- Nuclei formation
- Crystal growth

**Separation**

**Olein** → **Stearin**

**Growth rate:**
- Polymorphism
- Formation of mixed crystals

**Nucleation:**
- Number of nuclei
- Degree of supersaturation

- Foreign particles
- Insoluble matters
- Temperature (super cooling)
- TG composition
- Type of pre-treatment
Fractionation of milk fat by staging:

- **Milk fat** (MP 32-34)
  - **Olein** (MP 18-21)
  - **Stearin** (MP 42-46)
- **Soft-Stearin** (MP 24-30)
- **Super-Olein** (MP 12-16)
- **Top-Olein** (MP 6-10)
- **Recycle** (MP 18-21)

**Stage 1**

**Stage 2**

**Stage 3**
Phytosterol

- Phytosterols, also called plant sterols, are a group of steroid alcohol, naturally occurring in plants. (sitosterol, campesterol, stigmasterol)

- Nutritional Importance: Cholesterol-lowering effect

- Functional food (margarine, yoghurt, spreads, salad dressings, beverages etc.)
Occurrence of Phytosterol in Vegetable Oil
Mass Flow

A two stage crystallization

Crude phytosterol 1 2

Solvent

Final residue

Yield = 90 %

product >99 %
Crystallization Stage

- **Solution Preparation**
  - CRUDE (liquid)
  - SOLVENT (liquid)
  - SOLVENT (vapor)
- **Crystallization**
  - CRYSTAL GROWTH
  - DRAIN RESIDUE
- **Sweating**
  - MELT OUT INCLUSIONS
- **Solvent Evaporation**
  - SEPARATE SOLVENT
- **Melting**
  - PURE (liquid)
- **Cooling**
  - HEATING

- **Residue**
  - (liquid)
Final Product
Features of SULZER Process

Fully automated control of the mass balance guarantees constant product quality.

Extremely flexible operation allows adaptation to changes in feed quality or product requirements.

No addition equipment such as centrifuge or filter system is required for the phase separation.

No scale-up uncertainty; pilot plant results correlate 1:1 with the industrial plant.

Very low maintenance costs since the plant has no moving parts except standard pumps and valves.
Vielen Dank für Ihre Aufmerksamkeit

Sulzer Chemtech AG
Dr.-Ing. Manfred Stepanski
Sulzer-Allee 48
8404 Winterthur, Switzerland
Phone +41 52 262 3786
manfred.stepanski@sulzer.com
www.sulzer.com