IUPAC-AOCS Workshop on Fats, Oils & Oilseeds Analyses & Production
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DEODORIZATION AND PHYSICAL REFINING

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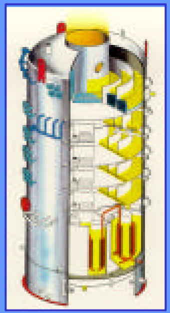
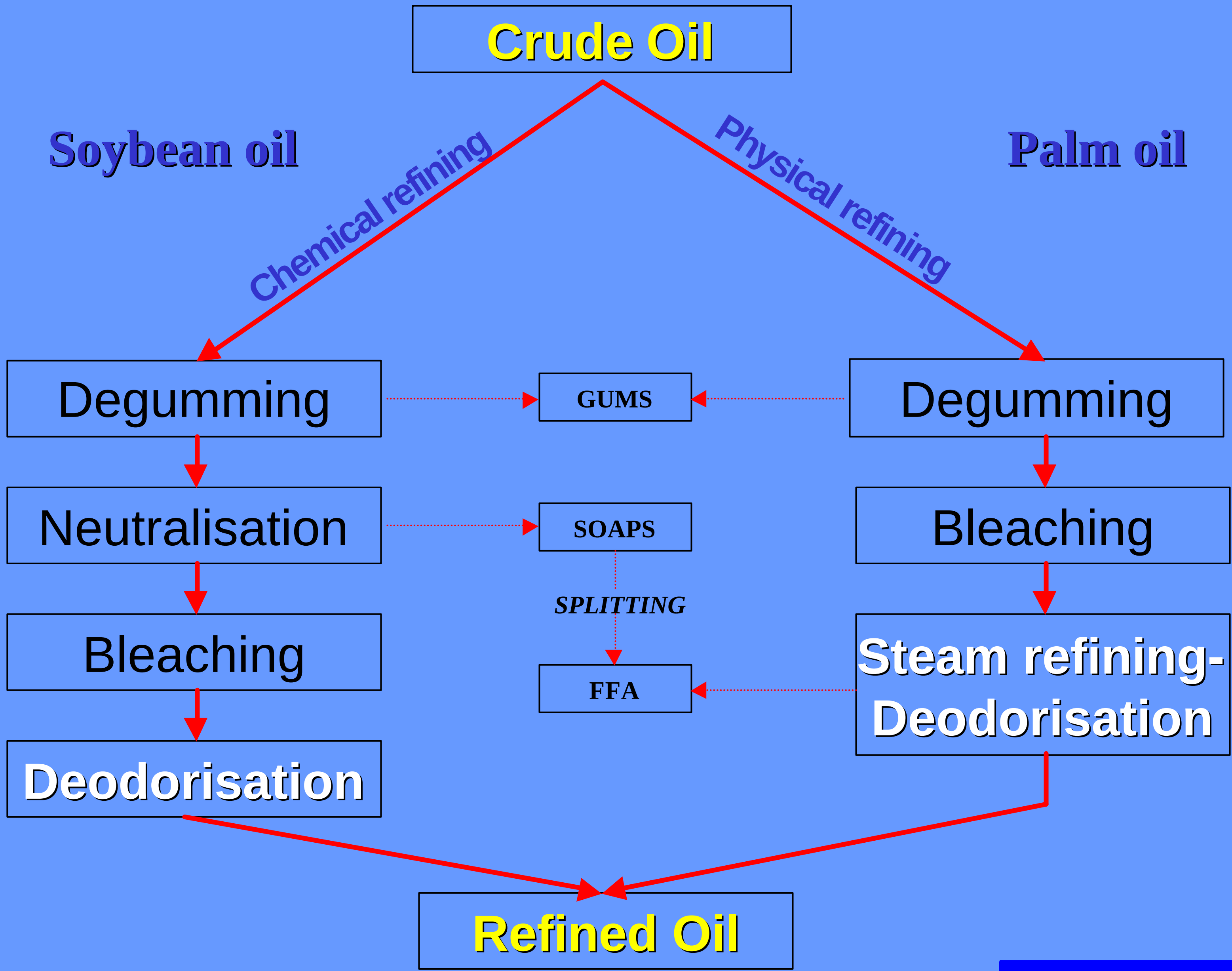
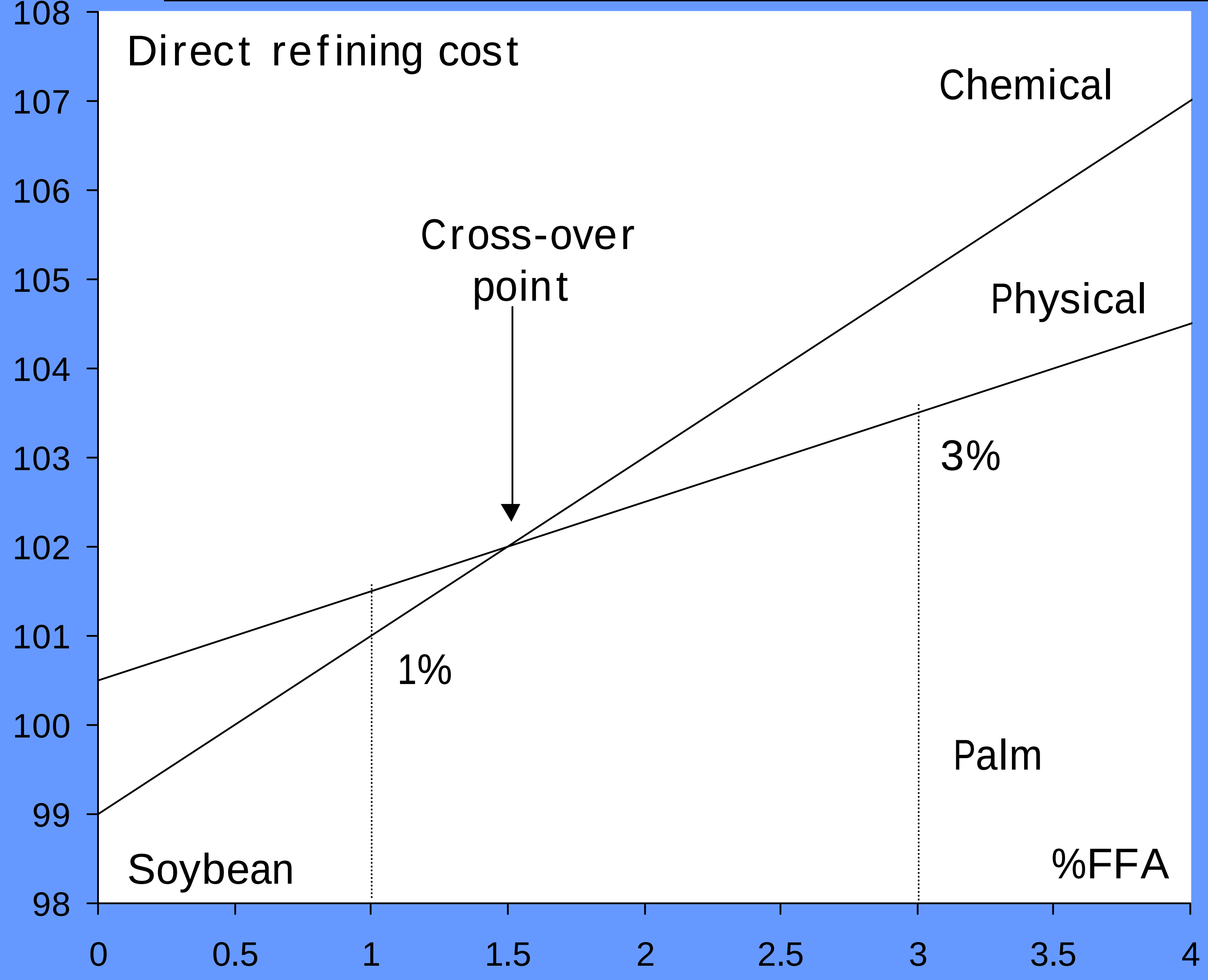
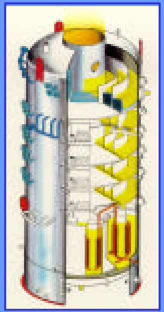




Crude Oil
Soybean oil
Palm oil
Chemical refining
Physical refining
Degumming
GUMS
Degumming
Neutralisation
SOAPS
Bleaching
SPLITTING
Bleaching
FFA
Steam refining-Deodorisation
Deodorisation
Refined Oil

Physical versus chemical refining

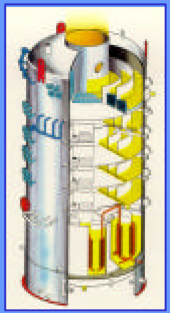




Deodorization conditions

Typical deodorization conditions

	Chemical Refining		Physical
Conditions	U.S.	Europe	Europe
Temperature (°C)	250-260	230-240	230-250
Pressure (mbar)	3-4	2-3	2
Sparge steam (%)	0.5-2.0	0.5-1.0	1-2
Time (min.)	20-40	40-60	60-90
Final FFA (%)	←	0.03-0.05	→



Deodorization principle

Stripping

FFA, volatile odoriferous components,

Valuable minor components (tocopherols,sterols,…..)

Contaminants (pesticides, light PAH, PCB, dioxins,…)

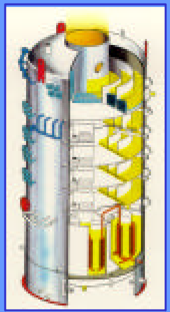
Odor and taste removal (actual Deodorization)

Hydrolytic/thermolytic degradation : f (steam/ time)

Temperature effect

Heat bleaching, *cis-trans* isomerisation,

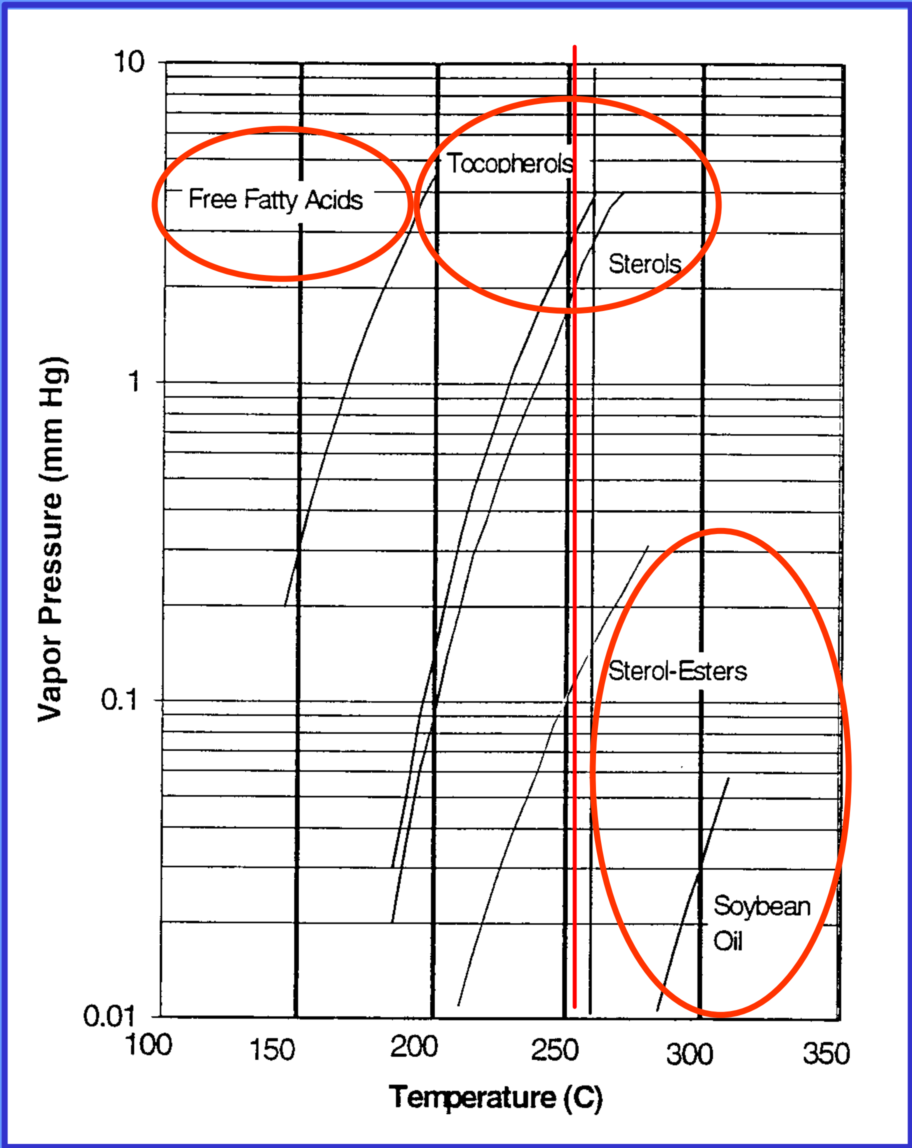
Polymerisation, interesterification,



Distillation-Determining Factors

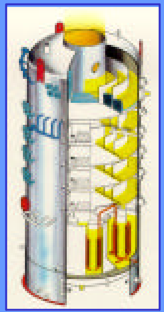
- **VOLATILITY of the components**
  - **Vapour pressure (at a given temperature)**
  - **General:heavier components are less volatile**
  - **FFA > Tocopherols > Sterols**
- **CONCENTRATION of the components**
  - **Partial pressure**
  - **Depends on vapour pressure and concentration**

Vapor pressure - temperature relationship for different components in oils



— 260ºC

Component	Mol. Weight	Relat. volatility
Fatty acid	280	2.5
Squalene	411	5
Tocopherol	415	1
Sterol	410	0.6
Sterol ester	675	0.04
Oil	885	<small>

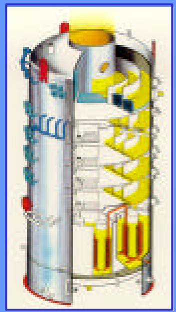


Stripping agent

- **Total pressure gas phase = S partial pressures**
  - **S partial pressures is low (mainly triglycerides)**
- **Distillation will only occur if :**
  - **S partial pressures > applied system pressure**

↓

Necessary to add stripping agent (steam, nitrogen)



Stripping agent

Required amount of stripping agent

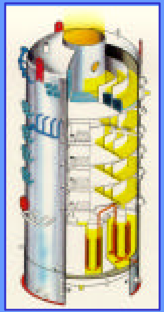
- directly proportional to its molecular weight
- low molecular weight is required (steam/nitrogen)

Nitrogen

- inert and non-condensable gas
- lower losses (no hydrolysis) and higher distillate quality
- more powerful vacuum system required
- profitability is very uncertain

Steam

- most 'evident' choice



Distillation

Simplified 'Bailey' Equation (initial FFA low)

$$S = \frac{P_t}{E.p_i^0}.\ln\frac{V_a}{V_0}$$

S = Total Moles of steam

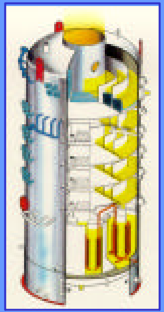
P_t = Total deodorization pressure

p_i^o = Vapour pressure of a given volatile component

V_a = Initial molar concentration of the component

V_o = Final molar concentration of the component

E = Vaporization efficiency



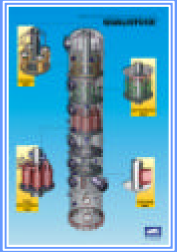
Stripping

$$S = \frac{P_t}{E.p_i^0}.\ln\frac{V_a}{V_0}$$

- Impossible to eliminate all volatile components

($V_0 = 0$ would require an infinite amount of steam)

- Halving the concentration of a given volatile requires same amount of steam irrespective of its absolute level



Refined Oil Quality

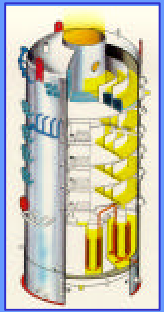
- Deodorization is a crucial refining stage
- Deodorizer design and process conditions have a determining effect on the refined oil quality
- Control of 'unwanted' and 'desired' effects :

- *trans* fatty acid formation
- positional isomerisation of PUFA
- polymerisation (dimers)

unwanted

- controlled stripping of tocopherols, sterols
- complete stripping of contaminants

desired



Trans Fatty Acids

- Unsaturated fatty acids with one or more double bond in *trans* configuration

- Structure similar to saturated fatty acids

  - Higher melting point than *cis* isomers

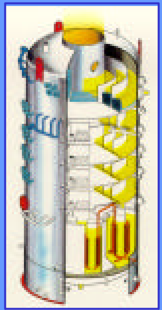
  - Negative nutritional properties : unwanted in food fats

- Renewed interest because of stricter legislation

  - *trans* labelling in USA from 2006

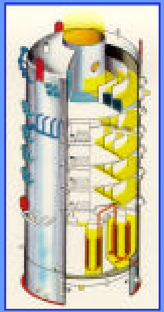
  - very strict Danish regulation : max. 2% in food fats

  - Canada considers to adopt same regulation



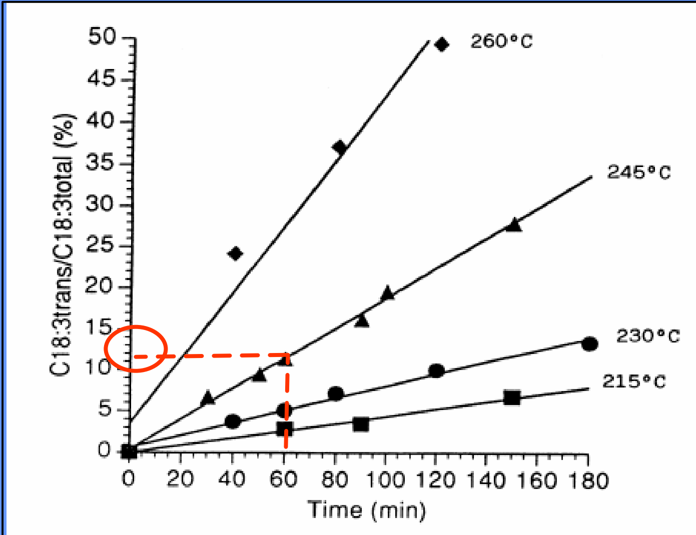
Trans Fatty Acids

- **Mainly formed during partial hydrogenation**
  - **- depending on hydrogenation process conditions**
  - **- typical levels : 10-50% (high in Cocoa Butter Replacers)**
- ***Trans* formation during bleaching**
  - **- 0.1-0.2% *trans* formation with acid activated BE**
- **Deodorisation**
  - **- % *trans* = f (time, temperature)**
  - **- T > 220°C detectable; T > 250°C exponential**
  - **- No significant influence of sparge steam and pressure**

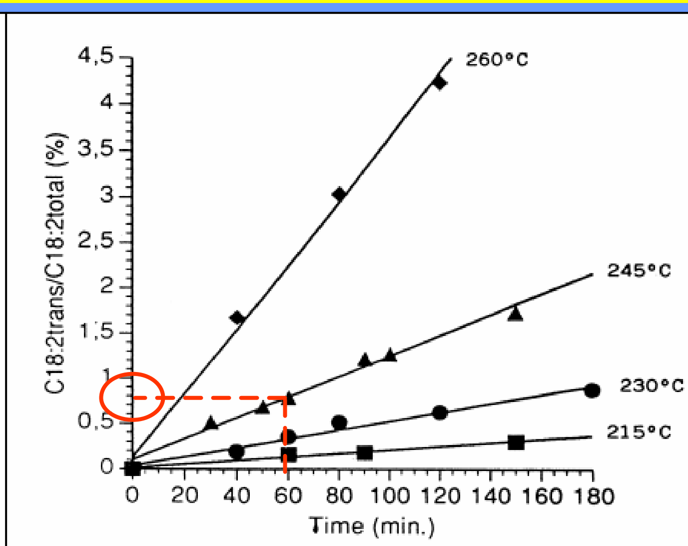


Trans Fatty Acids

Degree of isomerization (DI) $DI_{18:x} = \frac{C18:xtrans}{C18:x(cis+trans)} \cdot 100$



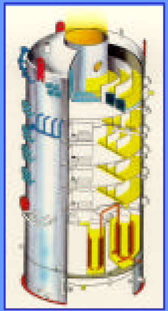
relative trans-isomerisation of C18:3



relative trans-isomerisation of C18:2

General rule : TFA= 10% of C18:3 + 1% of C18:2

For C18:3 rich oils : max. TFA = 1%; for other oils : max. TFA = 0.5%



Tocopherols

Losses during bleaching

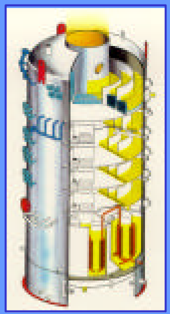
- Limited degradation (5-10%)
- Affected mostly by type and amount of BE

Losses deodorisation/deacidification

- Higher ‘losses’ possible (15.....> 60%)
- Tocopherol removal = f (steam, temp., pressure)

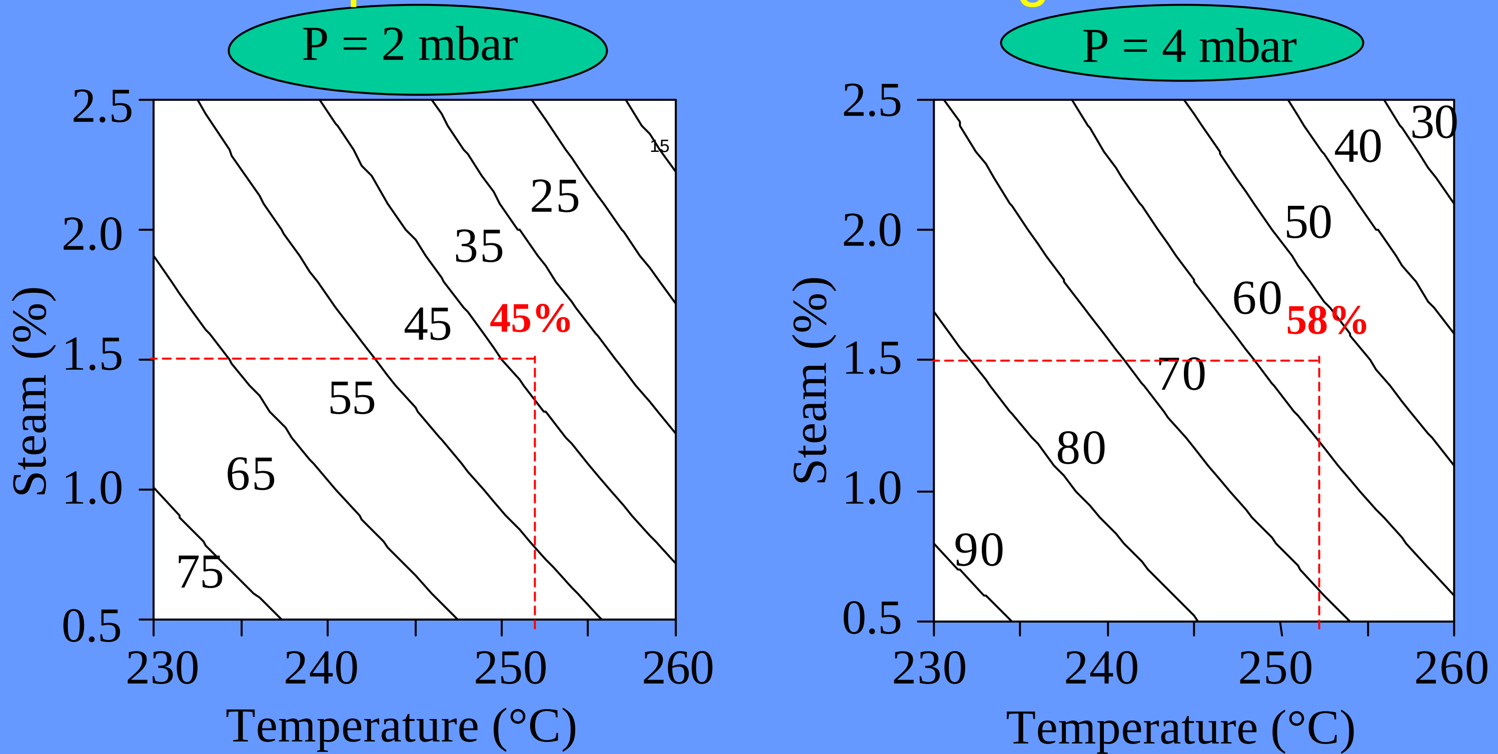
Distillation ⟷ Thermal breakdown

⟷ Oxidation

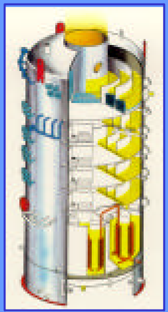


Controlled tocopherol stripping

Relative tocopherol **retention** during deodorization



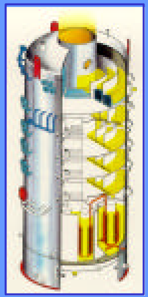
Higher retention/more stripping at higher P, lower T and less steam



Contaminant removal

- Adsorption on specific adsorbens (activated carbon)
  - **Heavy polycyclic aromatic hydrocarbons**
  - **Dioxins and furans from Fish Oils**
  - **PCB (only partially, less efficient than dioxins)**

- Deodorization (only 'volatile' contaminants)
  - **Pesticides (organo-chlorine)**
  - **Light polycyclic aromatic hydrocarbons (coconut oil)**
  - **PCB,dioxins, brominated flame retardants (fish oil)**



Pesticides

– *Today*

* Contamination usually below limit of detection (20-50 ppb)

* Occasionally : 1-2 ppm (improper post-harvest treatment)

– Efficient removal during deodorization *if*

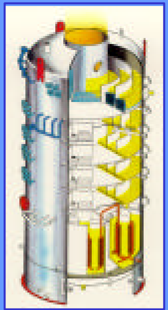
T >230°C, p< 4 mbar and steam > 1%

Distillation

Thermal decomposition

Pesticides can be removed efficiently during deodorization

→ Monitoring at regular intervals remains necessary (especially for *mild refined* oils)



PAH Removal during Refining

- *Heavy PAH*

  * Adsorption on activated carbon

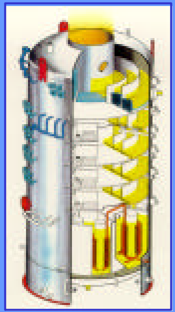
  * 0.1-0.4% added together with bleaching earth or separately

- *Light PAH*

  * Stripped under conventionally applied deodorizer conditions

  T >220°C, p <4 mbar and steam > 1%

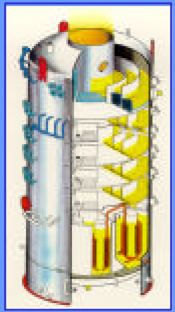
→ Levels > 25 ppb can still be detected in refined oils in case of highly contaminated crude oils



Deodorization Technology

Process stages

- Oil deaeration → Prevention oxidation
- Heating → Heat recovery
  Final heating
- Deodorization → Deacidification
  Injection of stripping steam
  Low pressure (vacuum)
  Condensation of volatiles
- Cooling → Heat recovery
  final cooling
- Polish filtration + AO dosing



Heating

Two stage process

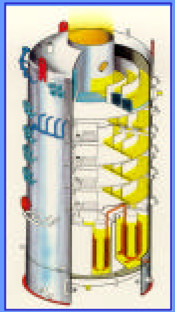
- preheating followed by final heating

Preheating

- heat recovery step
- oil/oil heat exchanger (incoming oil/finished oil)

Final heating

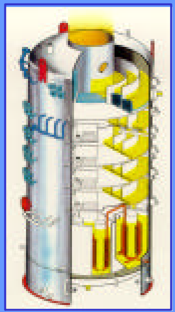
- High pressure steam (most used & recommended today)
- Thermal oil (avoided for food safety reasons)
- Electrical heating (rarely used)



Heating

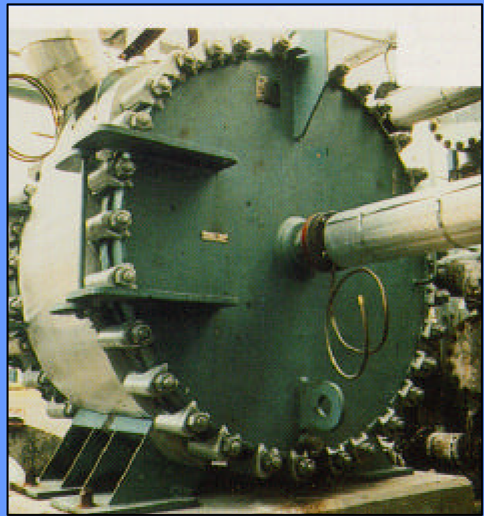
Temperature of high pressure steam

Pressure (bar)	Steam temperature (°C)	Latent heat (kJ/kg)	Specific volume (m^3/kg)
1	99.6	2258	1,694
2	120.2	2202	0,8853
3	133.5	2163	0,6056
5	151.8	2108	0,3747
7	164.9	2065	0,2762
10	179.9	2014	0,1943
15	198.3	1945	0,1316
20	212.4	1889	0,09952
30	233.8	1794	0,06663
40	250.3	1713	0,04975
50	263.9	1640	0,03943

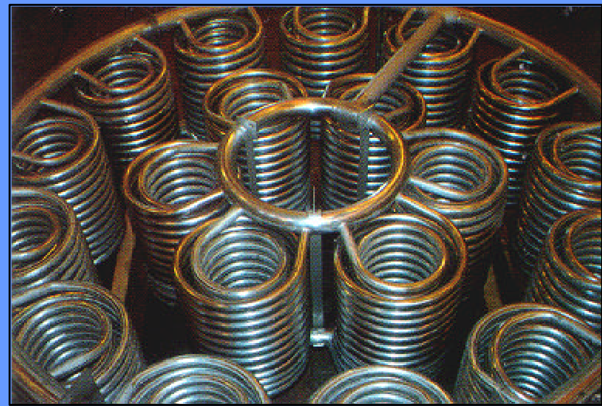


Heat recovery

plate



spiral



oil-steam heat exchanger

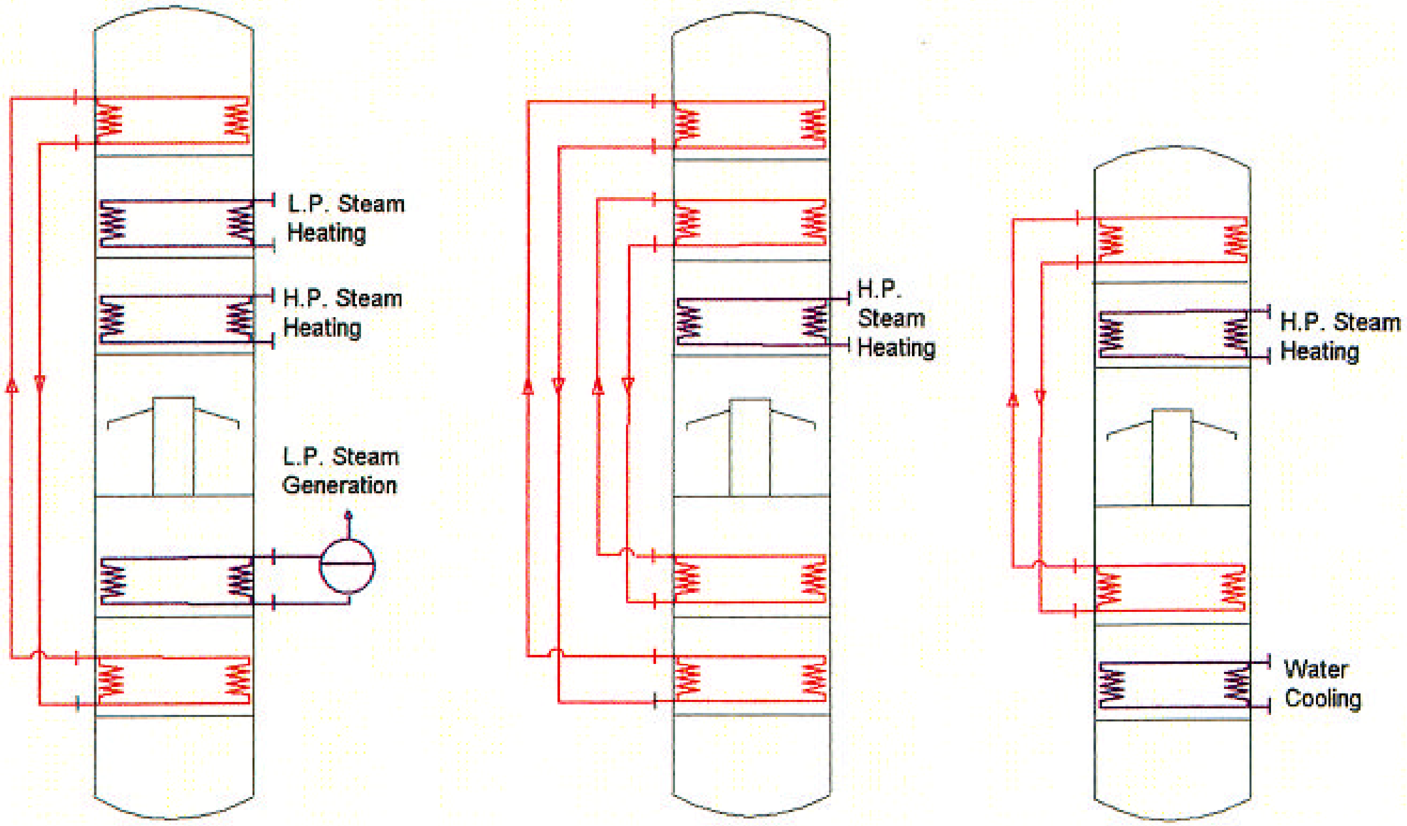
Internal heat exchangers

shell & tube

oil-oil heat exchanger

External heat exchanger

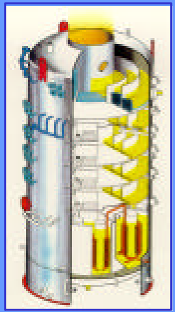
Heat recovery : Thermosyphon



L.P. Steam Generation &
Thermosyphon
Heat Recovery 75%

Double Thermosyphon
Heat Recovery 67%

Single Thermosyphon
Heat Recovery 45%



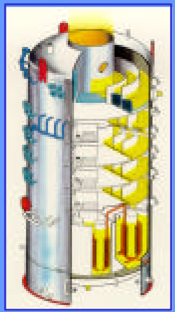
Vaporization efficiency

Steam distribution

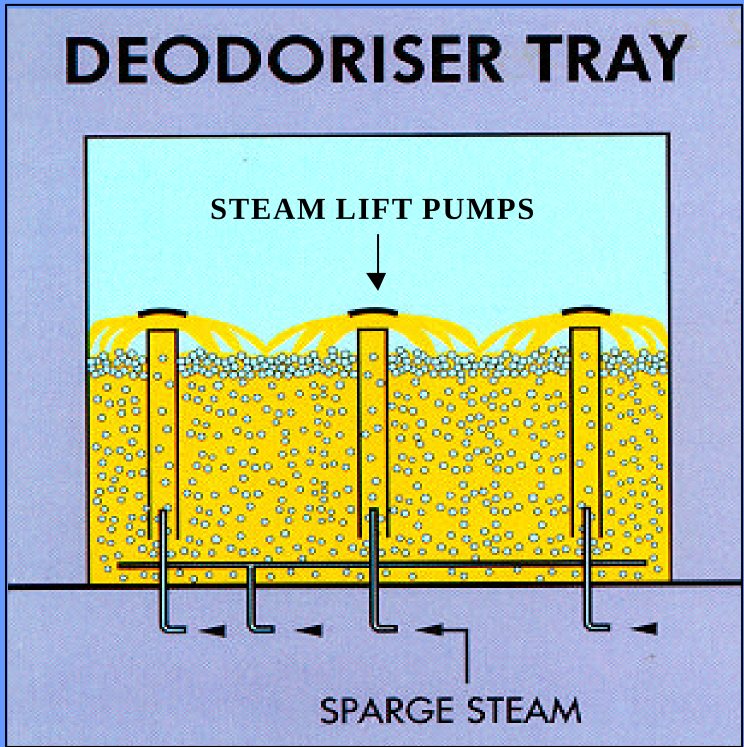
- sparge coils with very fine holes (Ø = 0.5-2.5 mm)
- steam lift pumps

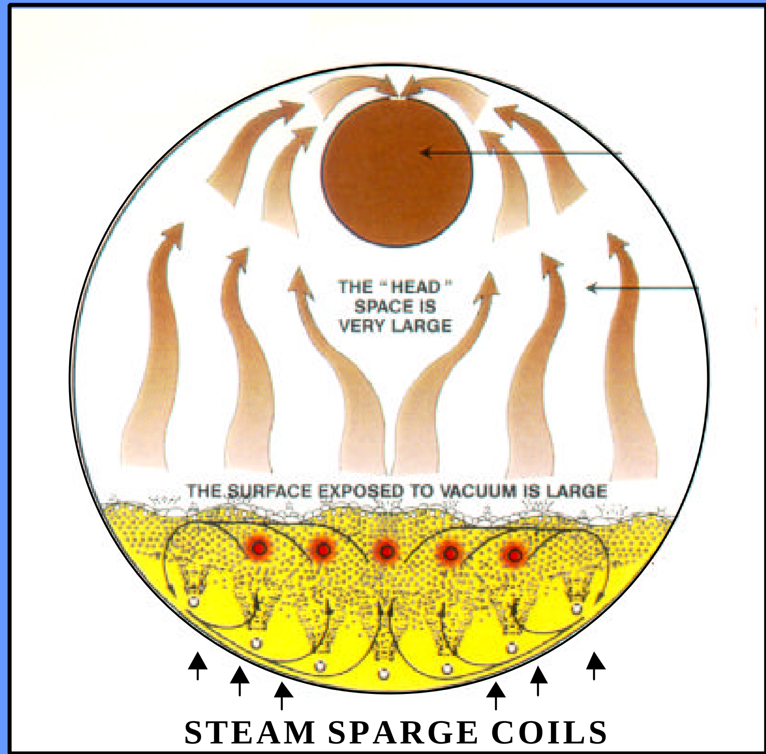
Deodorizer design

- Deep bed deodorizer (steam lift pumps)
- Shallow bed deodorizer (sparge coils)
- Continuous refreshing of the oil at vapor-liquid contact zone (lowest pressure)



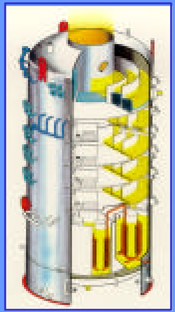
Deodorizer design





Deep bed deodoriser

Shallow bed deodoriser



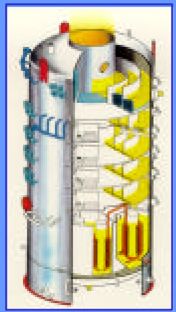
Vapor scrubbing system

Composition of vapor phase

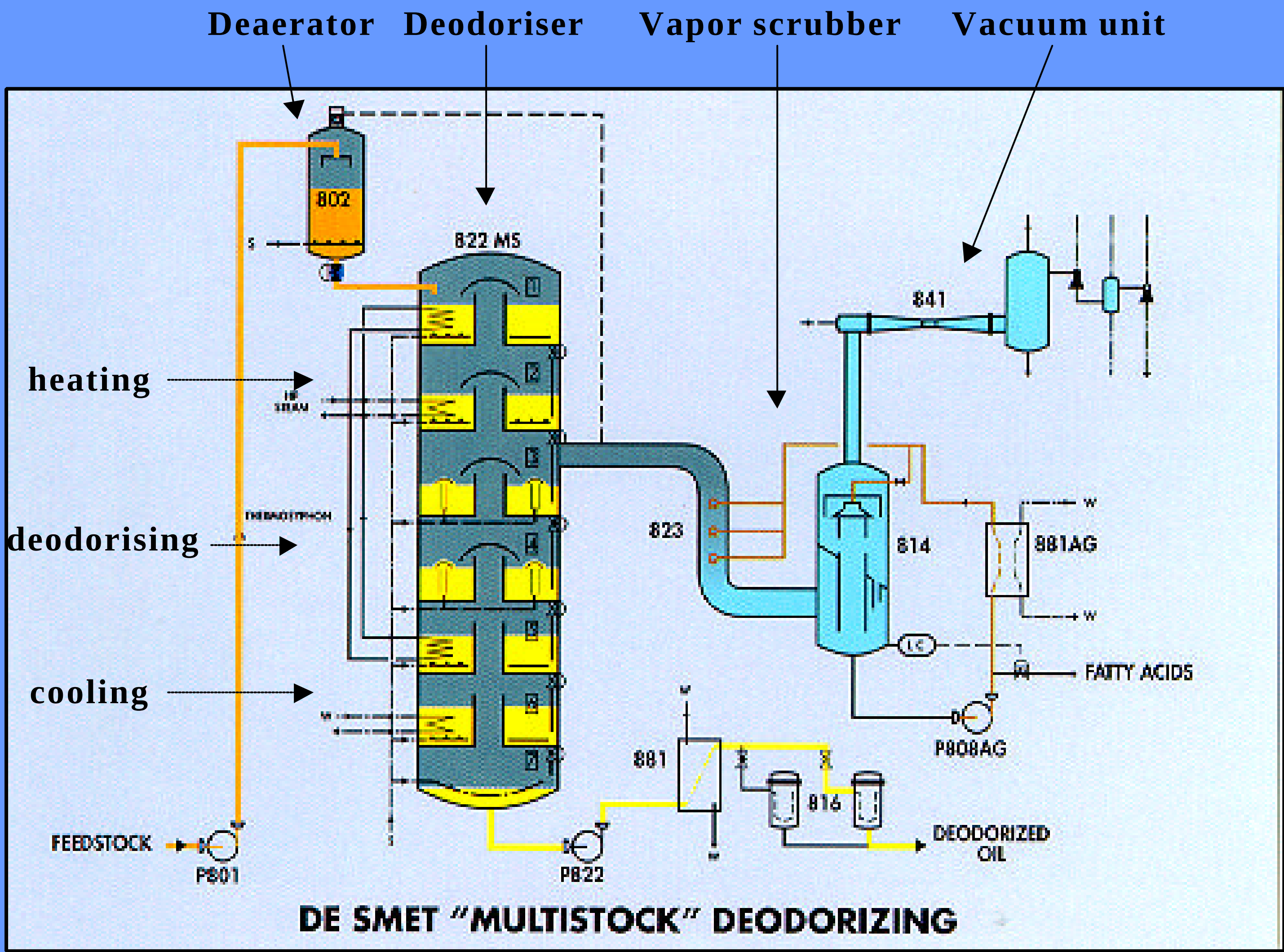
- Volatile components (FFA, odor components)
- Stripping steam
- Non condensable gases (air,...)

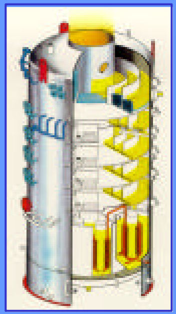
Condensation of volatile components

- intimate contact between vapor and recirculating distillate
- series of sprayers or packed bed in vacuum duct
- Distillate is recirculating at the lowest possible temp.
- Installation of demister at the top
- Designed to have a minimal pressure drop



Vapor scrubbing system



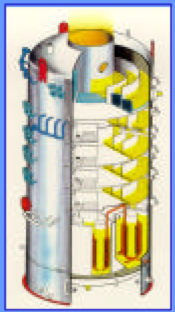


Deodorizer distillates

Composition of industrial deodorizer distillates

	Soybean		Corn	Sunflower	
Component	chemical	physical	physical	chemical	physical
Squalene (%)	1-2	0.5	0.5-1.0	0.5	0.5
Tocopherols (%)	16-20	5-7	2-4	5-7	1-2
Sterols (%)	19-23	11	3-6	12-14	4-5
Triglycerides (%)	5-6	4	1-2	2-3	1-2
FFA (%)	33	75	77-81	39	70

Concentration of contaminants (pesticides, PAH)



Vacuum systems

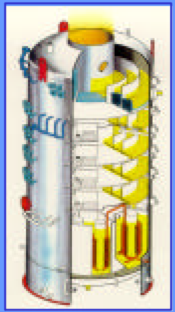
Conventional vacuum system

- Combination of steam jet ejectors (boosters), vapor condensers and mechanical (liquid-ring) vacuum pump

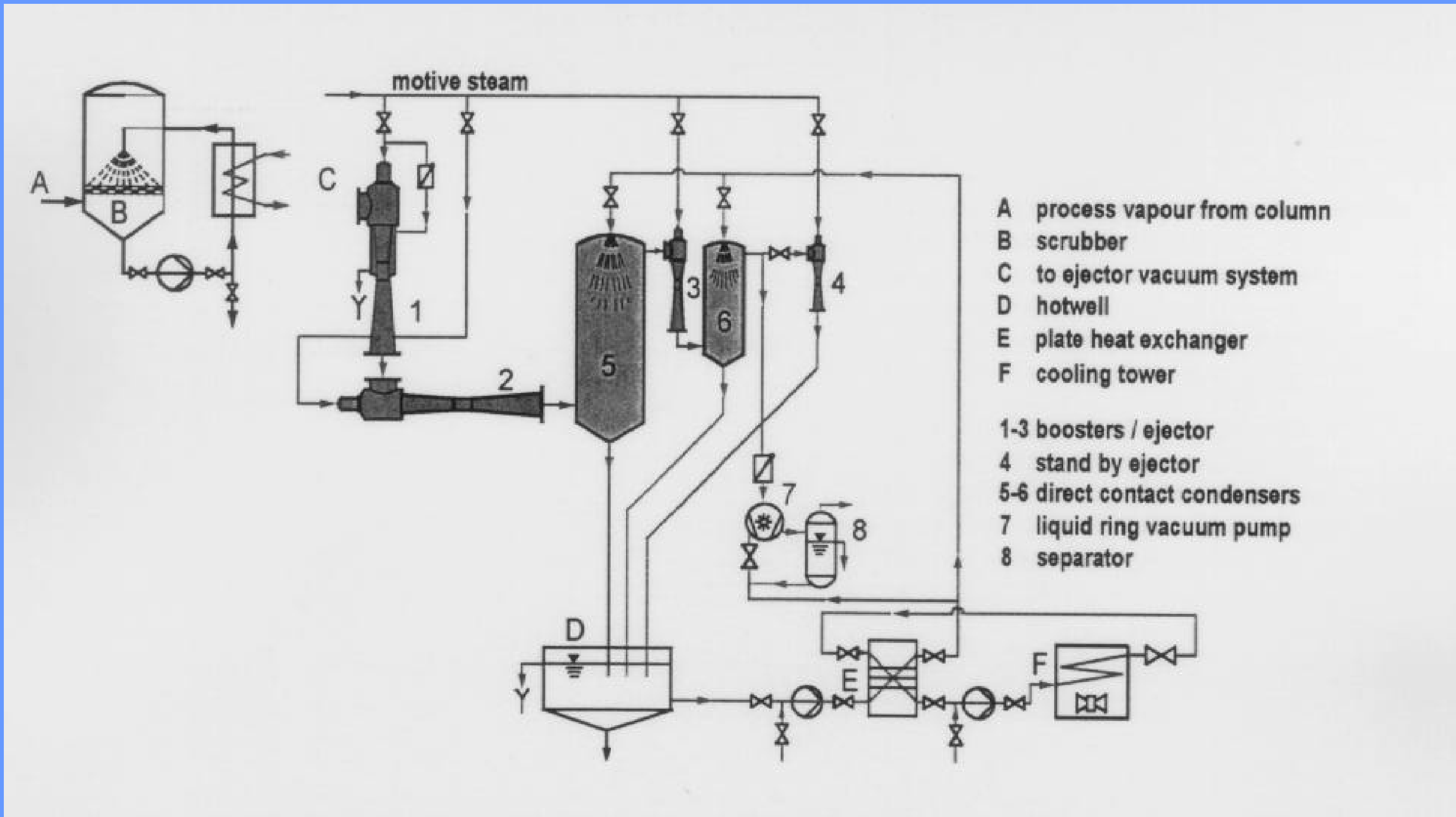
- High motive steam consumption (60-85% of total steam)

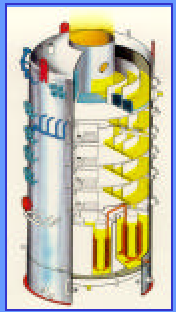
Pressure		**kg motive steam per kg strippng steam**	
Booster	**Deodorizer**	**30°C (1)**	**10°C (2)**
2.5	**3** mbar	4.5	1.6
1.5	**2** mbar	6.2	2.5

Note: (1) Barometric condenser water inlet temperature: 24°C; outlet temperature: 30°C
(2) Barometric condenser water inlet temperature: 5°C; outlet temperature: 10°C;



Vacuum systems

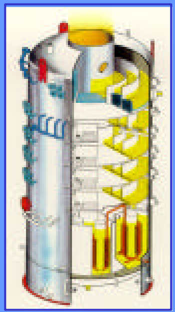




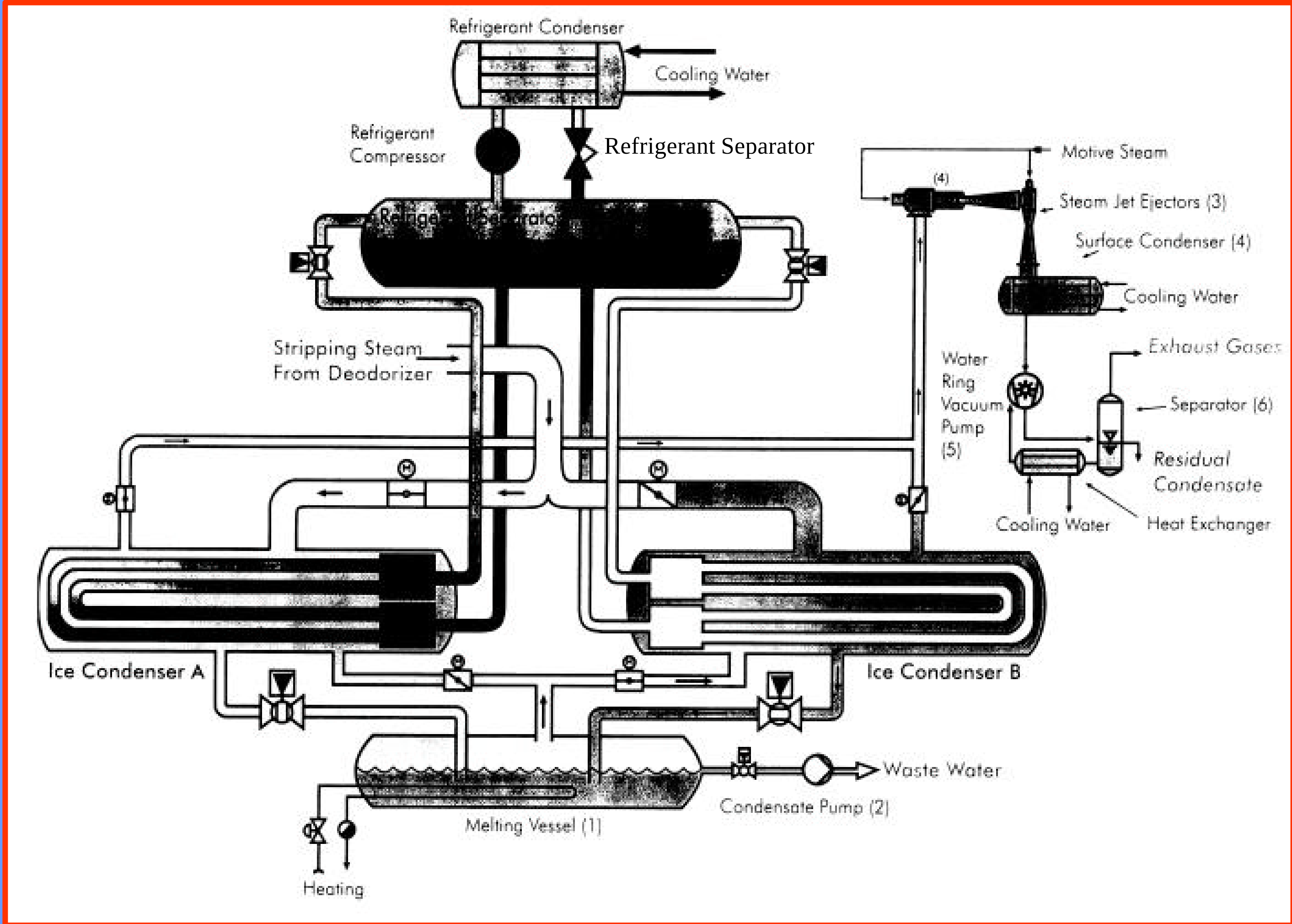
Dry condensing – Ice condensing

- Sublimation of steam (into ice) on surface condensers
- Low pressure can be reached (< 2 mbar in deodorizer)
- Strongly reduced odor emission
- Nearly no motive steam but higher electricity consumption
- Higher investment cost (compared to boosters)
- Operating cost (and ROI) will depend on ratio between cost of steam and electricity

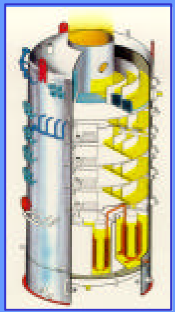
→ Generally shorter ROI in Europe

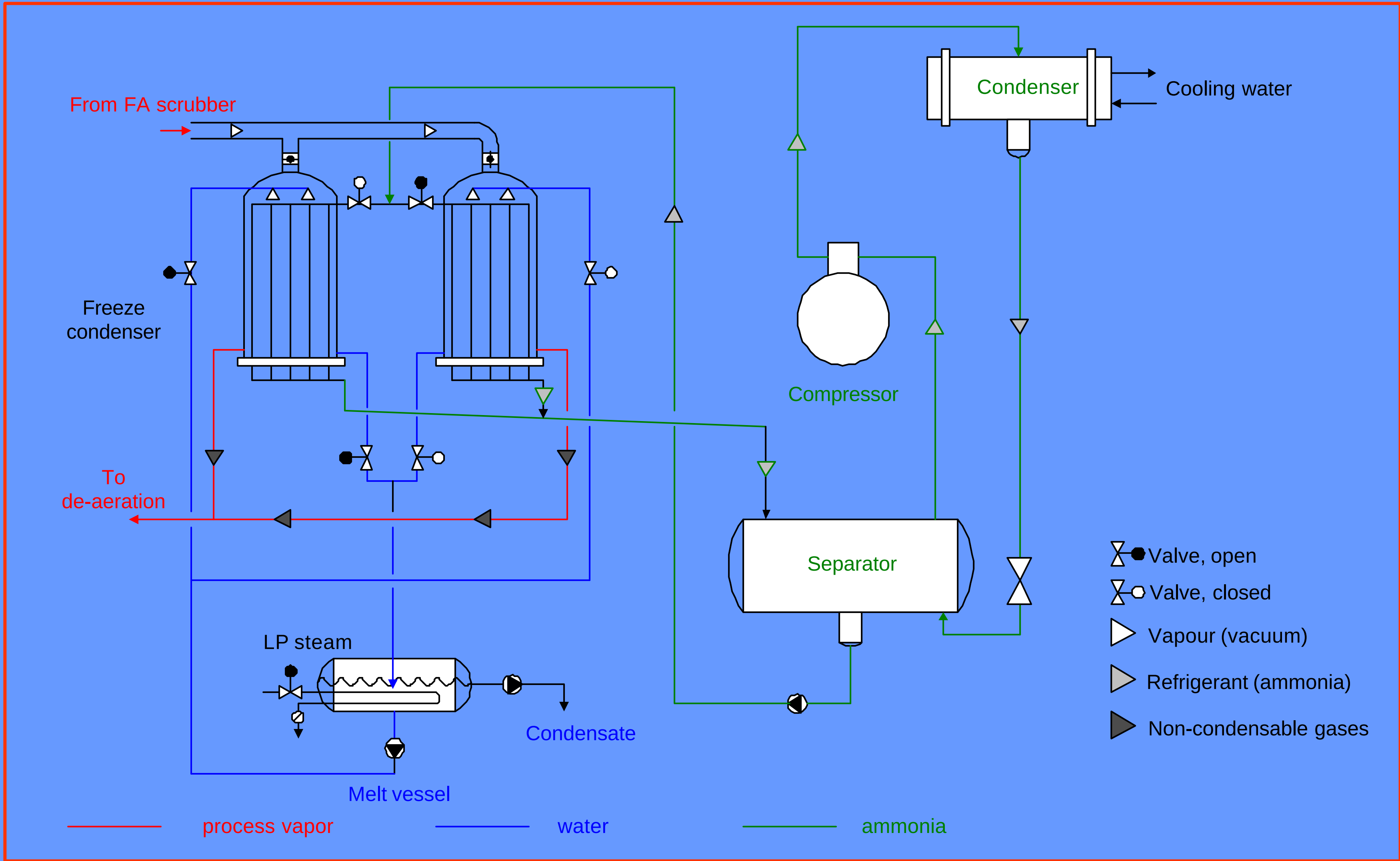


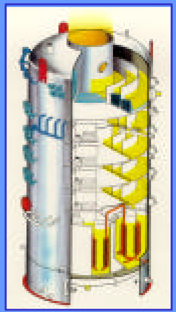
Dry condensing vacuum system with horizontal condensers



Dry Condensation Systems with vertical condensers







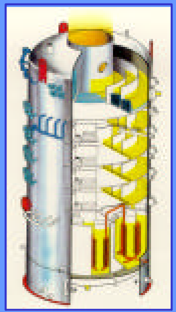
Deodorizer design

Batch deodorization

Continuous deodorization

- Horizontal deodorizer
- Single vessel vertical deodorizer
- Packed column technology

Semi-continuous deodorization

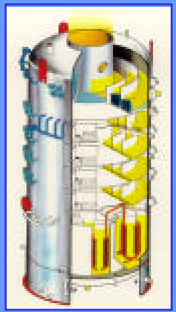


Continuous Deodorization

Limited feedstock changes

Advantages → Low utilities cost (high heat recovery)
→ Short residence time
→ Excellent control of all parameters

Disadvantage → Contamination during feedstock change



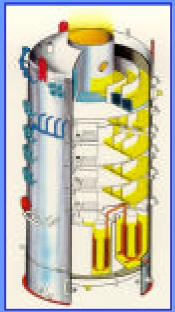
Continuous Deodorization

Continuous deodorizer types

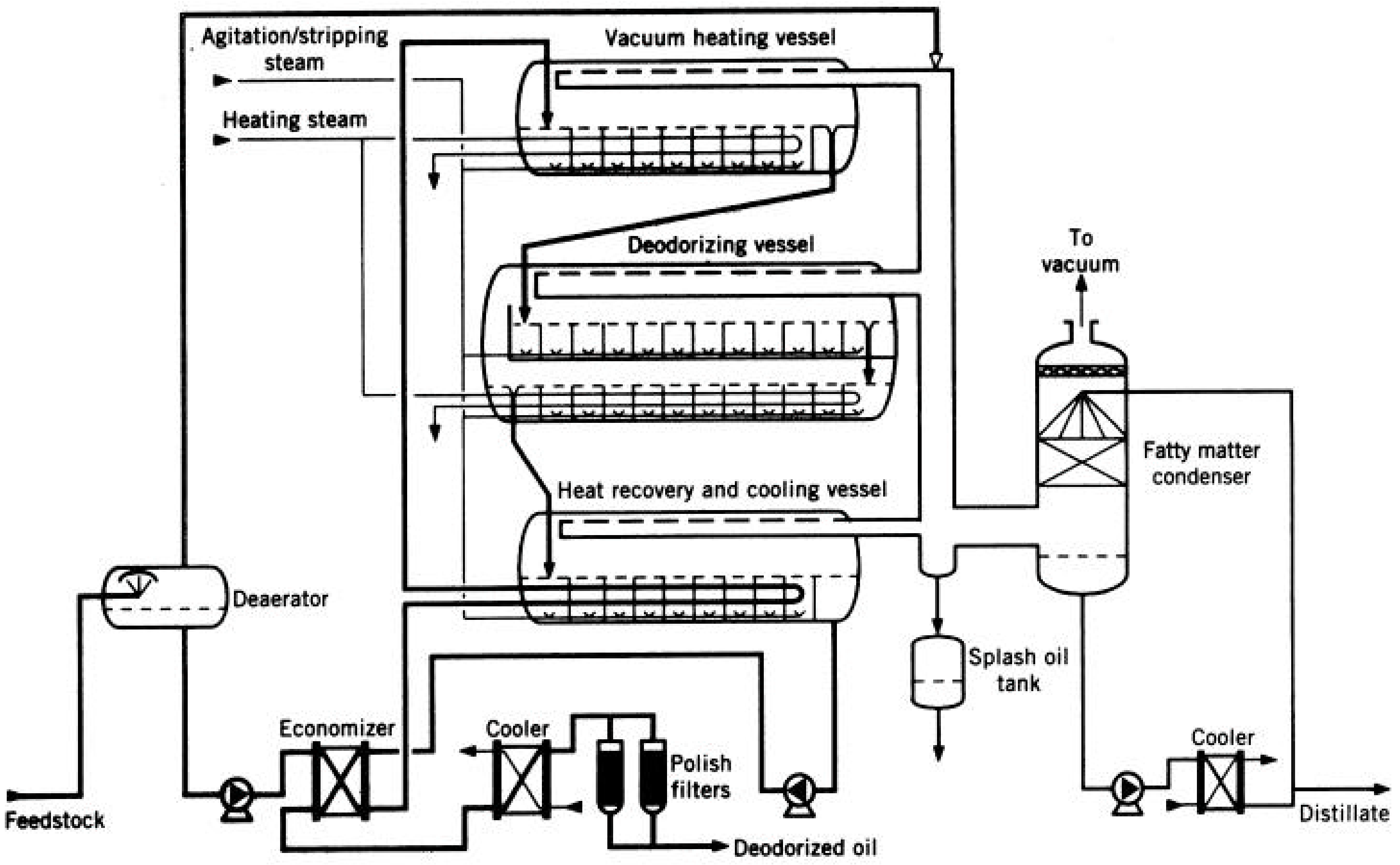
- Horizontal multi-vessel deodorizer

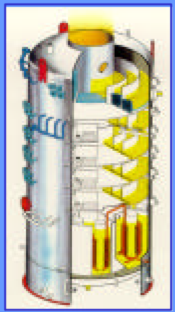
- Vertical deodorizer → most common
  - ↳ all operations integrated in single vessel

- Thin film deodorizer → packed column + retention vessel

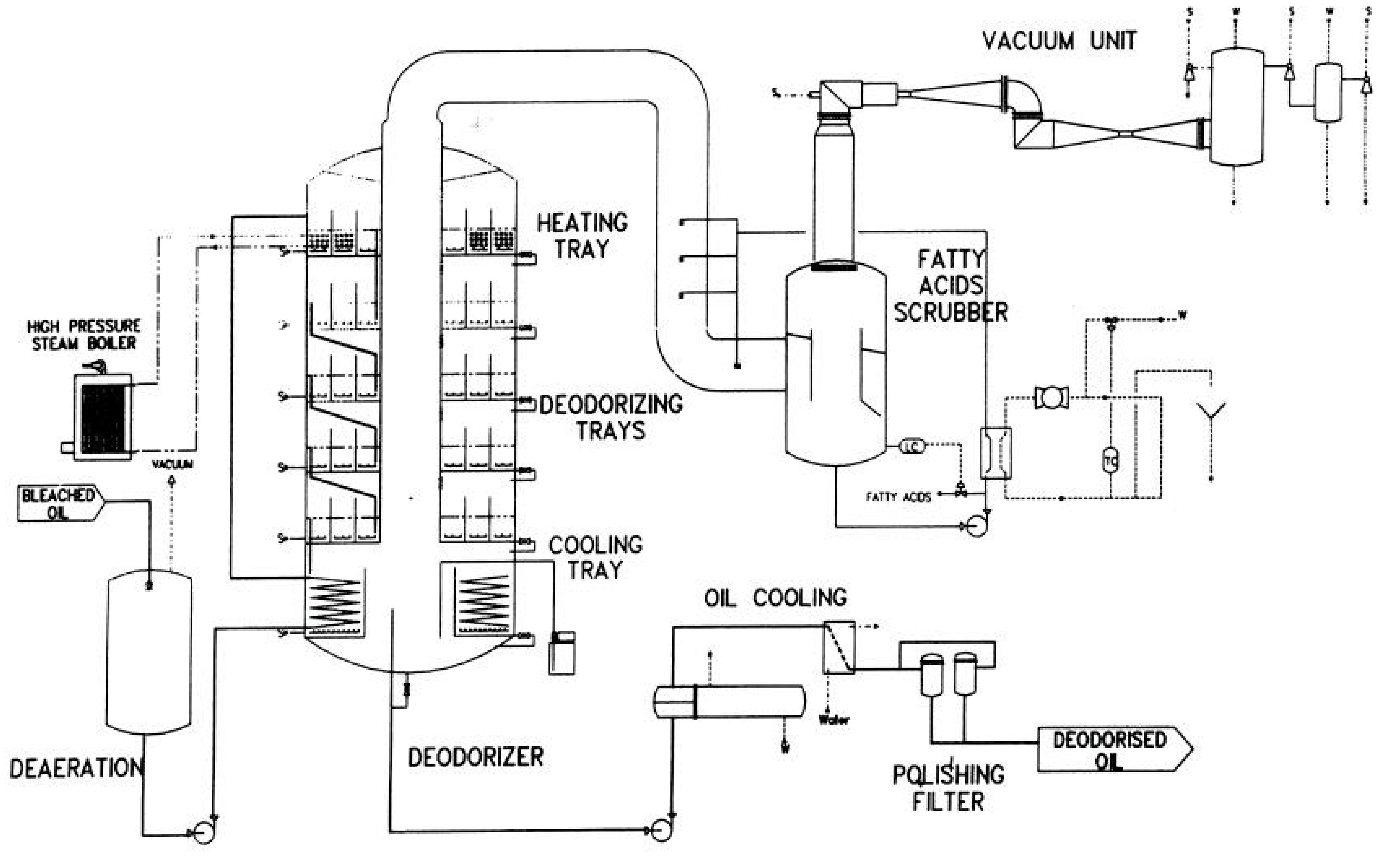


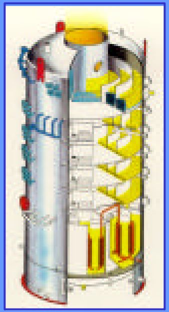
Continuous horizontal multi-vessel deodoriser



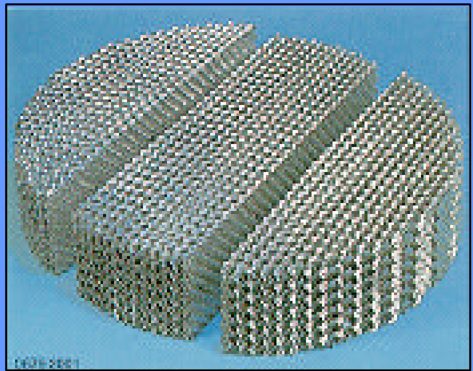


CONTINUOUS DEODORIZING PROCESS

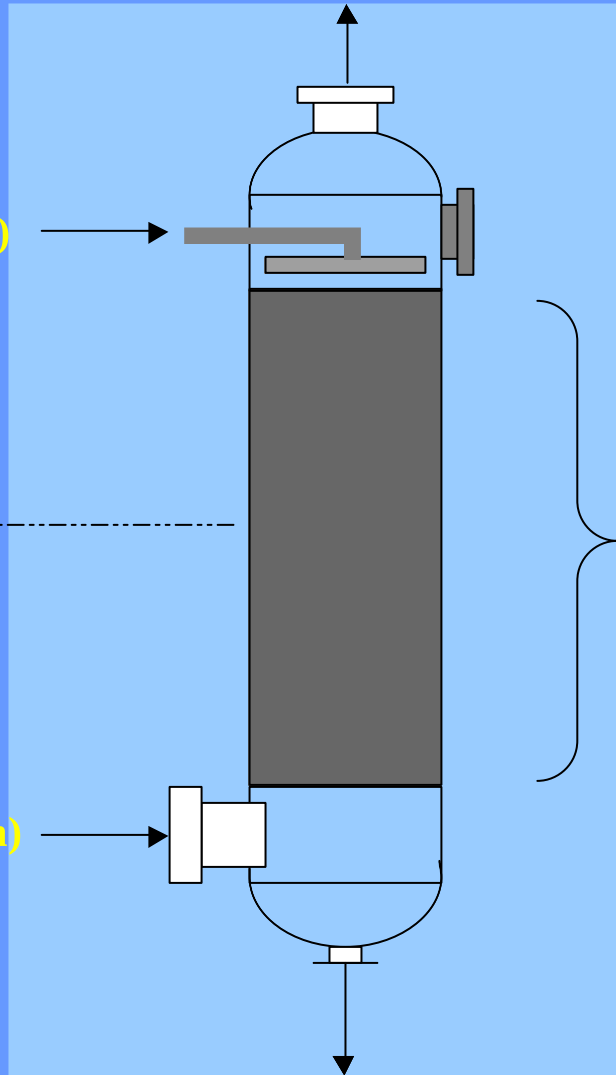




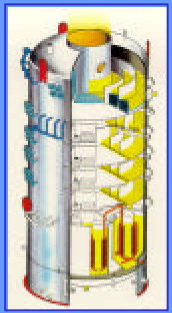
Packed column stripper



Structured packing



$$F = V_{vap} * \sqrt{r} * A$$



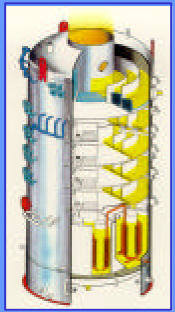
PACKED COLUMN TECHNOLOGY

- **Specific Process conditions**

  - **Structured packing : 100 - 300 m^2/m^3**
  - **Efficient stripping : Counter-current contact oil/steam**
  - **Short residence time : Few minutes at high temperature**

- Applications

  - **Stripping of valuable minor components or contaminants from heat sensitive oils**
  - **Preferably only in continuous operation**
  - **No deodoriser (too short residence time)**



Future challenges in deodorization

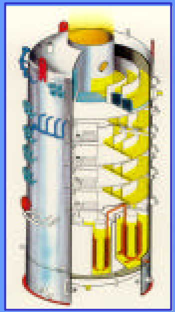
Lower 'heat load'

- Low *trans* and polymer formation
- No positional isomerisation of PUFA
- Preservation of natural character (color, aroma,…)

combined with

Efficient and controlled stripping

- Controlled stripping of tocopherols and sterols
- Complete removal of contaminants



Improved Deodorization Technology

- Dual temperature deodorization

  - Deodorization at two different temperatures

- Integration of packed columns

  - for specific application only
  - efficient stripping - lower steam consumption

- Dual condensation

  - Condensation at two different temperatures
  - Higher added value of deodorizer distillate (physical refining)

- Dry-Ice condensing

  - Lower deodorizing pressure (1 mbar)
  - Allows milder refining (lower temp)


Thank you for your attention