Soybean Oil Processing; Quality Criteria and Flavor Reversion

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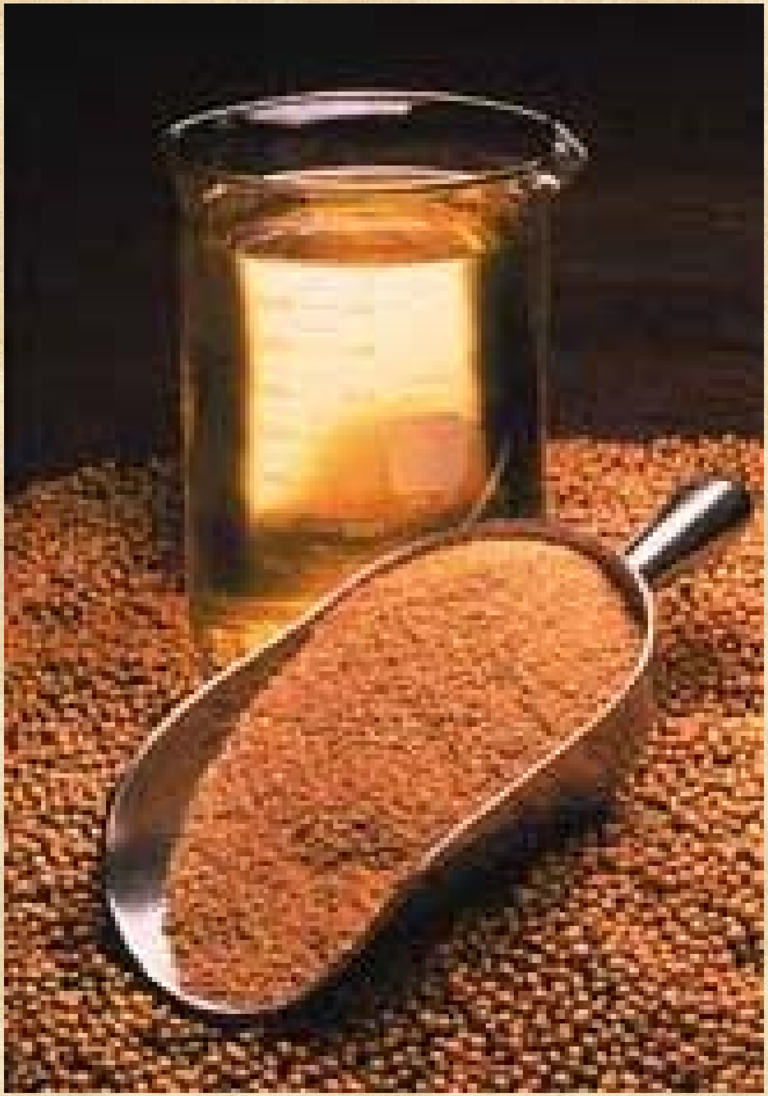
- Flavor Reversion
- Critical Parameters
- Quality Management



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

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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)

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Hypothesis flavor Reversion (3)

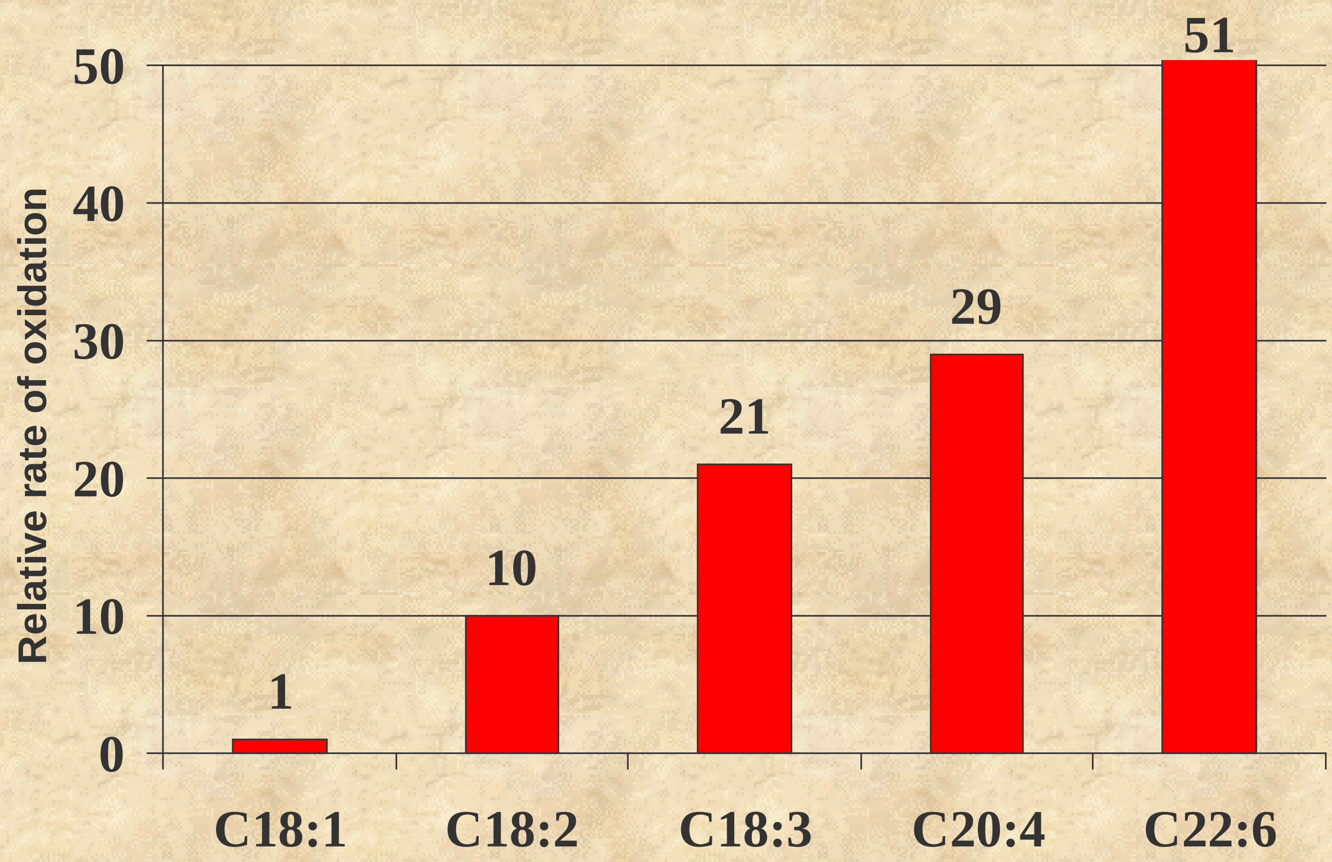
- Unsaponifiables
  - Induce reversion when added to other oils
  - Flavor reversion is improved by removing unsaponifiables with adsorbents or by drastic steam deodorization
- Oxidized polymers
  - Oxidized ethyl linolenic polymers could decompose under nitrogen
  - This yields flavor components identical 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

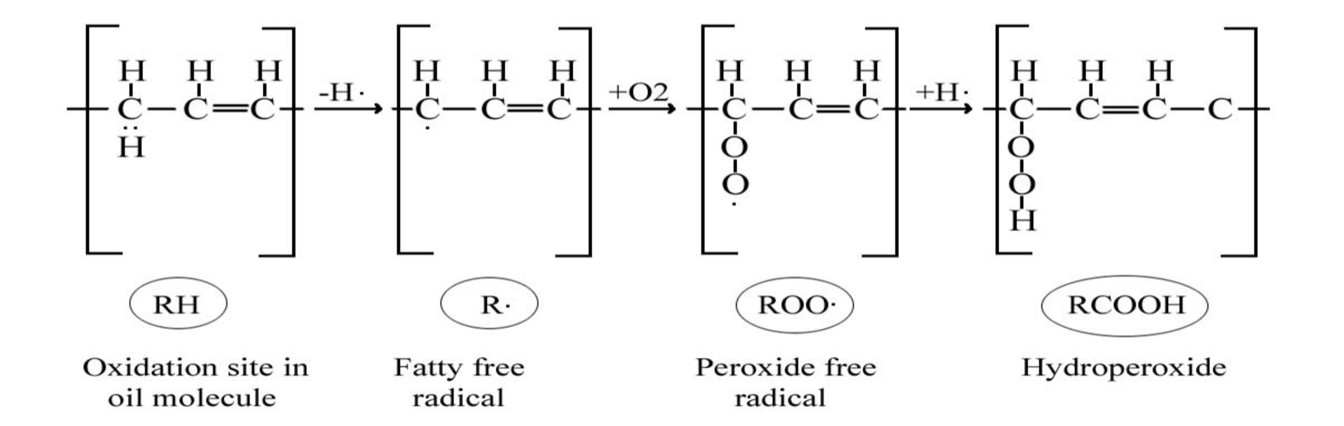


E.N.Frankel (1998) Lipid Oxidation, The Oily Press, Dundee

Relative stability of oils and fats

Oil type	OSI (h) @ 97.8°C	Relative stability
Fish oil	2-3	1
Linseed oil	1-2	< 1
Sunflower seed oil	8-10	4
Soybean oil	13-15	6
Rapeseed oil	16-20	7
Palm oil	40-65	20

Radical driven oxidation reactions



- Initiation $RH \xrightarrow{\text{Energy Catalyst}} R^{\bullet} + {}^{\bullet}H$
- Propagation $R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$

  $ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$
- Termination $R^{\bullet} + R^{\bullet} \longrightarrow RR$

  $RH + {}^{\bullet}OH \longrightarrow R^{\bullet} + H_2O$

  $ROO^{\bullet} + {}^{\bullet}R \longrightarrow ROOR$

  $ROO^{\bullet} + R_1OO^{\bullet} \longrightarrow ROOR_1 + O_2$

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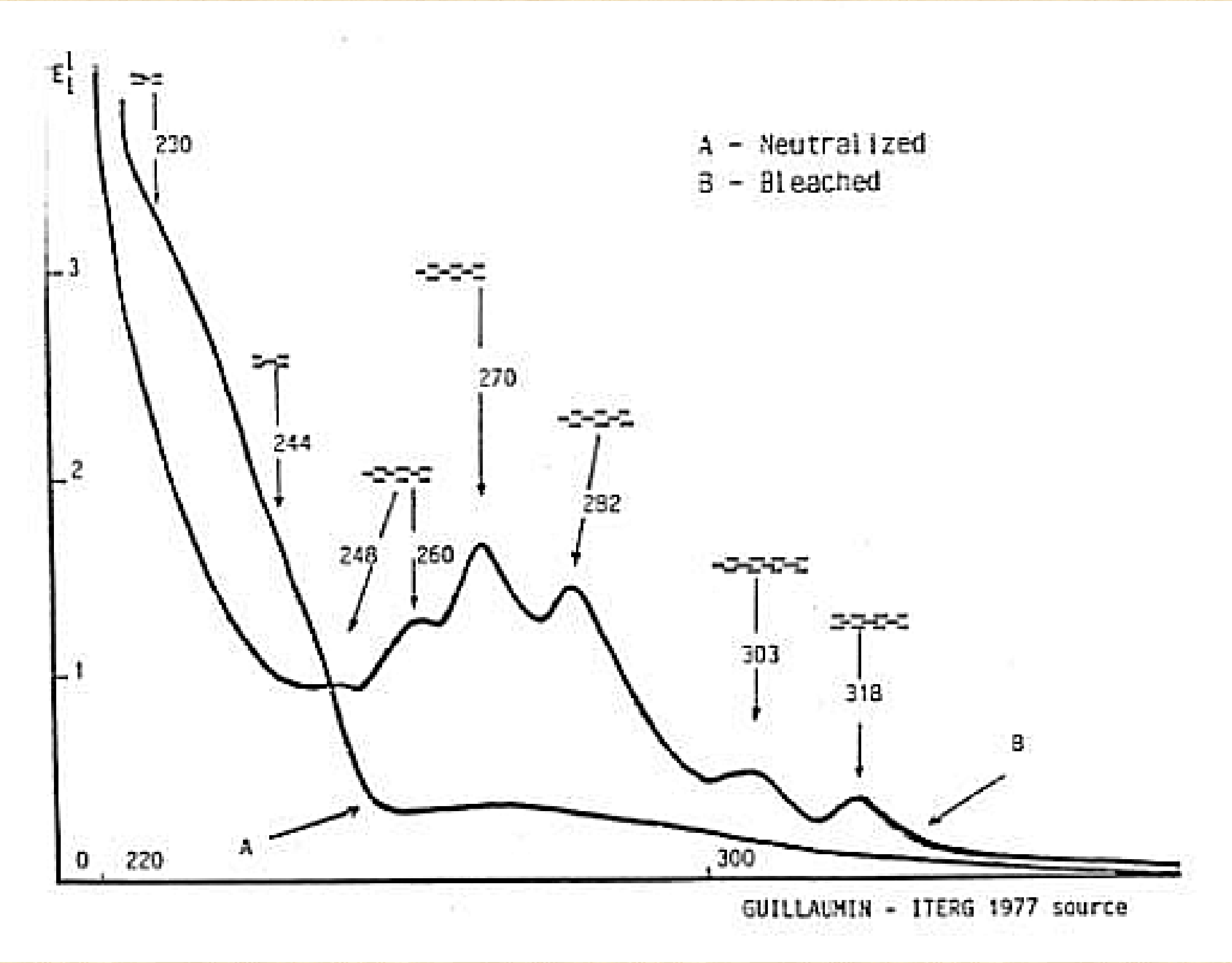
Oxidation: conjugated acids formed



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 (λ)
  - 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

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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 (λ)

- Protect the oil from exposure to light
- Add single oxygen quenchers such as beta-carotene and tocopherols
- Use appropriate refining conditions that reduce the photo-sensitizer content

Time (t)

- When given sufficient time, any fat or oil will deteriorate even if handled under ideal conditions

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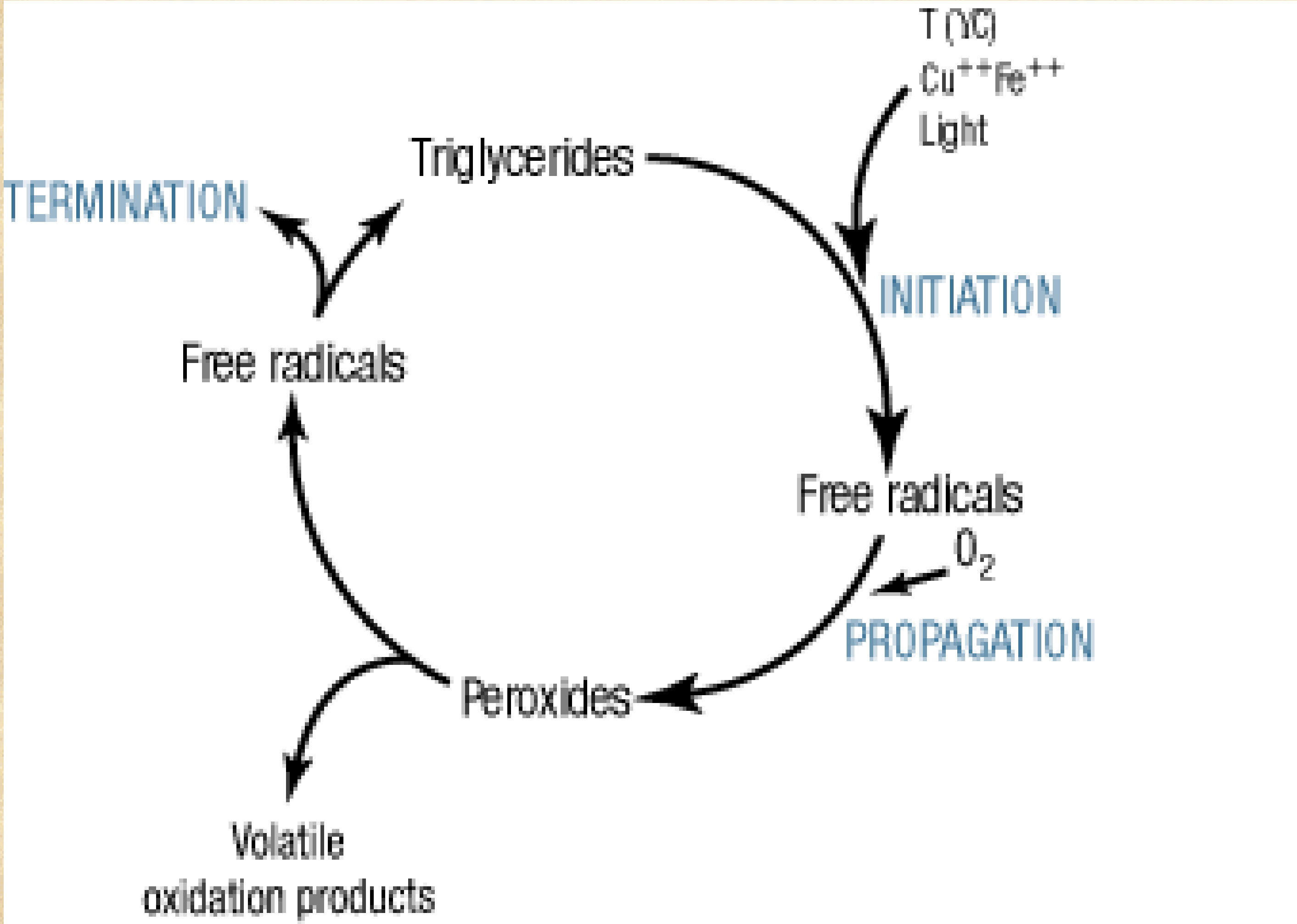
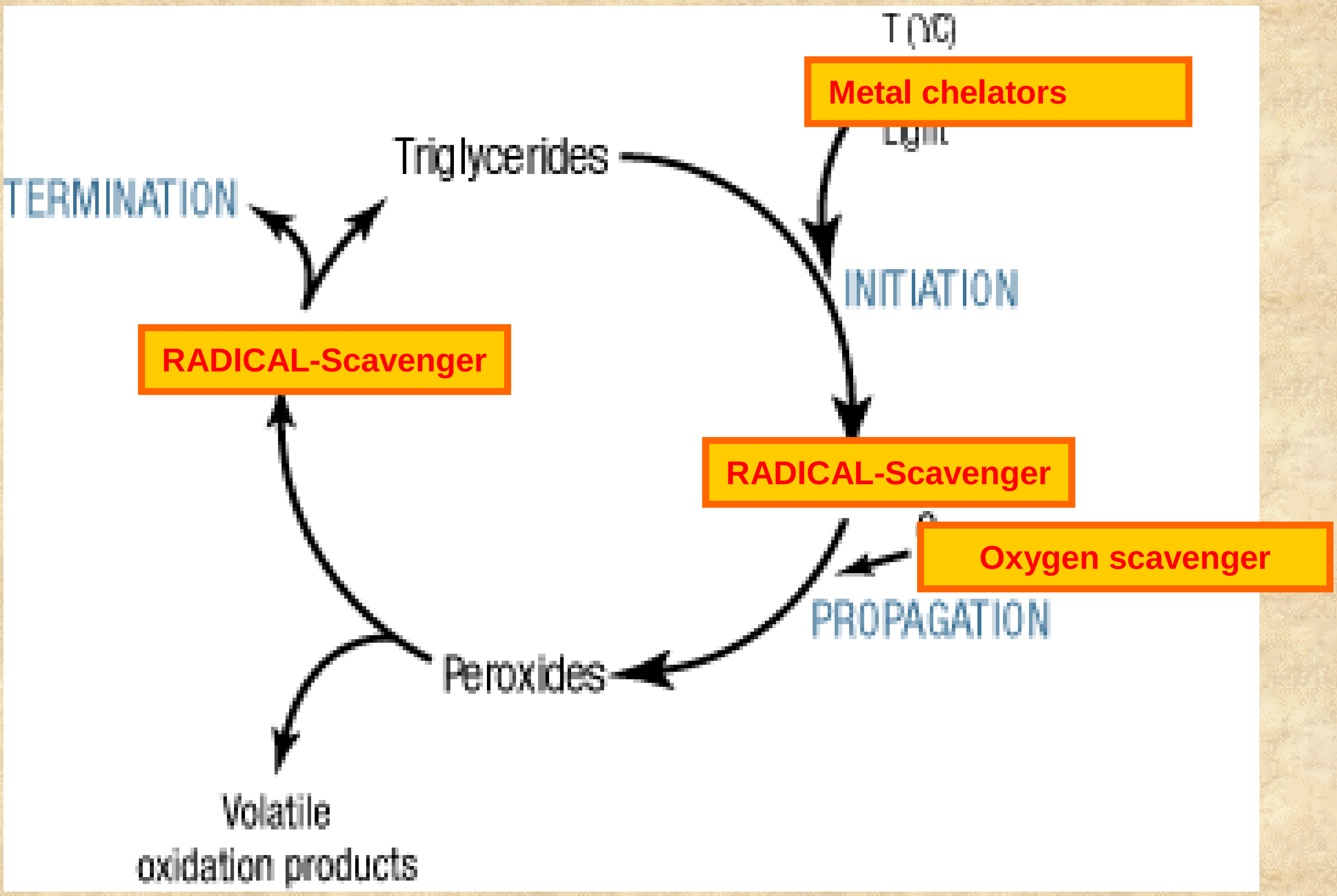
Cycle of lipid oxidation



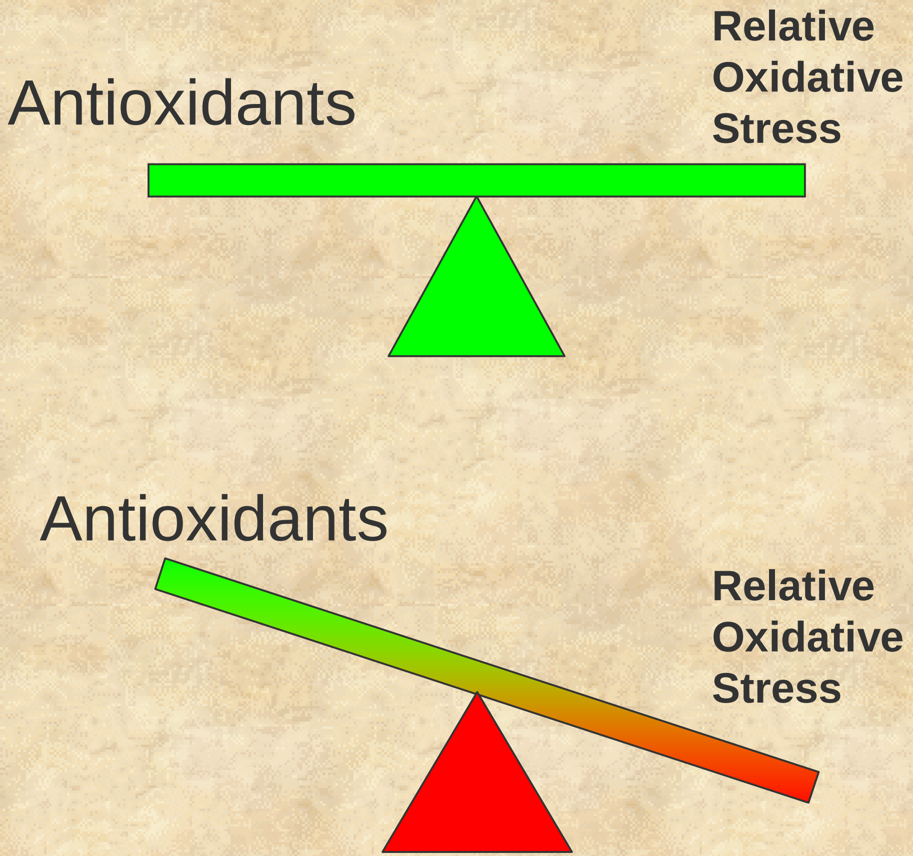
Cycle of lipid oxidation

Cycle of lipid oxidation



Balance antioxidants - radicals

In-vivo antioxidants
(e.g. α-tocopherol)
In-vitro antioxidants
BHA, BHT,…

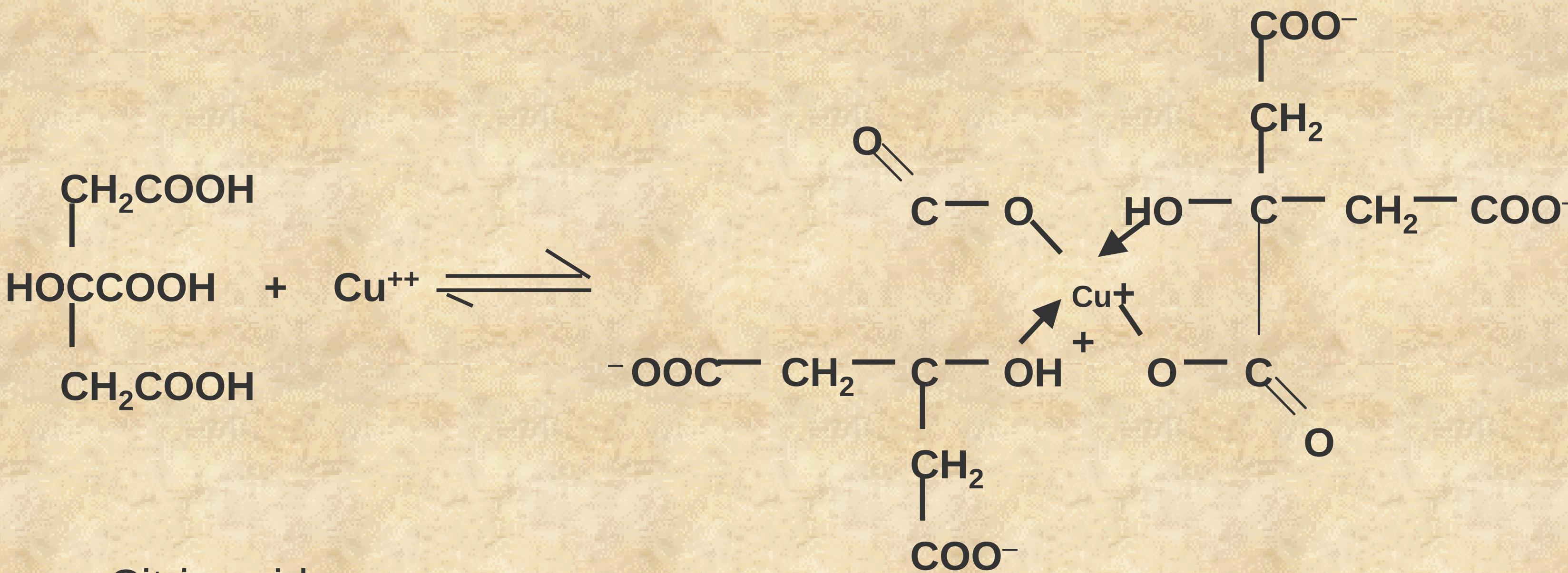


Types of antioxidants

- **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

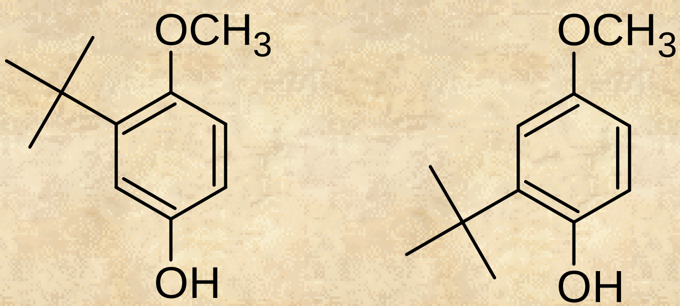
Metal chelators

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



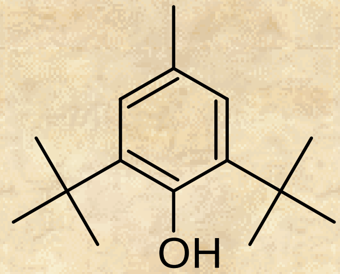
Citric acid

Radical Scavengers



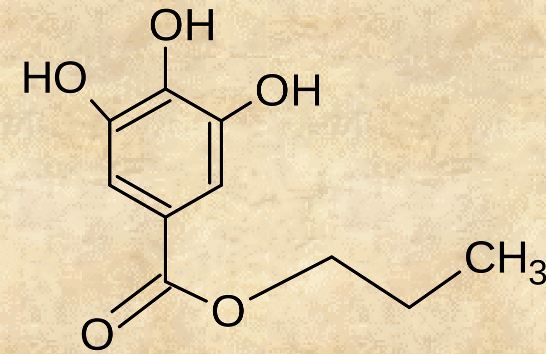
BHA

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



BHT

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



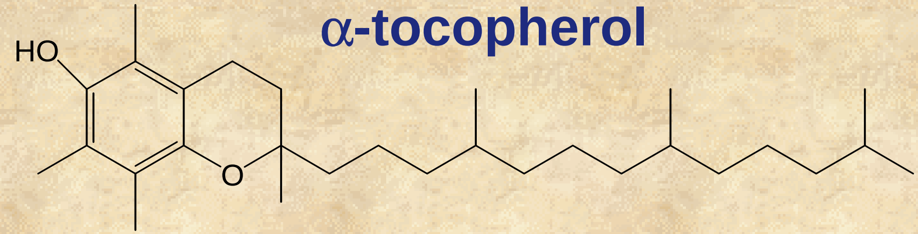
Propyl gallate

radical scavengers
“absorb” free radicals

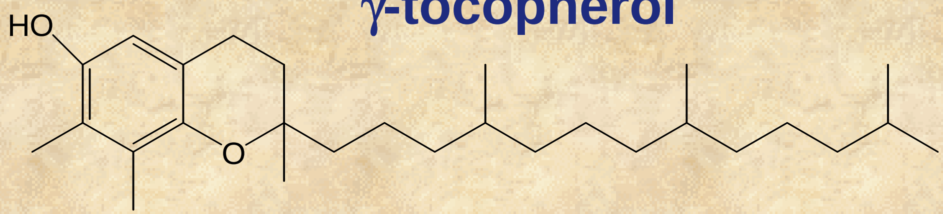
Tocopherols

Increasing antioxidant activity

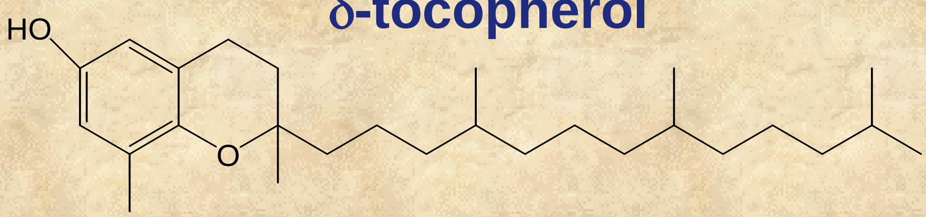
α-tocopherol



γ-tocopherol



δ-tocopherol



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

a	Total Gums/Phosphatides	b	Non-Hydratable Phosphatides
c	Free Fatty Acids	d	Oxidation Products
e	Iron/Metal Content	f	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**

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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)

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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

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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

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

Specifications may be added for moisture and secondary oxidation products

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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

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)

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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

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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

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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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