Degumming and Refining Technologies

Renewable Resources
Oscar Brückner
Degumming and refining technologies

- Basics of mechanical separation
- Objective of degumming and refining
- Different processes
  - Water degumming
  - Chemical refining
- Improvements of neutralization process
- Soapstock splitting
- Acid degumming
  - Enzymatic degumming
Clarification and Separation

**Definition:**
- **Clarification** is the separation of solids from a liquid
- **Separation** is the separation of two liquids

Liquid/Solid  Liquid/Liquid  Liquid/Liquid/Solid
Selection of centrifuges: Physical correlations

\[ V_s = \frac{D^2 \cdot \Delta \rho}{18 \cdot \eta} \cdot g \]

Stokes’ Law

\[ z = \frac{r \cdot \omega^2}{g} \]

Centrifugal acceleration

Settling by Gravity

- \( z = 10^5 \) – \( 10^6 \)
- \( z = 13,000 \) – \( 17,000 \)
- \( z = 5,000 \) – \( 13,000 \)
- \( z = 1,500 \) – \( 5,000 \)
- \( z = 300 \) – \( 1,500 \)
Selection of centrifuges: Function principle of separators

Decantation vessel with dividing plates

Feed

Clarified liquid

Centrifugal force

Engineering for a better world
Selection of centrifuges: Function principle of decanters

Sedimentation

Sedimentation + Centrifugal Force

Sedimentation + Centrifugal Force + Continuous Solids Discharge
Selection of centrifuges: Types of centrifuges

**Solid wall Disc Separator**
- up to 0.5 vol.\% solids
- manual cleaning

**Self-cleaning Separator**
- up to 3 vol.\% solids
- automatic desludging
- can be clarifier or separator

**Nozzle Bowl Separator**
- up to 25 vol.\% solids
- continuous discharge

**Decanter**
- up to 60 vol.\% solids
- continuous discharge
Selection of centrifuges: decanter vs. centrifuge

Decanters – Pressoil Clarification

- High solids loads in the feed (up to 50%)
- Coarse particles (up to 10 mm size)
- Reasonable dryness of the discharged solids
- Lower g-force than with a disc-type centrifuge

Separators – Degumming / Neutral.

- Solids load in the feed is limited to approx. 3%
- Removal of even fine particles \( D_{\text{lim}} < 1 \text{ micron} \)
- High clarification capacity => high throughputs
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Objectives of degumming and refining

- **Removal of undesired products from crude oils**
  - Free fatty acids (FFA)
  - Phospholipids (gums)
  - Oxidized products
  - Metal ions
  - Color pigments
  - Waxes
  - Others

- **Preservation of valuable minor components**
  (e.g. vitamin E or tocopherol – natural anti-oxidants)

- **Minimize oil losses**

- **Production of valuable by-products – i.e. Lecithin**

- **Protection of the oil against degradation**
Composition of phospholipids

<table>
<thead>
<tr>
<th></th>
<th>Soybean Oil</th>
<th>Rapeseed Oil</th>
<th>Sunflower Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphor content [ppm]</td>
<td>400 - 1200</td>
<td>200 – 900</td>
<td>300 – 700</td>
</tr>
<tr>
<td>Phospholipids content [%] (Conversion factor: 30)</td>
<td>1.0 – 2.9</td>
<td>0.5 – 2.3</td>
<td>0.8 – 1.8</td>
</tr>
<tr>
<td>Phospholipids distribution [%]</td>
<td>PC (MW 784) 47</td>
<td>27</td>
<td>29 – 52</td>
</tr>
<tr>
<td></td>
<td>PI (MW 861) 24</td>
<td>17</td>
<td>11 – 22</td>
</tr>
<tr>
<td></td>
<td>PE (MW 742) 20</td>
<td>17</td>
<td>17 – 26</td>
</tr>
<tr>
<td></td>
<td>PA (MW 699) 9</td>
<td>39</td>
<td>15 -30</td>
</tr>
</tbody>
</table>

- **Hydratable phospholipids**
  - Phosphatidyl choline (PC)
  - Phosphatidylinositol (PI)

- **Non-hydratable phospholipids** (calcium, magnesium and iron salts)
  - Phosphatitic acid (PA)
  - Phosphatidyl etholamine (PE)

**Remark:** Simplified model, not all PA and PE are NHP
Phospholipids content of different oils and fats

<table>
<thead>
<tr>
<th>Type of oil</th>
<th>P-content [ppm]</th>
<th>Phospholipids [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>10 - 20</td>
<td>0.025 – 0.05</td>
</tr>
<tr>
<td>Palm</td>
<td>15 – 40</td>
<td>0.04 – 0.1</td>
</tr>
<tr>
<td>Sunflower</td>
<td>200 – 500</td>
<td>0.5 – 1.3</td>
</tr>
<tr>
<td>Maiz germ (corn)</td>
<td>300 - 800</td>
<td>0.7 – 2.0</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>200 - 800</td>
<td>0.5 – 2.0</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>400 - 1000</td>
<td>1.0 – 2.5</td>
</tr>
<tr>
<td>Soyabean</td>
<td>600 - 1200</td>
<td>1.5 – 3.0</td>
</tr>
</tbody>
</table>
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  - Enzymatic degumming
Integration of degumming in refining processes

**Physical Refining**
- Crude oils
  - Gums
    - Acid-Degumming
    - Dewaxing
    - Bleaching
    - Deacidification/Deodorisation
    - Edible oil
  - Fatty acids

**Chemical Refining**
- Water-Degumming
- Alkali-Neutralisation
- Dewaxing
- Bleaching
- Deodorisation
- Distilled fatty acids
- Acid oil
- Lecithin
- Soapstock Splitting
- Gums Drying
- Edible oil
Water Degumming - Reasons

• Prevention of sediments in storage tanks
• Reduction of losses in advanced degumming processes, alkali-neutralisation and soapstock splitting
• Production of a crude oil according trading standards
• Production of lecithin used as:
  • Emulsifier for food products
    • Bread, Margarine, Chocolate, instant drinks
  • Animal feed
    • Emulsification, digestion and binding of dust during production
    • Fish Farming
  • Non food applications / technical applications
    • Cosmetics, Pesticides, Paint industry etc.
Water Degumming - Process parameters

- Oil temperature: 75 - 90 °C
- Water addition: corresponding to the phosphatised content
- Hydration time: with static mixers 20 - 30 minutes with high shear mixing not required but recommended to increase the yield
Water Degumming - Results

• **P-content**
  - depends very much on factors which cannot be influenced by the process, especially on the NHP-content:
    - Quality of the seed / beans
    - Conditions during pre-pressing and extraction
    - Storage conditions
  - P-content variations: 50 – 200 ppm
  - Usual warranty: NHP + 0,1 % HP

• **Loss measurement – oil content in gums:**
  - Measured as acetone insoluble (A.I. = phospholipids)
  - A.I. variations: 60 – 72 %
  - Usual warranty: 67 % (68 % with dynamic mixer and hydration vessel)
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Chemical Refining

Physical Refining

Crude oils

Chemical Refining

Water-Degumming → Gums Drying → Lecithin

Acid-Degumming

Dewaxing

Bleaching

Deacidification/Deodorisation → Edible oil

Edible oil

Soapstock Splitting → Acid oil

Distilled fatty acids

Gums

Physical Refining

Acid oil

Edible oil

Gums Drying

Soapstock Splitting

Acid oil

Lecithin

Renewable Resources – Oscar Brückner
Target for oil quality before bleaching

- P-content: $< 10$ ppm
- Iron content: $< 0.2$ ppm
- Sulphur content: $< 10$ ppm
- Polymer content: $< 2.0\%$
- Moisture: $< 0.25 \%$ (by weight)
- Impurities/filterable solid matter: $< 0.30 \%$ (by weight)
- Unsaponifiables: $< 1.50 \%$ (by weight)
Alkali neutralization - Process
Optional crystallization
Process steps

- **Conditioning** Transformation of the non-hydratable phospholipids into their hydratable form by breaking down the metal / phospholipid complexes with a strong acid

- **Crystallization** Optional stage for crystallization of wax

- **Neutralization** Saponification of the free fatty acids by alkali (caustic soda)

- **Washing** Removal of residual soaps by hot water. Alternative: Dry wash (i.e. with Silica)

- **Drying** Removal of moisture under vacuum.
Advantages:

• High Oil quality
• Low bleaching earth consumption
• Well know process
• Simple process control
• Low energy consumption

Disadvantages:

• Lower Yield compared with physical refining especially for high FFA oils
  • But Acid Oil can be recovered in soap-stock splitting
• Effluent stream after soap-stock splitting
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Improvement of neutralization process

- **More efficient technology to**
  - Reduce oil losses to the soapstock / gums
  - Increased oil quality due to improved separation
  - Reduction in consumption of chemicals
- **Important is the mixing of acid and caustic**
  - Trend towards more intensive mixing

static  ➔  dynamic  ➔  High Shear  ➔  Nano Reactor®
Nano neutralization: Advantages

- Easy implementation in existing process lines
- Reduction of reaction times – less space required
- Increased oil quality
  - Improved separation due to Nano Reaction
  - Less soap in oil after 1st separation
- Improved yield
  - Less neutral oil in soapstock
  - Less salts in soapstock – less contaminated waste water
- Less chemical consumption
  - Up to 90% reduction of acid
  - Approx. 30% reduction of caustic
    - Less acid must be neutralized
    - Only stoichiometric amount for FFA
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Chemical Refining – Soapstock splitting

Physical Refining

- Crude oils
  - Acid-Degumming
  - Dewaxing
  - Bleaching
  - Deacidification/Deodorisation

Chemical Refining

- Water-Degumming
- Alkali-Neutralisation
- Dewaxing
- Bleaching
- Deodorisation
- Gums Drying
- Soapstock Splitting
- Lecithin
- Acid oil
- Distilled fatty acids

Renewable Resources – Oscar Brückner
Chemical Refining – Soapstock composition

• Constituents of Soapstock
  • Soap (sodium salts of fatty acids)
  • Phosphatides
  • Sugars
  • Proteins
  • Solids
  • Water

• Total fatty matter (TFM): 15 – 50 %
  • For a continuous splitting (acidulation) the soapstock has to be liquid - TFM 15 – 20 %
  • The phosphatides are disturbing the splitting by forming a stable emulsion between the fatty acid and water phase
Soapstock splitting

• Reasons for soapstock splitting:
  • Dispose the soapstock
  • Recover fatty acids.

• The TFM of the Soapstock contains
  • Soap (sodium salt of fatty acids)
  • Neutral oil
  • Phospholipids

• Phospholipids are main cause for emulsions in soapstock splitting
  • Degumming before alkali neutralization
  • Post saponification
    • Phospholipids partly decomposed – reduced emulsification
    • Convert the Neutral oil to Soap – increased FFA content in Acid oil
Saponification of triglycerides

• The saponification is done by caustic under high pressure (10 bar) and high temperature (150°C).

• Neutral oil converted to Soap – increased FFA content in Acid oil

• Phospholipids partly decomposed – reduced emulsification
Soapstock splitting - Reaction stage

• Splitting temperature min. 90°C

• Acidulation by sulphuric acid to pH 2 – 3.

• Reaction time in agitated tank approx. 1 hour
Soapstock splitting - Process

- **Soapstock**
  - **Condensed steam**
  - **Sulfuric acid**
  - **Saponification column**
  - **Splitting tank**
  - **Intermediate tank**
  - **Cooling water**
- **Sulfuric acid**
  - **Water**
  - **Splitting tank**
  - **Decantation tanks**
- **Caustic soda**
  - **Washing water**
  - **Neutralization tank**
  - **Vapor washer**
  - **Decantation tank**
  - **Air**

**Processes**:
- **Soapstock splitting**
- **Decantation**
- **Splitting**
Soapstock splitting - Decantation

• Separation of acid oil (fatty acids) and acid water
  • Decantation vessels
    • Decantation time 3 - 8 hours depending on feed stock
  • Separator
    • Only possible in case of low emulsions
    • Special material due to aggressive media

• Back-up decantation for separate treatment of emulsion

• Optional:
  • Washing of fatty acid to improve quality
New application for centrifuges

- Replacement of decantation vessels for acid oil / acid water separation

- **Self-cleaning separator RSE 90 successfully tested in biodiesel plants**
  - Special machine with high corrosive resistant materials (Super Duplex, 1.4539, etc.)

- **Advantages:**
  - Reduced space requirement
  - Higher acid oil and acid water quality
  - Higher Degree of automation / easier operation
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Simple acid degumming

- First simple attempt to remove also NHP
  - Not able to remove NHP to an extent required for physical refining
- Used to pre-treat palm oil, coconut oil, olive oil and animal fat prior to physical refining
  - Removal of phosphatides, metal ions and proteins
  - Consumption of bleaching earth can be reduced by up to 50%
Simple acid degumming - Process parameters

- Oil temperature: 75°C – 90°C
- Acid addition: 0,1 - 0,3 % w/w phosphoric or citric acid
- Mixing: high shear mixing
- Retention time: min. 5 minutes
- Water addition: 2 - 3 % vol.
- Mixing: dynamic mixer
Acid degumming - Targets

• **P-content**
  - depends very much on factors which cannot be influenced by the process, especially on the NHP-content:
  - P-content variations: 10 – 50 ppm

• **Oil content in gums:**
  - Measured as acetone insolubles (A.I.= phospholipids)
  - A.I. variations: 65 – 72 %
Special degumming

• **Flexible plant**
  - Can be used for degumming and neutralization

• **Degumming with one or two stages**
  - One stage, without washing
    - less effective but no waste water
  - Two stages, with washing
    - Lower P-content but wash water as additional effluent stream
Special degumming - Process parameters

- Oil temperature: 60 - 75 °C
- Acid addition: 0,1 - 0,3 % w/w phosphoric or citric acid
- Mixing: high shear mixer
- Acid retention time: min. 5 minutes
- Caustic soda addition: partial neutralisation of acid, not FFA
- Water addition: corresponding to phosphatides content
- Mixing: dynamic mixer
- Hydration time: min. 60 minutes
- Heating for separation: 75 – 90 °C
- Wash water addition: 3 – 5 % vol.
Special degumming - Results

• **P-content:**
  - One stage process, no washing: 20 – 30 ppm
  - Two stage process, with washing: 15 – 20 ppm

• **Oil content in gums**
  - Acetone insoluble (AI): 50 – 60 %
  - Oil content on dry base: 40 – 50 %

• **Waste water quality:**
  - Oil content: approx. 5 %

• **Moisture content in degummed oil:**
  - Without vacuum drying: < 0,5 %
  - With vacuum drying: < 0,1 %
Top degumming

- **High effective and specialized degumming process**
  - Process based on a combination of two centrifuges
    - Separator to remove the bulk of phosphatides
    - High Speed Clarifier with nozzles for removal of fines

- **The process is very simple and the plant very compact**
  - Short retention times
  - Works with crude and pre-degummed oils
Top degumming - Process parameters

• Oil temperatures: 90 - 105 °C
• Acid addition: 0,1 - 0,3 % w/w phosphoric or citric acid
• Mixing: high shear mixer
• Acid retention time: 3 minutes
• Caustic soda addition: partial neutralisation of acid, not FFA
• Gums separation: by standard refining separator
• Wash water addition: 3 % vol.
• Water retention time: 3 minutes
• Water separation: by high speed nozzle separator
• Recycling: water, fine gums, oil to the first separator
Top degumming - Results

- P-content: < 10 ppm P
- Fe-content: < 0.2 ppm
- Losses: \( \frac{\Delta P \times 30 + \text{impurities}}{0.6} + \text{moisture} \)
- Moisture content in gums: > 50%
- Oil content in gums
  - Acetone insoluble (AI): 60–70%
  - Oil content on dry base: 30–40%
Enzymatic degumming

- **EnzyMax** – process originally developed in 1992 by LURGI and Roehm
  - Process was not further promoted due to limited availability and acceptance of phospholipase produced from pig pancreas
  - Problems in centrifuges with citrate layers
- **Revitalization of the process by NOVOZYMES**
  - Developed a microbiological enzyme
  - Better availability and acceptance (Kosher and Halal regulations)
  - Less citrate formation
- **Remark:**
  - Gums from enzymatic water degumming cannot be sold as lecithin
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Products with the use of specific enzyme:

- **PLA₁**: MonoAcylGlycerol - Phospholipid (Lyso-Phospholipid) + Free Fatty Acid
- **PLA₂**: Mono-Acyl-Glycerol - Phospholipid + Free Fatty Acid
- **PLC**: Di-Acyl-Glyceride + Phosphoroester
Basic principle of PLA 1 degumming

- Only Mono-Acyl-Glyceride-Phospholipids separated from oil
- Free Fatty Acid stays in oil $\Rightarrow$ reduction of losses
- Better emulsification of Mono-Acyl-Glyceride-Phospholipid in the water phase $\Rightarrow$ reduction of losses
Basic principle of PLA 2 degumming

- Mono-Acyl-Glyceride-Phospholipids separated from oil
- Free Fatty Acid stays in oil ⇒ reduction of losses
- Better emulsification of Mono-Acyl-Glyceride-Phospholipid in the water phase ⇒ reduction of losses
Basic principle of PLC degumming

- Only the Phosphor-ester is separated from the oil
- Di-Acyl-Glycerides stay in the oil \(\Rightarrow\) reduction of losses
- But the PLC will **not** reduce the level of PA/PI
Enzymatic degumming – typical process parameters

- Oil temperature: 70 – 75 °C
- Acid addition: 0,04 – 0,1 % w/w citric acid
- Acid retention time: 10 minutes
- Oil temperature: cooling to 55 °C
- Caustic soda addition: to adjust pH 4.5 – 7 (depending on enzyme)
- Enzyme addition: approx. 30 - 100 g/t (depending on enzyme)
- Water addition: corresponding to phosphatides content
- Hydration time: 2 – 6 hours
- Oil temperature: heating to 70 °C for separation
Enzymatic degumming – Results

• **Losses:**
  \[ 0.75 \times \frac{\Delta P \times 30}{0.55} + \frac{impurities}{0.55} + moisture \]
  factor depending on enzyme and crude oil

• **P – content:**
  < 10 ppm (for 2-stage process)

• Works with un-degummed and pre-degummed oils
Cost comparison for oil with 150 ppmP

Crude Oil specification:
- FFA: 1%
- Phosphorous: 150ppmP
- Moisture: 0.1%
- Impurities: 0.1%

Enzyme dosing: 50 g/t
Enzyme price: 30 €/kg

Water degummed oil:
Typical if Lecithin Processing is applied

Costs for utilities plus oil losses for 400 tpd
Comparison for oils with 500 ppmP
Costs for utilities plus oil losses for 400 tpd

Crude Oil specification:
FFA: 1%
Phosphorous: 150ppmP
Moisture: 0.1%
Impurities: 0.1%

Enzyme dosing: 50 g/t
Enzyme price: 30 €/kg

Utility Costs [TEUR / Year]
## Matrix for choosing the right Degumming Process (according to theoretical cost calculations)

<table>
<thead>
<tr>
<th>&lt; 50 ppm P</th>
<th>50 – 150 ppm P</th>
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<tr>
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<td>TOP-Degumming</td>
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</tr>
</tbody>
</table>

**Remark:**

- For enzyme costs of 30 EUR / kg and enzyme dosage of approx. 50 g / t crude oil
- Combined process of TOP and Enzymatic Degumming is possible
- For oils between 150ppmP and 500 ppmP more accurate calculations need to be done.
Enzymatic TOP-Degumming for all options

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