Soybean Oil Processing; Quality Criteria and Flavor Reversion

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♦ Flavor Reversion
♦ Critical Parameters
♦ Quality Management
**Soybean Oil Flavor Reversion**

- Soybean oil is highly susceptible to oxidation
  - The polyunsaturated fatty acid content is high: 57-58%
  - The linolenic acid content is high: about 7%

- The flavor of the refined oil reverts back to that of the crude oil

  **Flavor is changing to slight beany, which in advanced stages is described as painty or fishy**
Hypothesis flavor Reversion (1)

- Oxidation of linolenic acid
  - Oxidative decomposition of linolenic acid
  - Low linolenic soybean oil develops less reversion flavor
  - However, nitrogen blanketing does not prevent it completely
  - Oxidation of iso-linoleic acid? But reversion taste is not the same in brush-hydrogenated oil
Hypothesis flavor Reversion (2)

♦ Phosphatide reaction
  - Nitrogen is part of molecules found in the flavor extracts of reverted soybean oil
  - Lecithin provides the trimethylamine oxide, which in the presence of linolenic acid and hydroperoxides from auto-oxidation, releases formaldehyde and dimethylamine (= fishy odor)
Hypothesis flavor Reversion (3)

♦ Unsaponifiables
  - Induce reversion when added to other oils
  - Flavor reversion is improved by removing unsaponifiables with adsorbents or by drastic steam deodorization

♦ Oxidized polymers
  - Oxidized ethyl linolenic polymers could decompose under nitrogen
  - This yields flavor components identical to those isolated from reverted soybean oil
Summary: flavor reversion

Flavor reversion is an oxidation process involving:

- (Poly)unsaturated fatty acids: Linolenic > Linoleic > Oleic
- Unsaponifiable components
- Nitrogenous materials: phosphatides; other
Relative oxidation rate of poly-unsaturated fatty acids at 37°C

E.N. Frankel (1998) Lipid Oxidation, The Oily Press, Dundee
## Relative stability of oils and fats

<table>
<thead>
<tr>
<th>Oil type</th>
<th>OSI (h) @ 97.8°C</th>
<th>Relative stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fish oil</td>
<td>2-3</td>
<td>1</td>
</tr>
<tr>
<td>Linseed oil</td>
<td>1-2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Sunflower seed oil</td>
<td>8-10</td>
<td>4</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>13-15</td>
<td>6</td>
</tr>
<tr>
<td>Rapeseed oil</td>
<td>16-20</td>
<td>7</td>
</tr>
<tr>
<td>Palm oil</td>
<td>40-65</td>
<td>20</td>
</tr>
</tbody>
</table>
Radical driven oxidation reactions

Initiation

RH $\xrightarrow{\text{Energy Catalyst}}$ R$^\cdot$ + H$^\cdot$

Propagation

R$^\cdot$ + O$_2$ $\rightarrow$ ROO$^\cdot$

ROO$^\cdot$ + RH $\rightarrow$ ROOH + R$^\cdot$

Termination

R$^\cdot$ + R$^\cdot$ $\rightarrow$ RR

RH + OH $\rightarrow$ R$^\cdot$ + H$_2$O

ROO$^\cdot$ + R$^\cdot$ $\rightarrow$ ROOR

ROO$^\cdot$ + R$_1$OO$^\cdot$ $\rightarrow$ ROOR$_1$ + O$_2$
Oxidation: conjugated acids formed
Critical Factors in flavor Reversion

♦ Factors contributing to the oxidative deterioration of finished oil (according to decreasing importance)
  - Oxygen or air ($O_2$)
  - Heat (T)
  - Pro-oxidants (metals)
  - Light ($\lambda$)
  - Time (t)

♦ Factors related to processing (in)efficiency
  - Crude oil quality
  - Processing specifications
Oxygen or air (O$_2$)

Solubility of O$_2$ in oil is high: 3.2 ml / 100 ml. But oxidation can be initiated at much lower O$_2$ concentrations!

- Avoid exposure to air during processing
- Avoid spraying in the air during filling and emptying of storage or holding tanks
- Use proper agitation systems in holding / storage tanks
  - Avoid leakage at joints, fittings, or faulty pump seals
- Maintain vacuum where possible
- Avoid / eliminate the blowing of lines with air (use N$_2$)
- Protect oil with nitrogen blanketing or sparging
- Use anti-oxidant where possible
Heat (T)

Chemical reactions, incl. oxidation, accelerate with increasing temperature

♦ Keep the oil no warmer than needed
♦ Avoid localized overheating by agitating the oil when it is heated
♦ Keep the storage temperature as low as possible

Remark: even at low temperature sensitive lipids are prone to oxidation: e.g. frozen meat will oxidize upon storage at –20°C
Pro-oxidants (metals)

Copper (Cu), the most potent oxidation catalyst and Iron (Fe) should be kept as low as possible

Cu < 5 ppb
Fe < 150 ppb

Role for cobalt, manganese and chromium?

♦ Use a chelating agent such as citric acid or phosphoric acid
♦ Avoid using iron or copper (bronze) in systems coming into contact with (finished) oil
Light ($\lambda$)  
- Protect the oil from exposure to light  
- Add single oxygen quenchers such as beta-carotene and tocopherols  
- Use appropriate refining conditions that reduce the photosensitizer content

Time ($t$)  
- When given sufficient time, any fat or oil will deteriorate even if handled under ideal conditions
Cycle of lipid oxidation

- **Initiation**: T (UVC), Cu++, Fe++ with Light
- **Propagation**: Free radicals, 
  Oxygen (O₂)
- **Termination**: Free radicals, Triglycerides
- **Peroxides**: Volatile oxidation products
Cycle of lipid oxidation

One Way Reaction
Cycle of lipid oxidation

- Metal chelators
- RADICAL-Scavenger
- Oxygen scavenger
Balance antioxidants - radicals

*In-vivo* antioxidants
(e.g. $\alpha$-tocopherol)

*In-vitro* antioxidants
BHA, BHT,…
Types of antioxidants

♦ Metal chelators
  - Citric acid
  - Phosphoric acid

♦ Oxygen scavengers
  - Ascorbic acid

♦ Radical scavengers
  - Synthetic antioxidants: BHA, BHT
  - Semi-natural antioxidants: gallic acid, propyl gallate
  - Natural antioxidants: tocopherols, rosemary extract
Metal chelators

bind metal ions, e.g. neutralization of copper or metal ions with citric acid (or with EDTA)

\[
\text{HOCCOOH} + \text{Cu}^{++} \rightleftharpoons \text{CH}_2\text{COOH} \quad \text{Citric acid}
\]
Radical Scavengers

2- and 3-tert-butyl-4-methoxyphenol

2,6-di-tert-butyl-4-methylphenol

Propyl gallate

radical scavengers “absorb” free radicals
Tocopherols

Increasing antioxidant activity

Increasing vitamin E activity
Factors related to processing (in)efficiency

♦ The quality of fully refined soybean oil is influenced by the quality of the crude oil and the quality of soybeans from which it was extracted.

♦ The refining, bleaching and deodorizing should be done according to the best available technology – agreed Process Standards.
Factors in crude SB/SBO affecting quality

- Total Gums/Phosphatides  
- Non-Hydratable Phosphatides
- Free Fatty Acids  
- Oxidation Products
- Iron/Metal Content  
- Pigments

- Field Damaged Beans  
  - a, b, c, e
- Weed Seed  
  - d, f
- Immature Beans  
  - f
- Splits (Loading/Transport/Unloading)  
  - a, b, c
- Bean Drying & Storage (t/T/Humidity)  
  - a, b, c, d
- Conditioning Beans for Extraction  
  - a, b, d, e
- Solvent Stripping Oil (Overheating)  
  - b, d
- Oil from Stripper (Overheating)  
  - b
- Crude Oil Storage (Time/Temp)  
  - c, d
Quality soybeans ⇒ Quality Crude oil

♦ Optimal range for effective crushing and dehulling: DM = 9.5-10.5%.

Depends on:
- Growing conditions
- Harvesting conditions
- Storage conditions (cleanliness? open air contact in silos, containers, trucks, trains and ships?)

♦ Poor drying and storage conditions induce hydrolysis and oxidation that will partially be found in the crude oil

♦ (Heat) damage
  - Ground or weather damage
  - Frost damage
  - Immature soybeans
  - Insect damage
  - Mould damage
  - Microbial damage
  - Sprout damage
  - Heat damage (inappropriate drying)
Effect of Soybean Damage on SBO Quality

- Lower yield of crude soybean oil
- Problems in the oil extractor
- Too high green color in RBD SBO
- Higher levels of Free Fatty Acids
- Losses in the refining process of SBO
- More impurities to remove in bleaching
- Changes in the flavor and odor of SBO
- Shorter shelf-life of the SBO
In-Process (Oil) Standards

This is the heart of quality management
Process & quality personnel need to know and be able to follow-up all in-process standards

♦ Standards
  - Start at the oilseed quality and crude oil production
  - End at the warehousing & distribution

♦ Standards are set
  - On the basis of oil type and specific processes applied
  - To maintain the best quality and maximum shelf life for the oil product
# Average Compositions for Crude and Refined Soybean Oil

<table>
<thead>
<tr>
<th></th>
<th>Crude Oil</th>
<th>Refined Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglycerides (%)</td>
<td>95-97</td>
<td>99</td>
</tr>
<tr>
<td>Phosphatides (%)</td>
<td>1.5 – 2.5</td>
<td>0.003 – 0.045</td>
</tr>
<tr>
<td>Unsaponifiable matter (%)</td>
<td>1.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Plant sterols (%)</td>
<td>0.33</td>
<td>0.13</td>
</tr>
<tr>
<td>Tocopherols (%)</td>
<td>0.15 – 0.21</td>
<td>0.11 – 0.18</td>
</tr>
<tr>
<td>Hydrocarbons(squalene) (%)</td>
<td>0.014</td>
<td>0.01</td>
</tr>
<tr>
<td>Free fatty acids (%)</td>
<td>0.3 – 0.7</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Trace metals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron (ppm)</td>
<td>1 – 3</td>
<td>0.10-0.20</td>
</tr>
<tr>
<td>Copper (ppb)</td>
<td>30-50</td>
<td>10-30</td>
</tr>
</tbody>
</table>

Specifications may be added for moisture and secondary oxidation products.
Critical parameters to be controlled in a good quality refining process (1)

Start with acceptable crude oil quality within basic quality parameters

- Moisture < 0.15 %
- Peroxide value < 5 meq/kg
- Anisidine value < 2
- Below limit secondary oxidation products
Critical parameters to be controlled in a good quality refining process (2)

Crude oil storage

- Fill and keep tanks below critical temperature
  - preferably at 35-40 °C; never exceed 65 °C!!!
- Bottom filling is preferred (minimize contact with air)
- Work with mechanically agitated storage tanks
Significance of Equipping Edible Oil Storage Tanks with Mechanical Agitators

This avoids sludge formation, reduces the losses and creates a more stabilized supply of feedstock crude oil.

It is also essential to achieve (1) product quality and (2) processing economic objectives.

♦ Maintain oil homogeneity from crude state to finished product
  - With static storage conditions, gravity-gradient stratification occurs
  - The quality of the oil constantly changes
  - It is impossible to establish stable optimum processing conditions
  - End result: reduced oil quality, higher oil loss, and increased operating expense

♦ Homogeneity in storage tanks
  - Cannot be obtained by expensive circulating of the oil with a pump
  - Is obtained with mechanical agitators

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Critical parameters to be controlled in a good quality refining process (3)

♦ Equipment constraints: no copper, zinc or bronze connections, valves, pipes

♦ Preferably equipment is made in stainless steel:
  - Inox 304 (high temperature), or
  - Inox 316 (bleaching, deodorizing)

♦ Oil contact with air: max. temperature 65°C

♦ Oil contact temperature in pumps: max. 100°C (risk for air contact at higher temperature)
Critical parameters to be controlled in a good quality refining process (4)

♦ Oil quality at entry of bleaching step:
  - phosphorus < 5 ppm P
  - soap < 50 ppm

♦ Avoid all contact with air during filtration at high temperature

♦ Oil quality at entry of deodorization step:
  - phosphorus (ppm P) < 3 ppm
  - iron (ppb Fe) < 150 ppb
  - phosphoric acid 0
  - soap 0
  - bleaching earth none
Critical parameters to be controlled in a good quality refining process (5)

♦ Vacuum in the deodorizer should be correct (3-4 mm Hg). This requires proper maintenance and cleaning, and elimination of all leaks (< 10 mbar pressure loss in 24 h)
♦ Avoid all contact with air during high temperature polishing filtration
♦ Cool to below 60°C before storage
♦ Sparge with nitrogen gas when possible
♦ Add citric acid (ppm range) to refined, bleached and deodorized oil (to chelate metal ions, and protect from oxidation)
Critical parameters to be controlled in a good quality refining process (6)

♦ Refined oil storage
  - Dish or cone-bottom stainless steel tanks
♦ Residual oils must be eliminated as much as possible
♦ If possible, use nitrogen blanketing or sparging
♦ Wash tanks at least twice a year
♦ Maximum storage temperature 30 °C
♦ Packaging materials
  Can > TetraPak > Glass > PET ≈ PVC > PE
DEFINITION OF QUALITY OF SOYBEAN OIL (1)

♦ Fully refined soybean oil = pure soybean oil
♦ Produced from fair average quality crude soybean oil, from which essentially all of the free fatty acids and non-oil substances have been removed by chemical treatment, and by mechanical or physical separation
♦ The oil shall be essentially free of polyaromatic hydrocarbons and related toxic substances
DEFINITION OF QUALITY OF SOYBEAN OIL (2)

♦ Three processing steps are used:
  - (Chemical) Neutralization
  - Bleaching
  - Deodorization.

♦ Citric acid is added to the oil after deodorization; preservative addition permitted (re: local legislation)

♦ The oil shall be **clear and brilliant** in appearance at 21-29 °C, and free from settlings or foreign matter

♦ The oil shall be **bland** and free from rancid, painty, musty, soapy, fishy, metallic, beany, and other foreign or undesirable odors and flavors
DEFINITION OF QUALITY OF SOYBEAN OIL (3)

♦ Color (Lovibond): ≤ 10Y/1.0R
  AOCS Cc 13b 45
♦ % FFA (% by wt): ≤ 0.05
  AOCS Ca 5a 40
♦ Phosphatide content: ≤ 3 ppm P
  AOCS Ca 12 55
  AOCS Ca 19-86
♦ Iron content: ≤ 0.1 ppm
  AOCS Ca 15 75
♦ Cold test: ≥ 5 1/2 hrs
  AOCS Cc 11 53
♦ Moisture and volatile matter: ≤ 0.10 %
  AOCS Ca 2d 25
♦ Soap: traces
♦ Unsaponifiable: ≤ 1.5 %
  AOCS Ca 6a 40
♦ Peroxide value (in meq/kg): ≤ 2.0
  AOCS Cd 8 53
♦ Stability – Oil Stability Index
  Rancimat or OSI ≥ 7.5 h onset time at 110°C AOCS Cd 12b-92
  AOM: ≥ 15 h to reach a POV=35 meq/kg  AOCS Cd 12 57
PRODUCTION OF TOP QUALITY
SOYBEAN OIL

♦ Avoid contamination
  - Metallic contamination: Fe < 0.15 ppm; Cu in ppb range
  - Use chelating agents: citric acid
  - Oxidation products itself act as pro-oxidants

♦ Avoid overheating
  - Will create a “set” color, difficult to bleach
  - Keep below 60°C when in contact with air

♦ Avoid undue exposure to air
  - Results in oxidation and reduced shelf life
  - Bottom fill tanks
  - Use nitrogen blanketing or sparging
  - Addition of antioxidants

Control each processing step to insure removal of the impurities it is intended to remove

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THANK YOU

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