Hydrocarbon processing

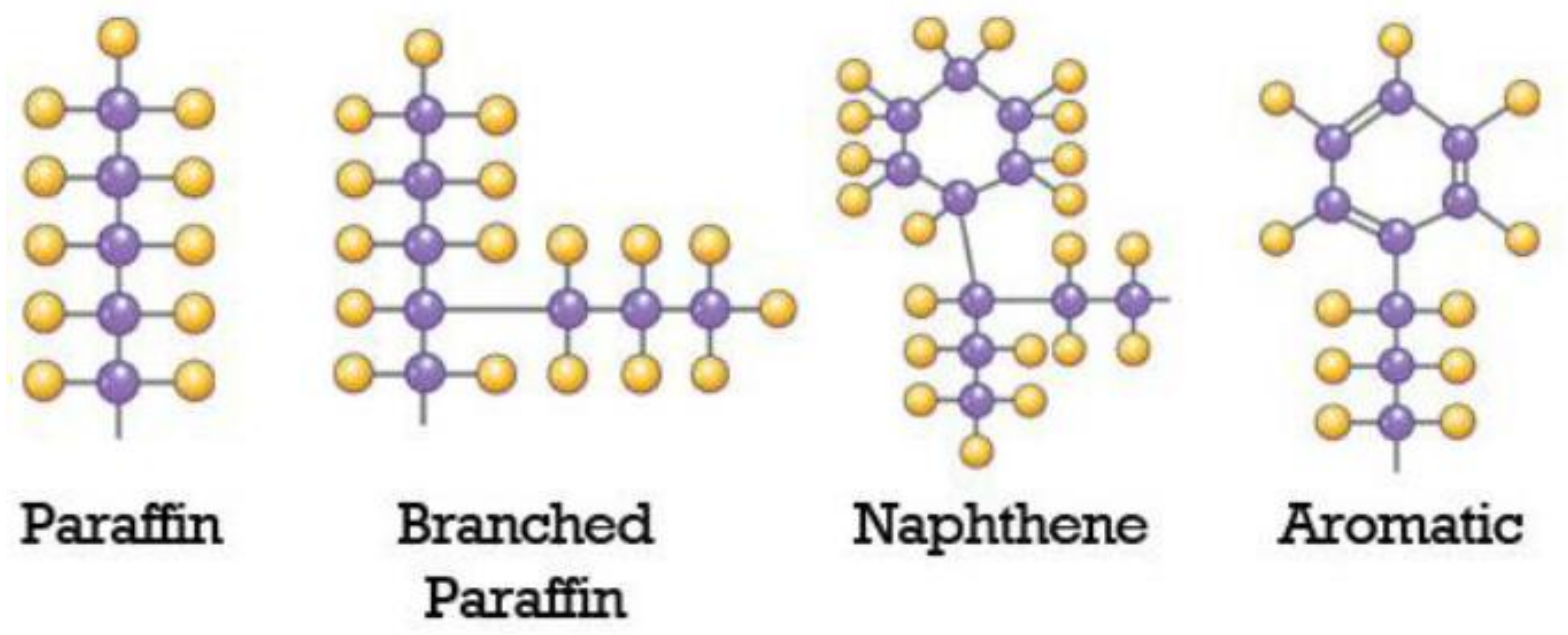
Crude oil

Dr. Ákos Fürcht

Definition

- „Crude oil” or petroleum, is a **mineral of organic origin**: anaerob decomposition (without oxygen) material derived from prehistoric algae and zooplankton remains
- Its main components are the **liquid phase hydrocarbons**, but it may contain dissolved gases and/or solid hydrocarbon as well
- The crude oil is a complex hydrocarbon mixture but also consists **sulphur**, **nitrogen** or **oxygen** containing compounds. There are **metallic components** (Ni, V, …) in complex form and some dissolved water present too.

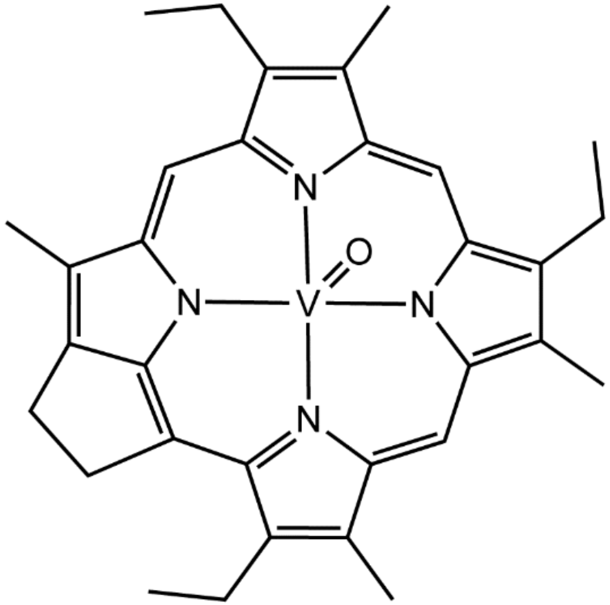
Composition: types of **hydrocarbons**



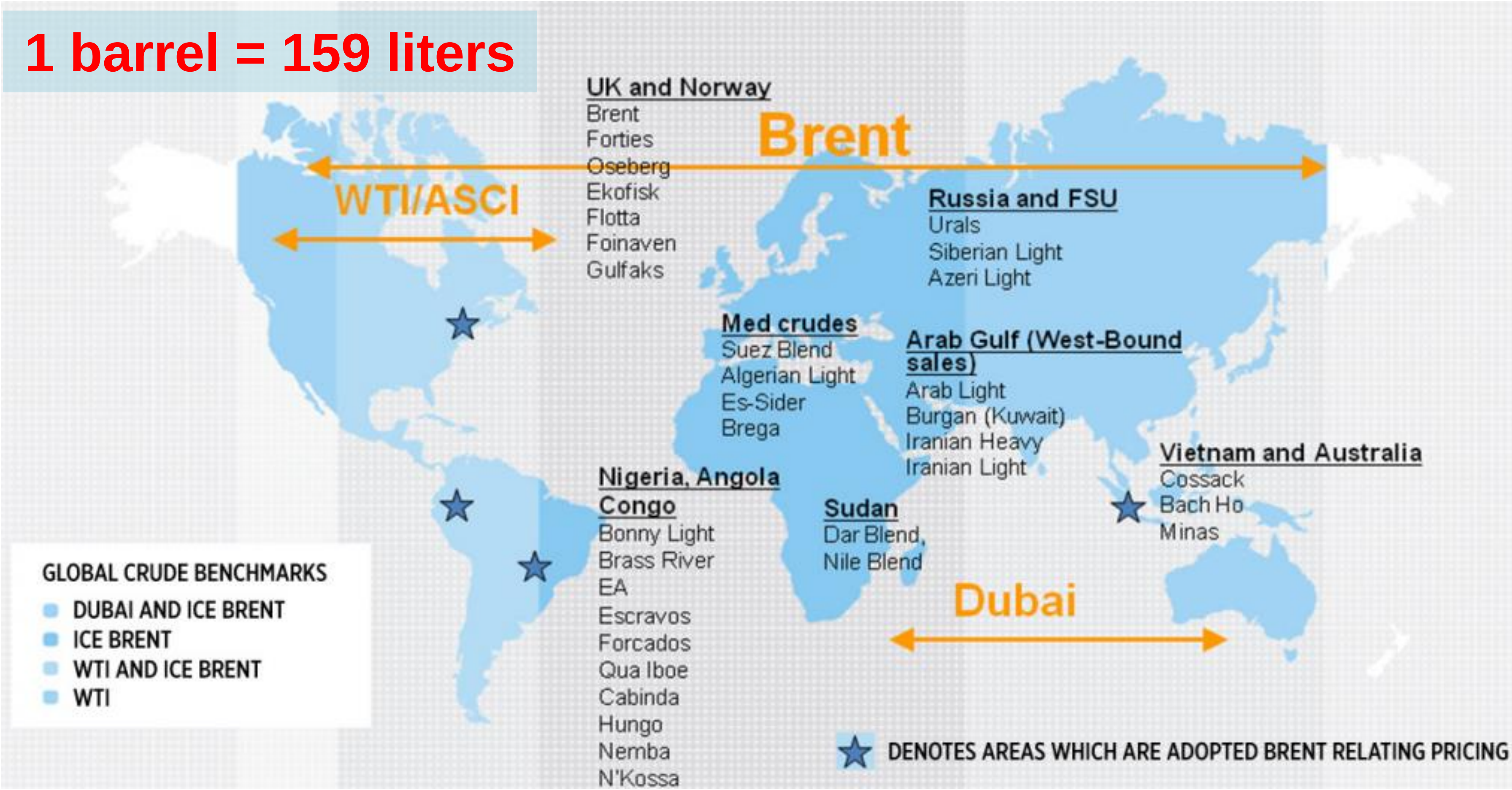
Missing: unsaturated hydrocarbons

Composition: types of **impurities**

- **Heteroatom compounds**
  - **Sulphurous** compounds
    - Elemental sulphur
    - Hydrogen sulphide
    - Mercapthanes
    - Sulphides-disulphides
    - Tiophenes and derivatives
  - **Nitrogeneous** compounds
    - Amines
    - Nitriles
    - Pirrols
  - **Oxygeneous** compounds
    - Organic acids
    - Phenols
- **Inorganic ions**
  - Dissolved in the water, present in the crude oil
  - Na^+, Cl^-, HCO_3^-, etc.
- **Organic metal complexes**
  - Mainly nickel (Ni) and vanadium (V)



Benchmark crude oils worldwide



Benchmark crude oil is crude oil that serves as **a pricing reference**, making it easier for sellers and buyers to determine the prices of multitudes of crude oil varieties and blends.

Source: Intercontinental Exchange (www.theice.com/publicdocs/ICE_Crude_Refined_Oil_Products.pdf)

General classification of crude oil

Crude are generally classified according to:

Location of origin	e.g. Brent
Density	Light, Intermediate, Heavy
Sulphur content	Sweet vs. Sour

Crude oil **quality**

Quality and Production Volume of Main Crudes 2014 (*)
(thousand barrels/day)

Source: ENI World Oil and Gas Review 2015

API gravity

- The American Petroleum Institute gravity, or API gravity, is a measure of how heavy or light a petroleum liquid is compared to water. If its API gravity is greater than 10, it is lighter and floats on water; if less than 10, it is heavier and sinks.

- API gravity = 141.5/SG - 131.5 where SG = ρ_{oil}/ρ_{water}

- Crude oil is classified as light, medium or heavy, according to its measured API gravity:
  - Light crude oil is defined as having an API gravity higher than 31.1 °API
  - Medium oil is defined as having an API gravity between 22.3 °API and 31.1 °API
  - Heavy oil is defined as having an API gravity below 22.3 °API.

Eg.: Urals (Russian Export Blend)
~900 kg/m3 specific gravityvs.
~26 API gravity

Classification of crude oil: UOP K

- The characterization factor was introduced by UOP. Is based on the observation that the specific gravity of the hydrocarbons are related to their H/C ratios and their boiling points are linked to the number of carbon atoms in their molecules.

- $K_{UOP} = (1.8T)^{1/3} / SG$

  - where $SG = \rho_{oil}/\rho_{water}$, T = (T20 + T50 + T80)/3 from the TBP distillation

  - TBP:
    - **Specifications for ASTM D2892 Packed Columns (True Boiling Point)**
      Distillation Column Efficiency: 15 Theoretical Plates
      Vacuum Range: 100 to 2 mmHg
      Packing Types: Propak, Helipak, Structured Packing

- K_{UOP}/K_W:
  - n-paraffins > i-paraffins > olefins > naphthens > aromatic hydrocarbons
  - Average K_W of crude oils: 10-13

Crude oil **assay**

Alaskan North Slope - Summary Crude Oil Assay Report

Source of Sample

Reference:	MM15ANS2
Name:	Alaskan North Slope
Origin:	United States of America
Sample Date:	2015.07.27
Comments:	

Light Hydrocarbon Analysis

H_2S*	ppm wt	-
Methane	%wt	0,00
Ethane	%wt	0,01
Propane	%wt	0,18
Isobutane	%wt	0,45
n-Butane	%wt	1,80
Isopentane	%wt	0,99
n-Pentane	%wt	1,42
Cyclopentane	%wt	0,17
C6 paraffins	%wt	2,11
C6 naphthenes	%wt	1,37
Benzene	%wt	0,34

*Dissolved in liquid

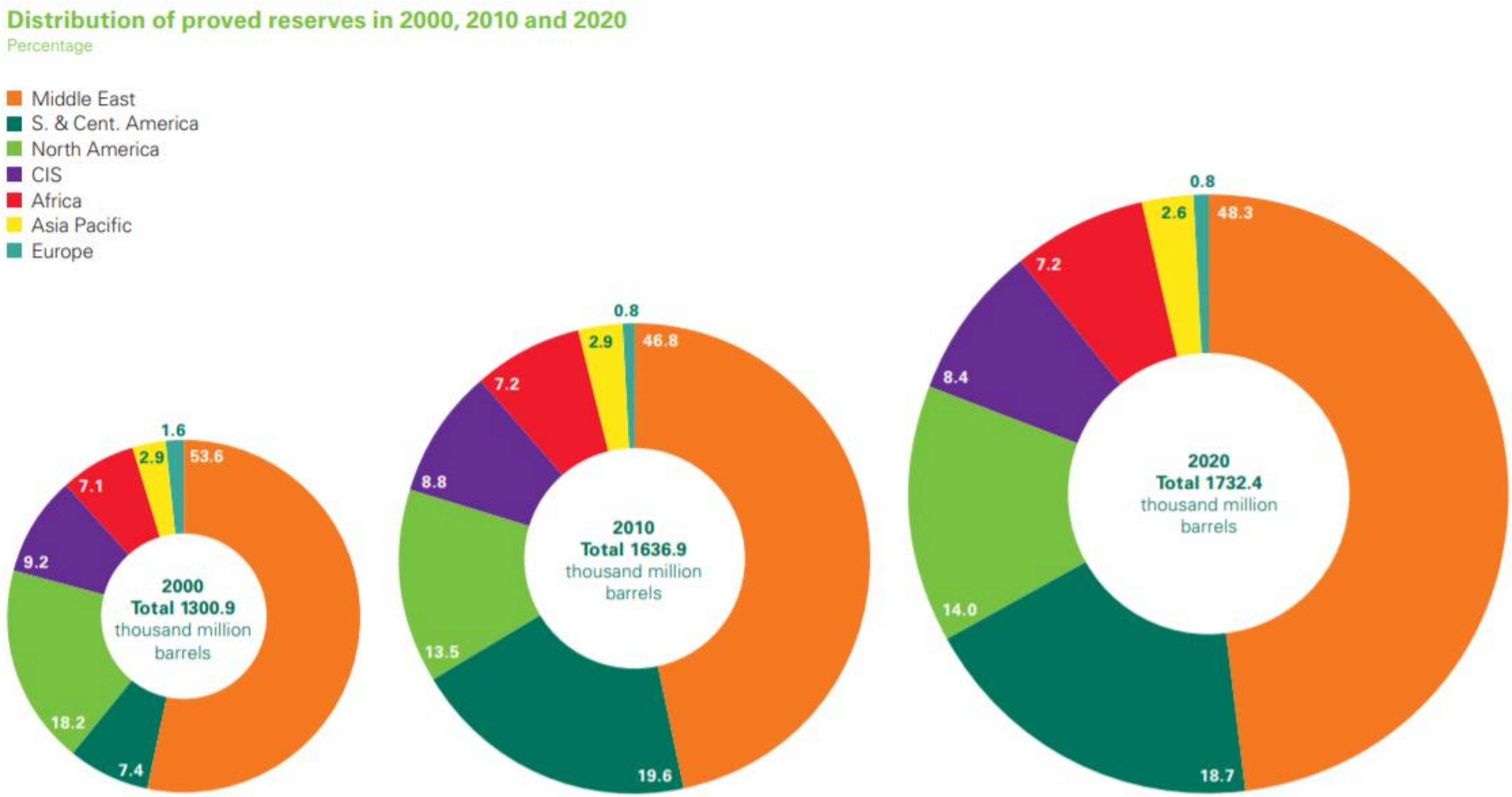
Assay Summary / TBP Data

Gravity (°API)	32,0	
Sulphur (%wt)	0,962	
Yield on Crude	%wt	%vol
Gas to C4	2,45	3,65
Light Distillate to 149°C	17,80	21,05
Kerosene 149 - 232°C	13,20	14,20
Gas Oil 232 - 369°C	23,35	23,05
Vacuum Gas Oil 369°C - 550°C	25,15	23,10
Residue above 550°C	18,05	14,95

Volume expansion: 0,3 per cent vol on crude distributed across whole distillation

Cut Data	Crude	Distillates									Residues			
		Light Naphtha	Heavy Naphtha		Kero	Light Gas Oil	Heavy Gas Oil	Light Vacuum Gas Oil	Heavy Vacuum Gas Oil		AtRes	VacRes		
Start (°C API)	IBP	C5	95	149	175	232	342	369	509	550	369	509	550	585
End (°C API)	FBP	95	149	175	232	342	369	509	550	585	FBP	FBP	FBP	FBP
Yield on crude (% wt)	100	7,95	9,85	4,05	9,10	19,00	4,35	20,35	4,80	3,60	43,20	22,85	18,05	14,45

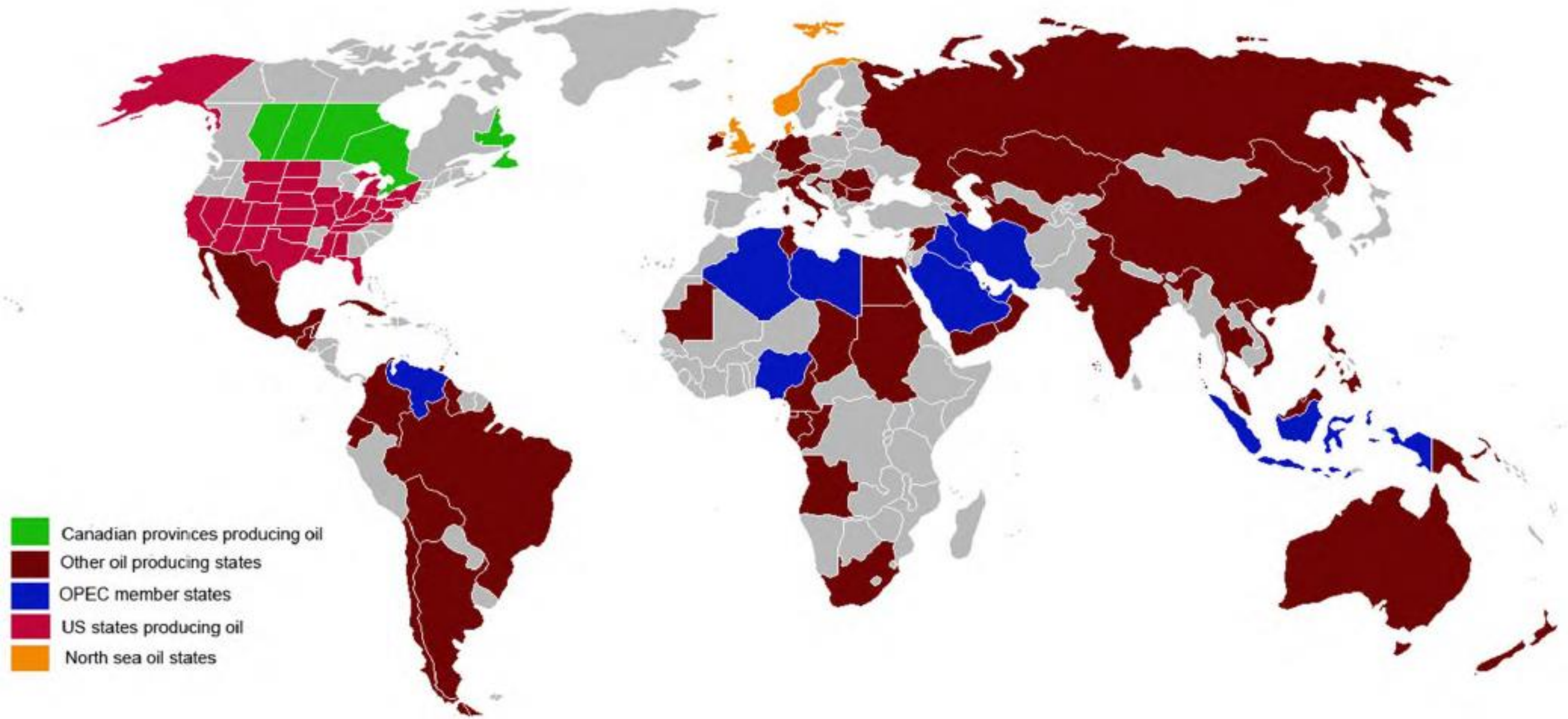
Proven crude oil **reserves**



According to estimations, proven reserves will reach its maximum around ~2040

Source: BP Statistical Review of World Energy 2021

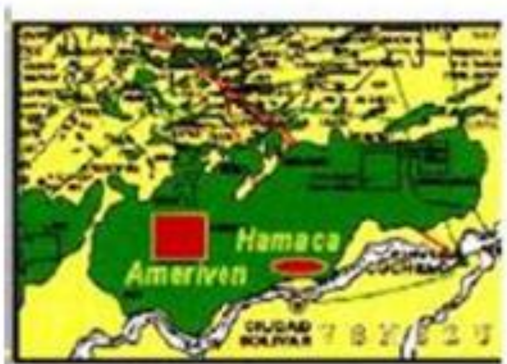
Oil producing **countries**



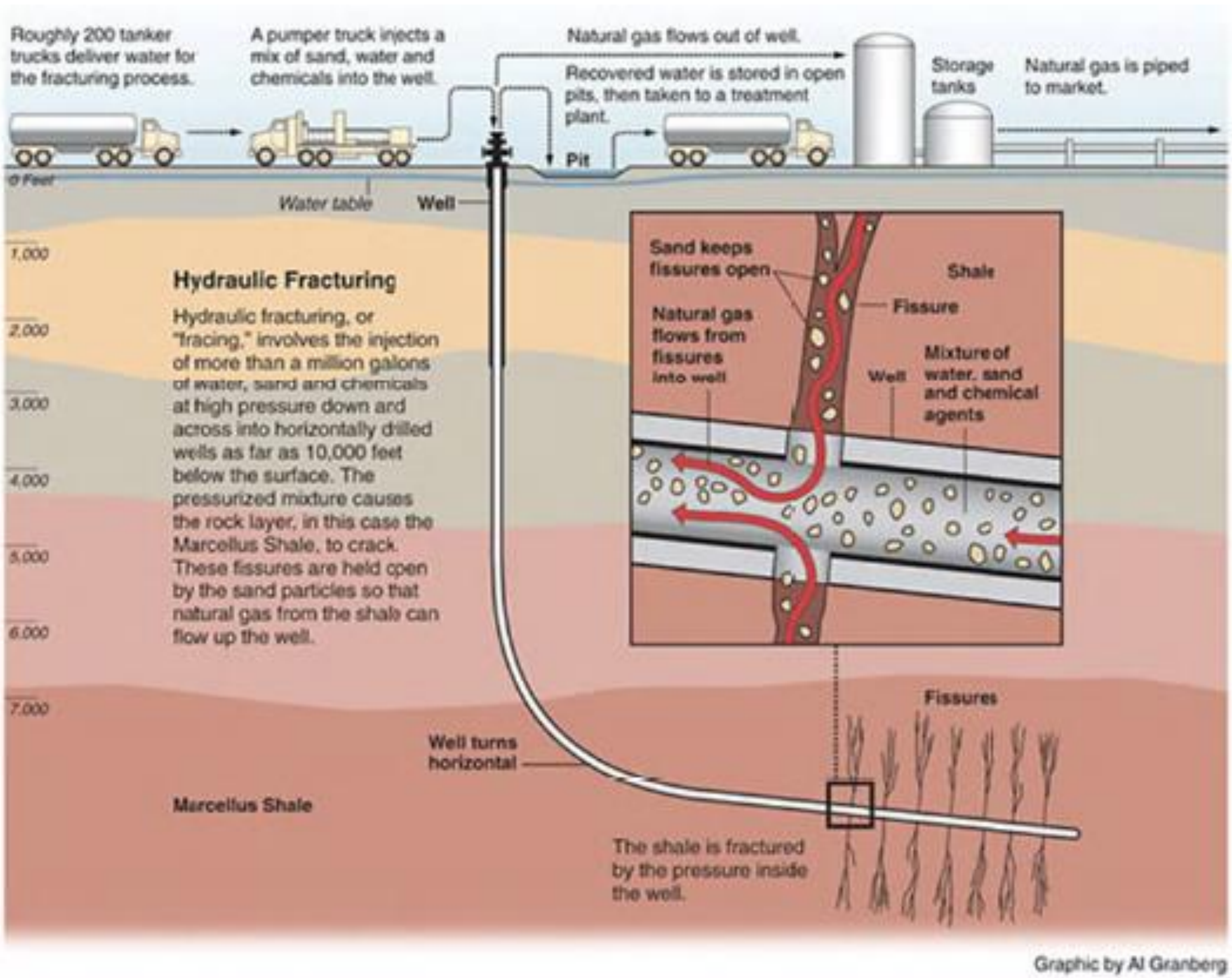
Crude type: **Extra heavy**

Canadian oil sands:1.7 trillion barrels

Venezuelan heavy crudes:
1.9 trillion barrels



Crude type: **Shale oil**

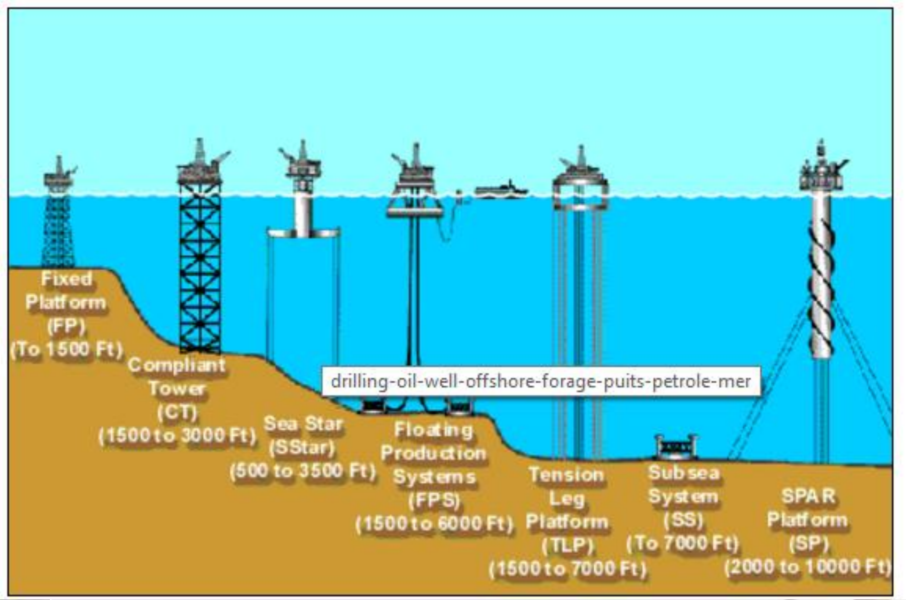


Source: www.vox.com

Crude oil **supply chain**

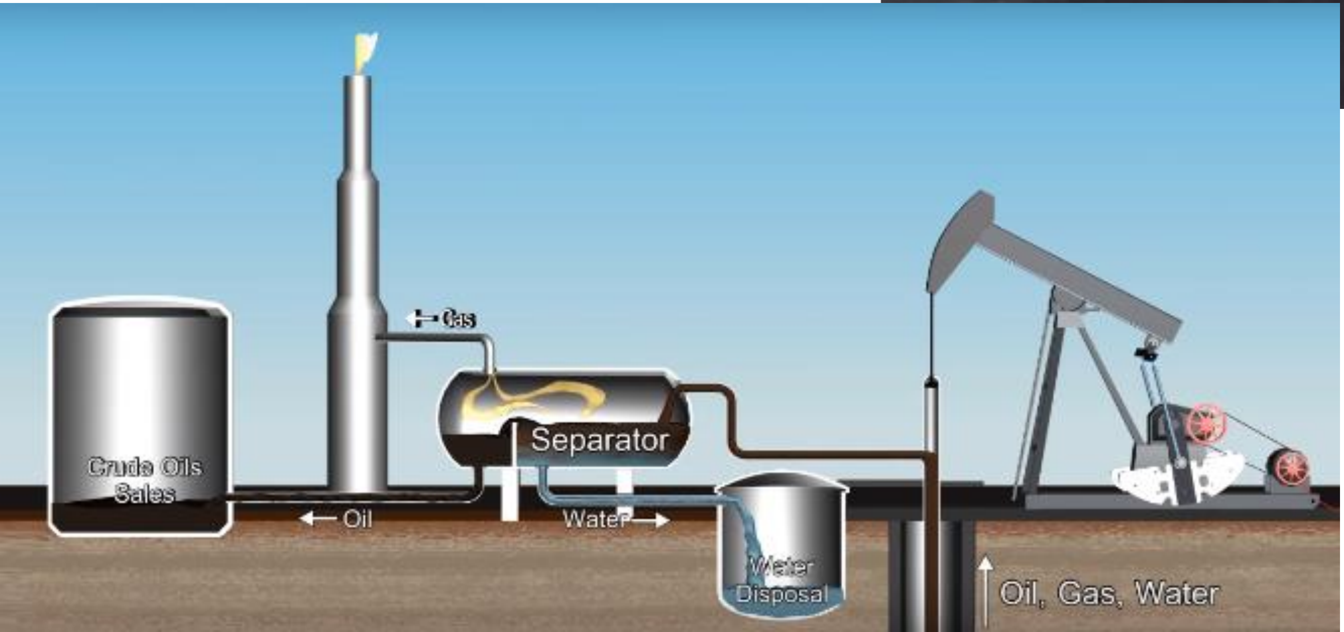
- Exploration
- Well creation
- **Production**
  - **Primary**: own pressure assists to come onto surface
  - **Secondary**: gas or water injected to assist to come onto surface
- **Pretreatement**: water and gas separation
- Storage
- Transport

Crude oil **production**



Crude oil **pretreatement**

- The oil is **collected** from individual wells at central collecting stations
- Here **free water** is setting out and **free gases** are separated: the oil become stabilised



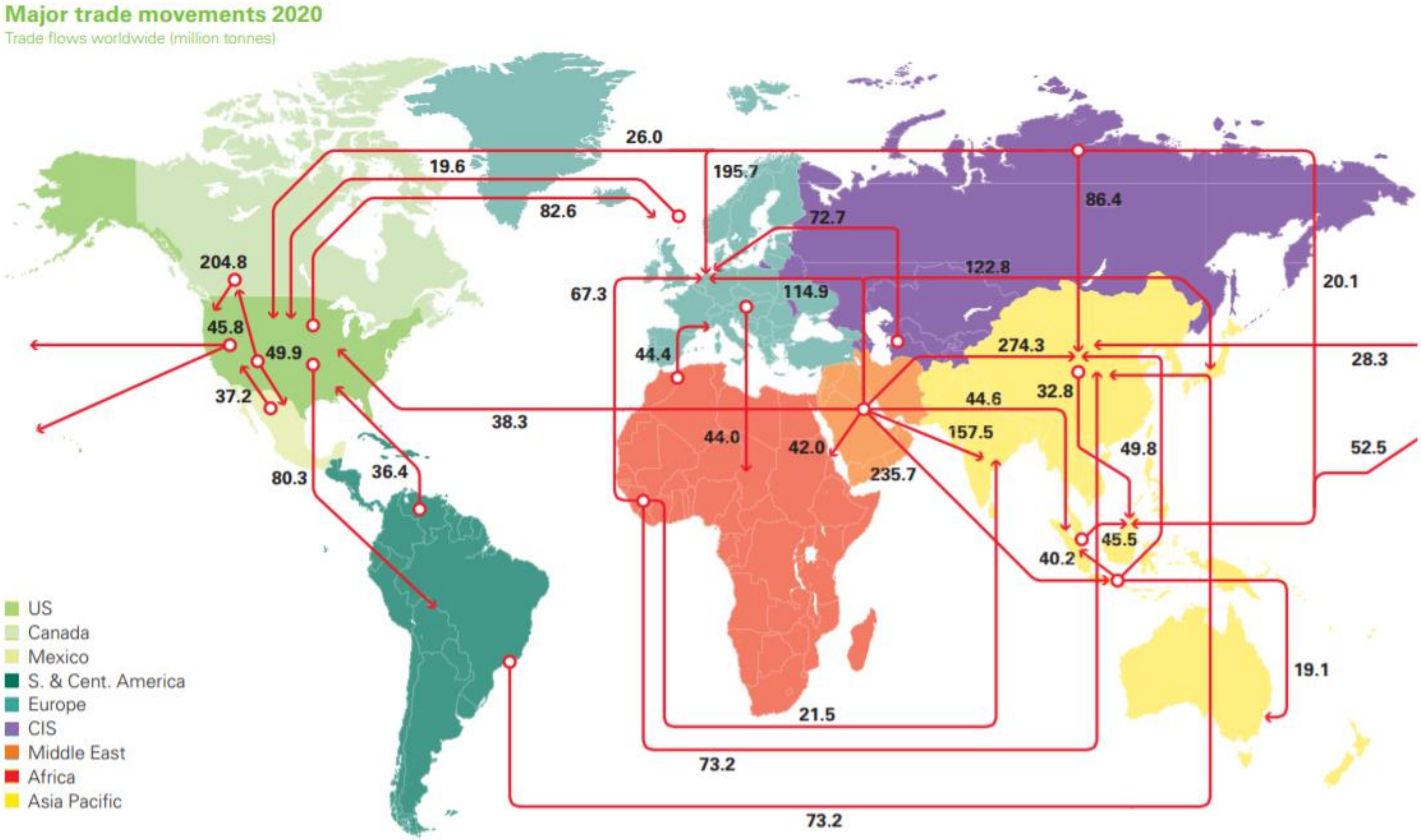
- The **stabilised oil** then may be transported

https://www.youtube.com/watch?v=K0WyqQe2W7k
https://www.youtube.com/watch?v=ioE8n93PsMs

Transportation of crude oil

- Via water
  - Long distance: see tankers
  - Short distance: barges
- Via land
  - Long distance: pipelines
  - Short distance: rail cars, trucks

Trade movements



Source: BP Statistical Review of World Energy 2021

Crude Oil Desalting

Problems with the salts

- **Why is it essential in virtually every cases?**

If your desalter is operating inefficiently, there is a direct effect on the atmospheric column operation

  - It will cause **deposits** in the fired heaters and heat exchangers
  - There will be **corrosion** in the top product line equipment (condenser, etc.)
  - Effect of atmospheric residue high sodium content (Na)
  - More deposition in the vacuum furnace
  - **Catalyst poison** in the catalytic processes
  - Deposition and corrosion in the superheater boilers
  - (Shorter cycle time in the Viscosity Breaker unit)

- **The Desalter is a crucial preparatory process upstream of the crude oil distillation and the downstream units!**

Salts in the crude oil

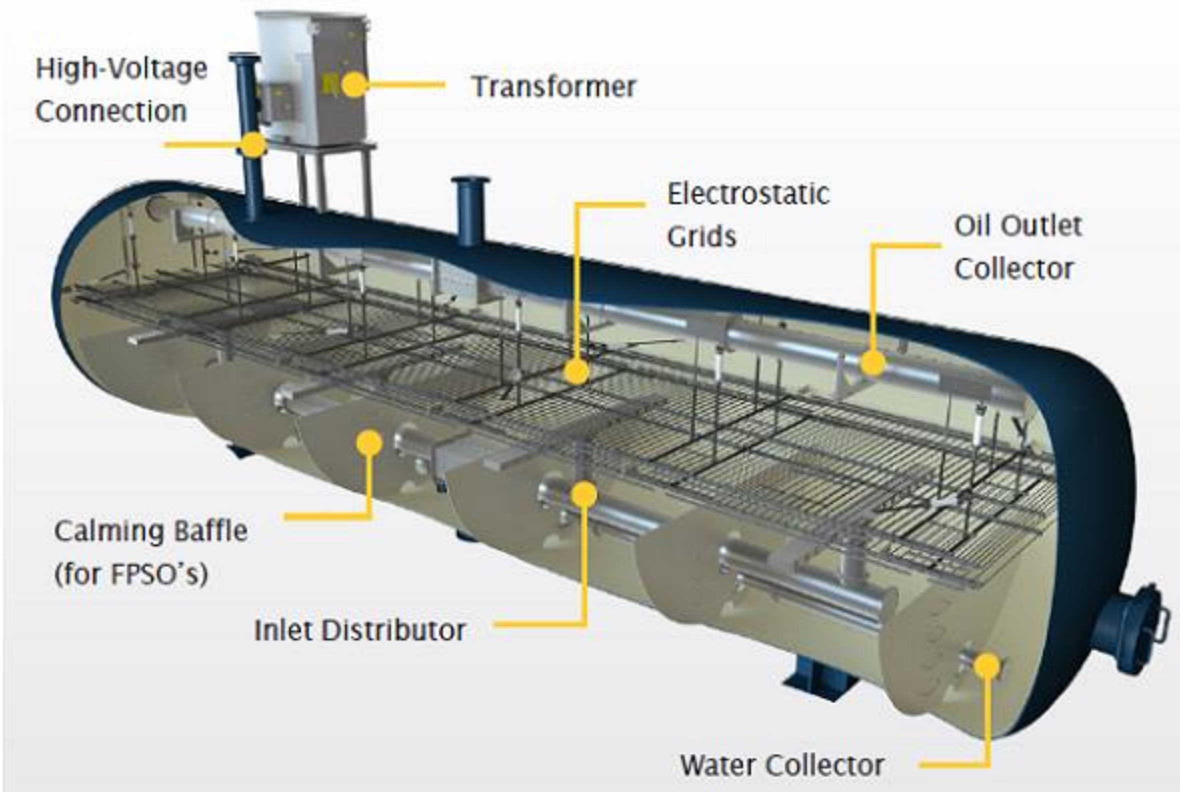
- Salts present in the crude oil are predominantly in **chloride form**:
  - **NaCl 70-80 wt %**
  - **$MgCl_2$ 20-10 wt %**
  - **$CaCl_2$ 10 wt %**

- The salts may be found in ionized or crystalline form **in the dissolved water**, which is always present in the crude oil.

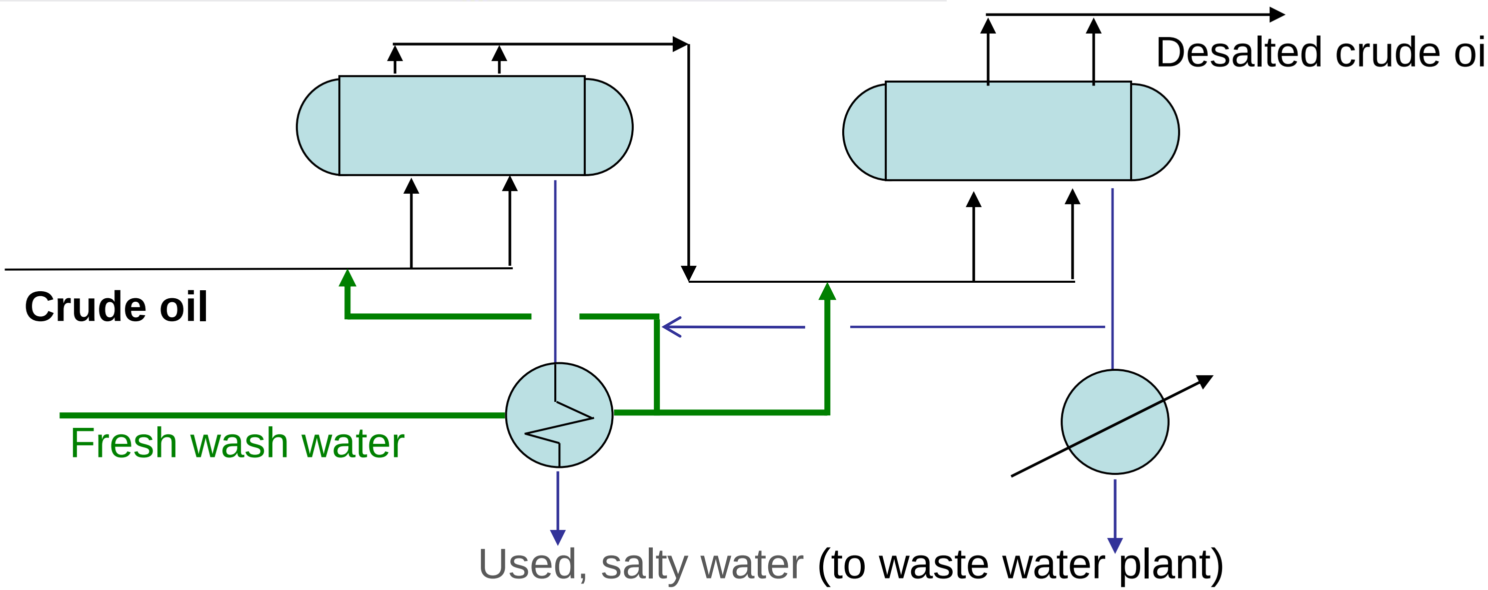
- The salts can be removed by adding sufficient amount of **wash water** in the desalter equipment (3-5%).

- Rule of thumb is that **the chloride content** in the effluent water from the **atmospheric column condenser** **shall be less than 10 ppm**. Otherwise severe corrosion may occur.

Operation

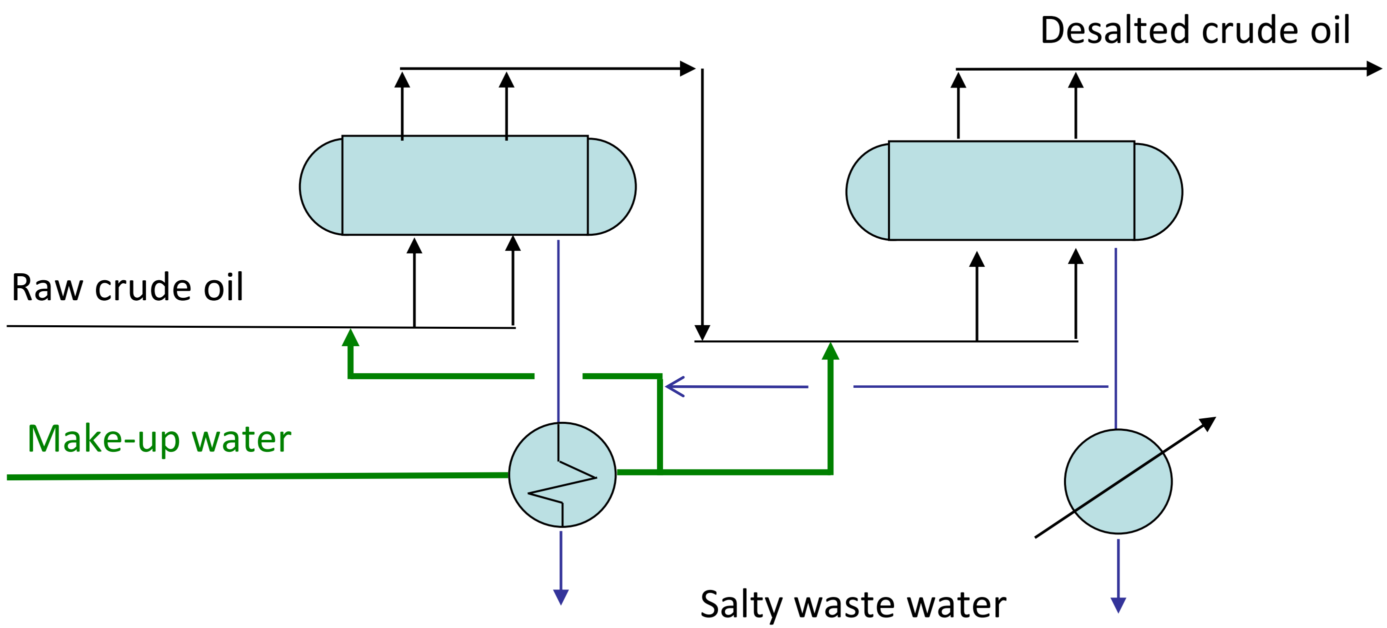


- The efficiency of a **two stage** desalter is better
- Average salt content of REB type crude is 20-40 ppm
- **The desalted crude oil salt content shall be as low as possible (<1ppm)**



Single slide summary: Desalter

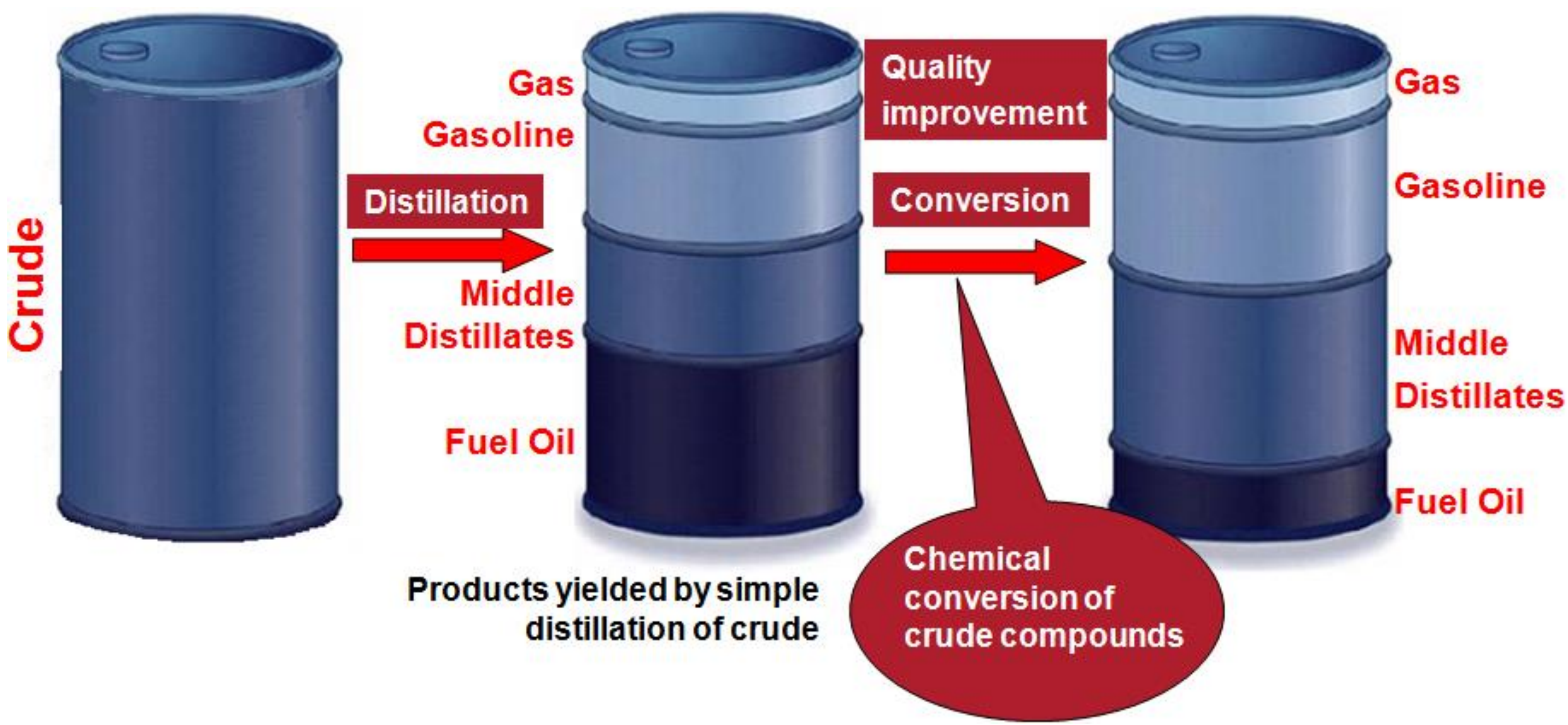
- **Aim:** removal of inorganic salt impurities from crude oil
- **Feedstock:** raw crude oil + make-up water
- **Process parameters:** ~140°C, 10-15 barg
- **Heat balance:** neutral
- **Additive:** demulsifier
- **Products:** desalted crude oil, salty waste water



Hydrocarbon processing
Separation processes - distillation

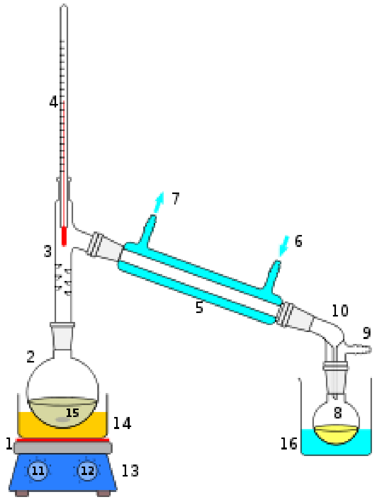
English version based on the presentation of István Rabi,
held on 18.09.2013.

Goal of the crude oil processing

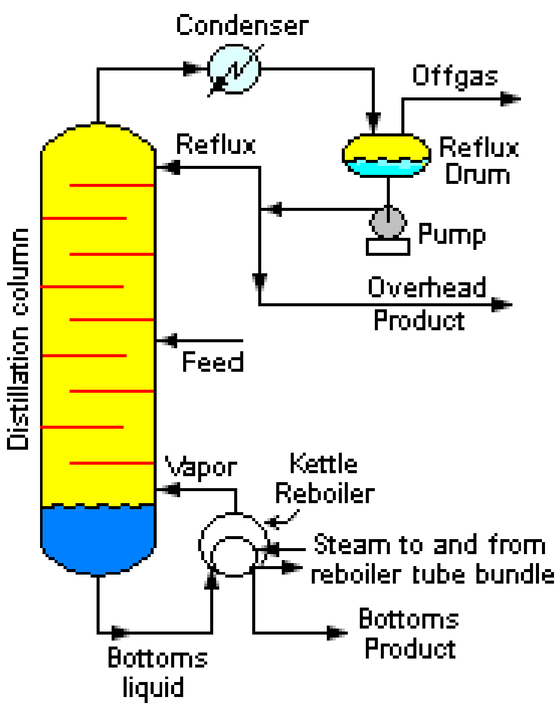


The whole process is called „refining”

Distillation



▶ The essence of distillation is to heat a given liquid until it became vapour and then condensing the vapours the material is converted to liquid again. Since there is no chemical alteration in the material structure, only phase transition, **the distillation is a physical process**.



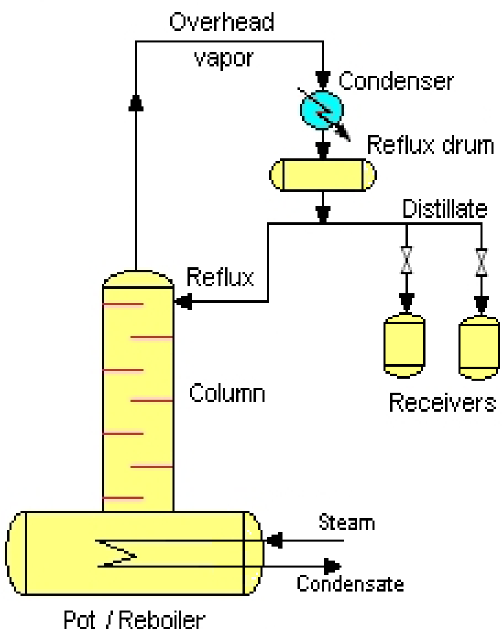
▶ Rectification provides sharper separation. The essence is that between **the contacted materials** (one in liquid, one in vapour phase), which **are not in equilibrium**, there is a two way material and heat transfer. The temperatures of the two phases are different and they are moving relative to each other. During the phase contact, the lower boiling point components are evaporated in greater extent, so the concentration in the vapour phase of that components will increase. On the other hand, the higher boiling point components are condensed in greater extent, so they will concentrate in the liquid phase better.

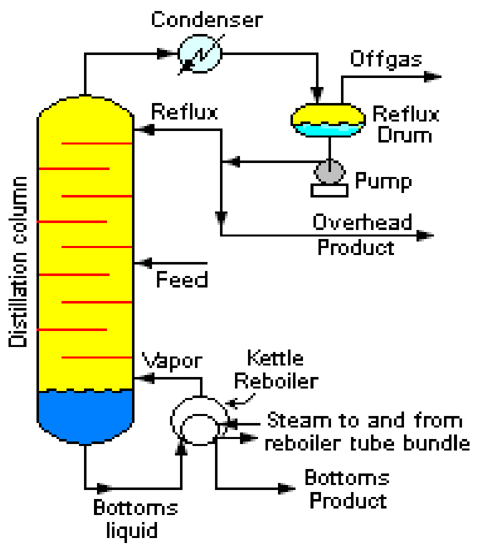
Principles of distillation

- Distillation may be used to separate liquid mixtures, where **all components are volatile.** That means all components have a definite, distinct vapour pressure, but still different from each other.

- The principle of separation by the means of distillation is the different vapour pressure of the components of the liquid mixture at the same temperature. Consequently, each component will evaporate into vapour phase, relative to its fugacity (volatility).

Main distillation types by method





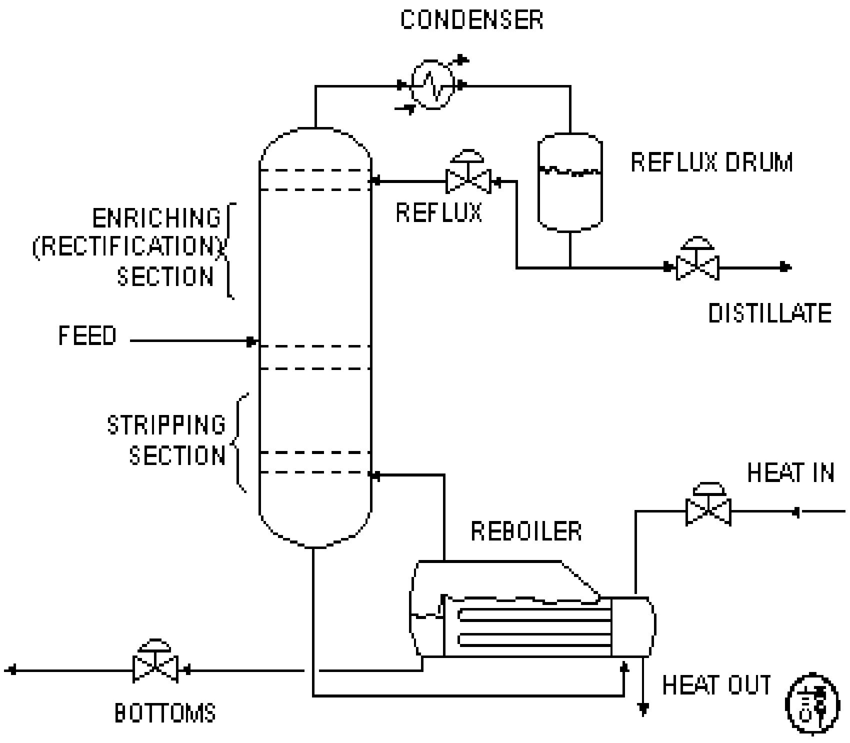
Batch distillation (dynamic fractionated distillation)

- The aim of the *batch distillation* is the purification or separation the liquid mixture into a couple of parts
- **start-up**: We fill up the reboiler and heat. The vapours are moving upwards through the rectification column and are condensed in the condenser. Usually **the process is started-up in total reflux.**
- When the top product quality reached the desired specification, the product draw is initiated into receivers. Still, part of the condensate is rerouted back to the column as reflux. The higher volatility components are separated earlier and the lower volatility components are concentrated in the reboiler.

Continuous distillation

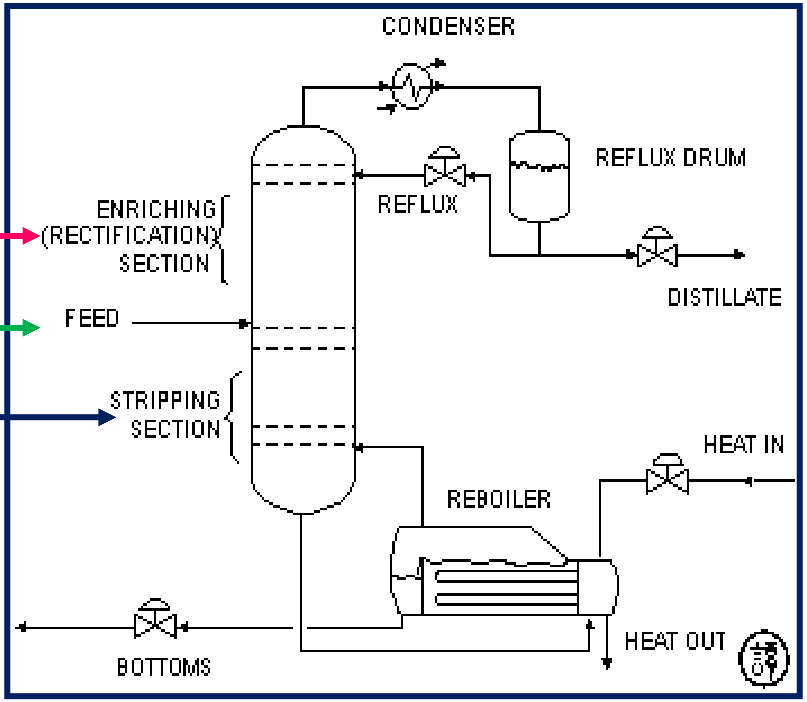
- The most frequently applied method in the chemical and oil industry. The feed and processing is continuous in this method

Main equipment types of a distillation column



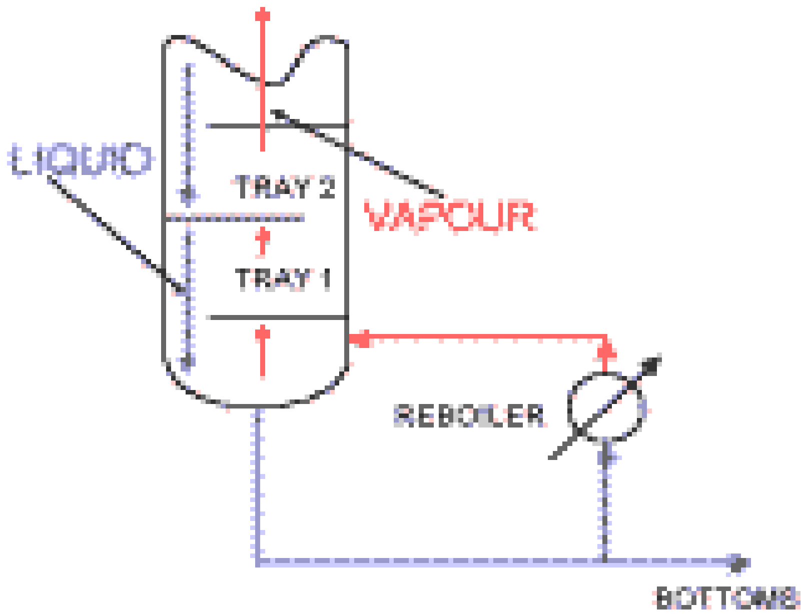
- **Shell** is the frame of the column
- **Column internals** are e.g. the trays and/or the packing, which are used to separate components
- **Reboiler** provides the heat necessary for evaporation
- **Condenser** is the place where the vapours are converted to liquid again
- **Reflux drum** is the receiver of the liquid (later the reflux and top product), condensed in the condenser

Operation of a distillation column 1



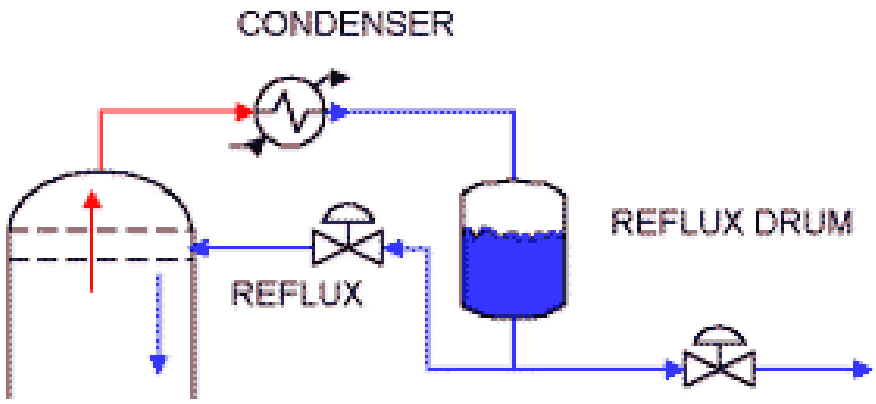
- The liquid feed is routed to the feed tray
- The feed tray split the column into two parts:
  - Upper part – rectification section
  - Lower part – stripping section
  - The section around the feed tray is also called evaporation section

Operation of a distillation column 2



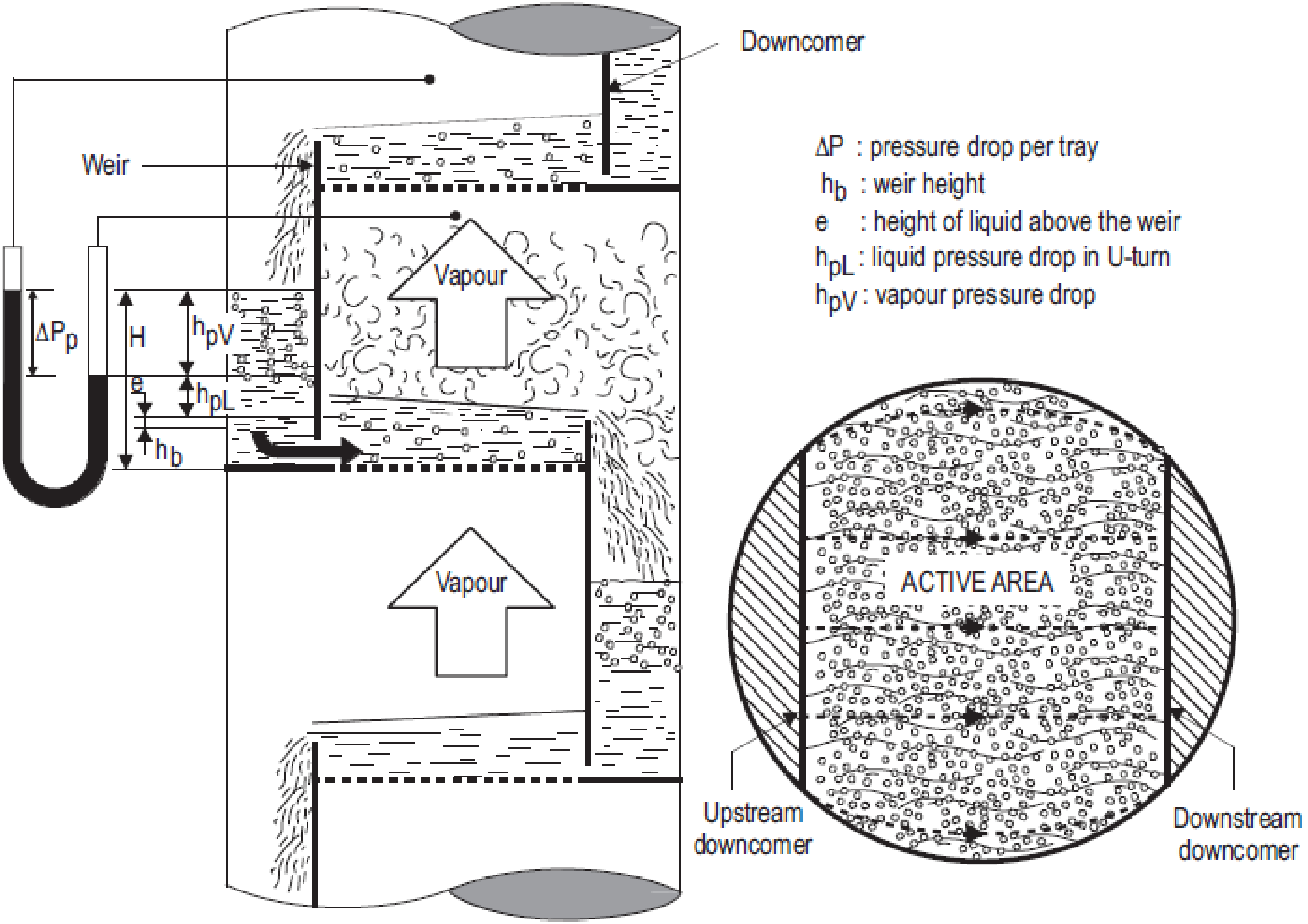
- **The liquid feed is flowing downwards** and accumulates in the column bottom and reboiler.
- The heat transferred in the reboiler will partly evaporate liquid. In most cases, the heat is transferred via steam, in the chemical industry. In the refinery the source of heat is an other product stream (most of the cases). The evaporated vapour is rerouted under the lowest tray of the column.
- The drawn liquid is **the bottom product**.

Operation of a distillation column 3



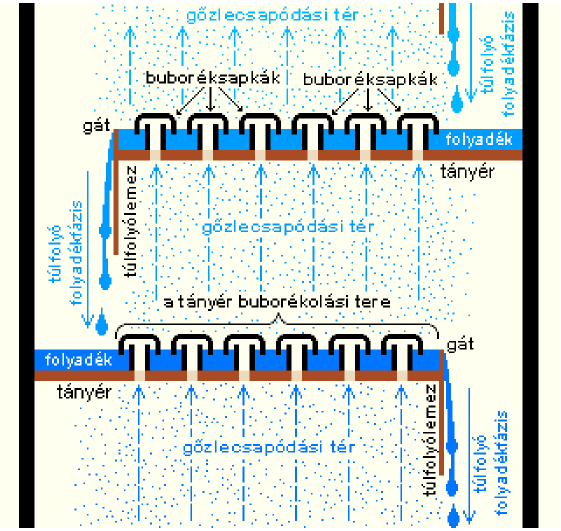
- **The vapour flows upwards,** and leaves the column at the top and reaches the condenser.
- The vapours are cooled and **condensed in the condenser**.
- The condensed liquid is collected in a receiver, which is called reflux drum. Part of that liquid is rerouted above the upper tray.
- The drawn liquid is **the top product**.

Tray operation and pressure drop

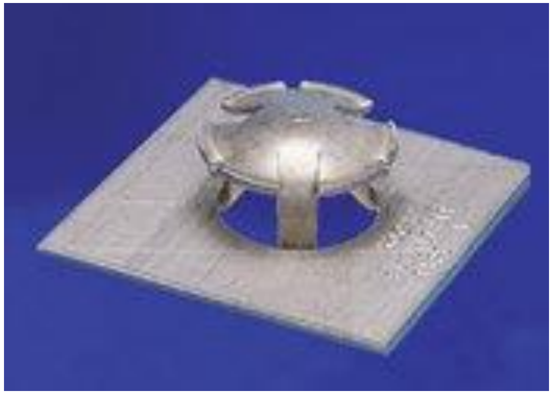


Column internals (trays)

Boubble cap tray

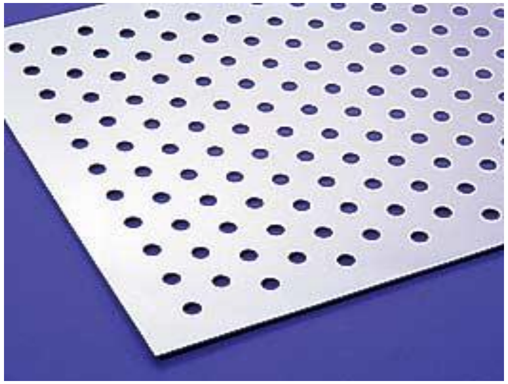


Moving valve tray



Fixed valve tray

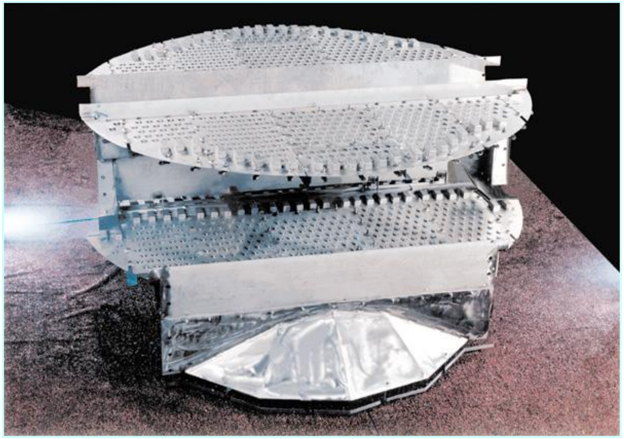
Perforated tray



High efficiency trays

- **Benefits:**
  - Lower specific energy consumption
  - Better product quality
  - Used in absorption columns, less absorbent liquid requirement will spare energy during solvent regeneration

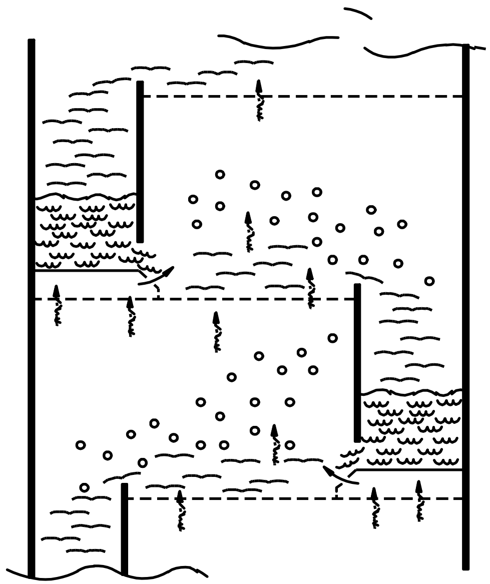
ULTRA-FRAC® trays

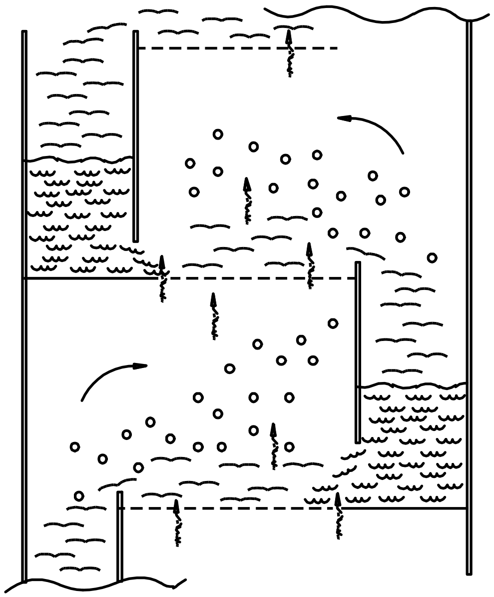


SUPERFRAC® trays

VGPlus Trays

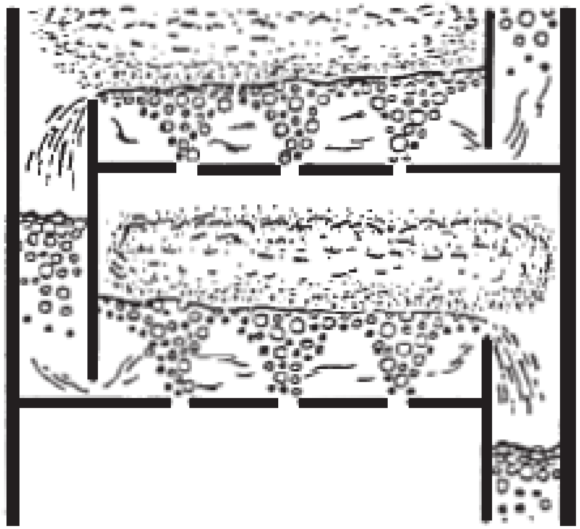
Conventional vs. high efficiency trays: comparison



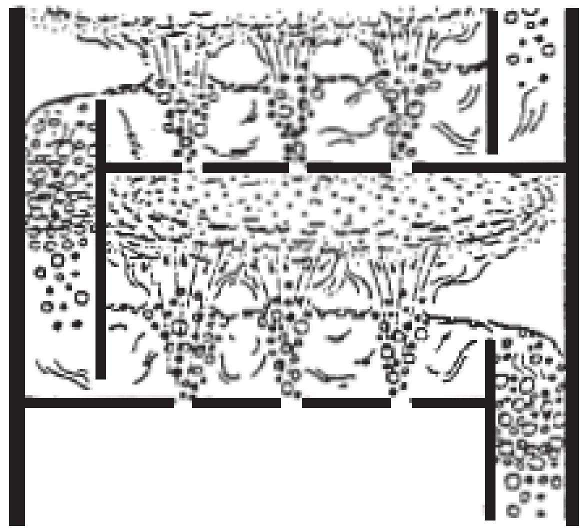


- **Benefits related to the conventional tray structure:**
  - Higher capacity: 30%
  - Lower pressure drop: 20%
  - Similar or better material transfer
  - More homogeneous liquid flow
  - More homogeneous vapour pattern
  - Lower sensitivity to impurity accumulation

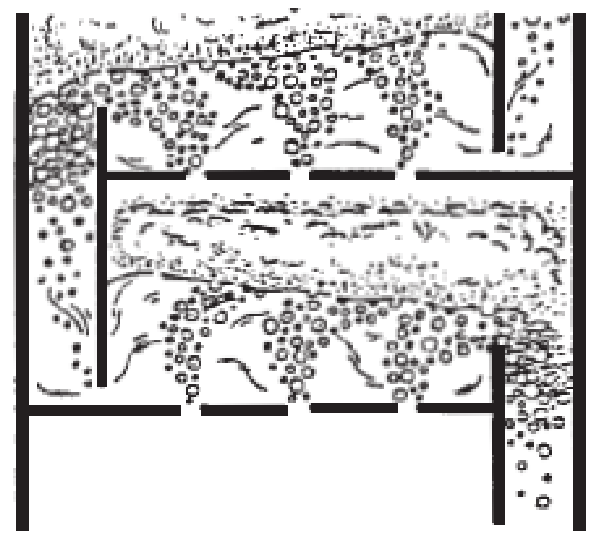
Tray malfunctions



Normal tray operation

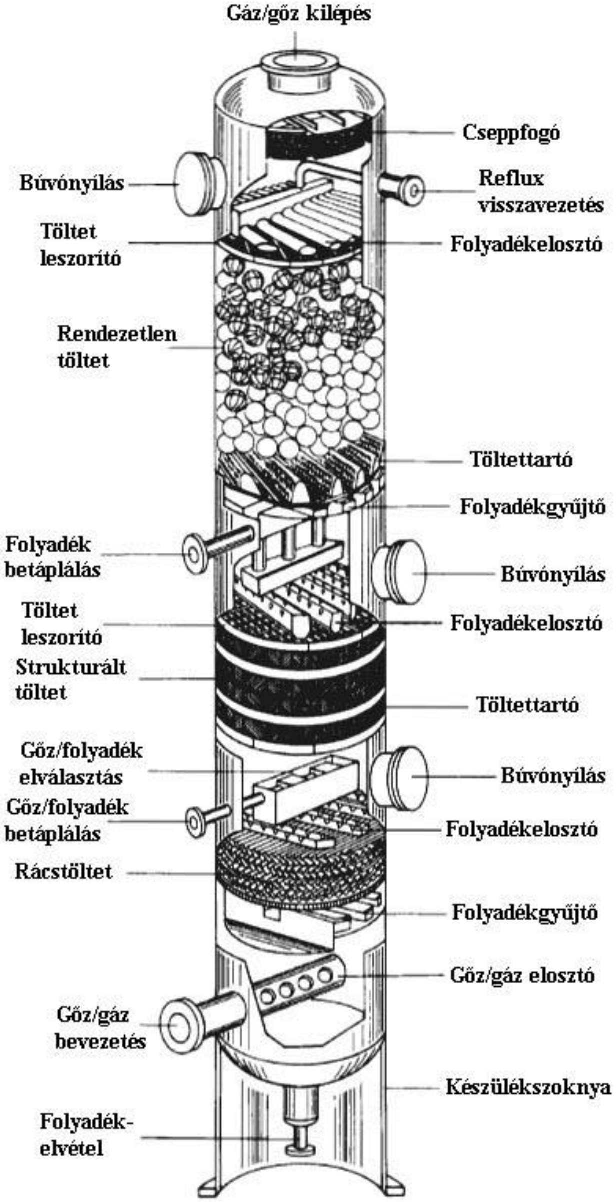


Carryover and flooding
(excess vapour)



Flooding
(excess liquid)

Packed distillation column ITT TARTOTTUNK 2020.09.30



MOLGROUP

Parts of packed distillation column

Shell

- The material is usually metal, but it can be ceramic or plastic as well.
- The shell may have an internal coating (e.g. plastic, enamel)

Packing

First generation:	1907-50, Raschig ring, Berl saddle
Second generation:	1950-70, Pall ring, Intalox saddle
Third generation:	since1970, derived from the above types

Material of packing

Metal:

- in case of non-corrosive substances
- higher capacity and efficiency
- wide geometrical possibility
- pressure proof
- price increases exponentially with specific needs (e.g. stainless steel 3-5x)

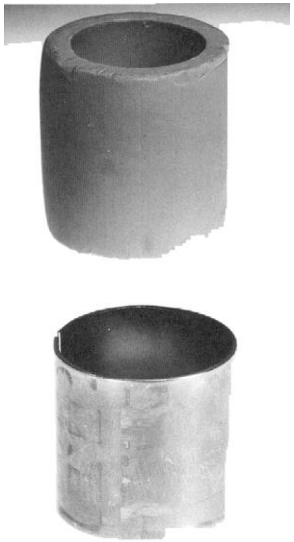
Ceramic:

- low capacity
- mechanically not durable
- usage under high temperature and reactive substances
- since the appearance of plastic packing limited usage

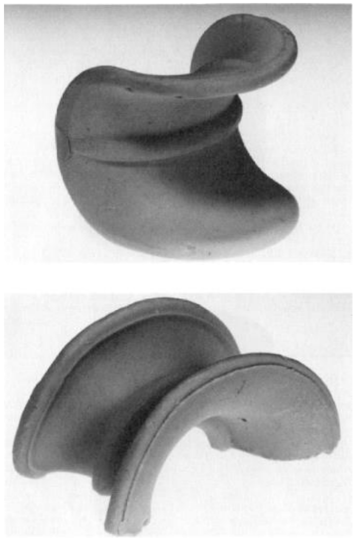
Plastic:

- polypropylene up to 120 °C
- low price
- degradation in oxidative atmosphere
- becomes rigid at low temperature
- bad wetting

Random packing

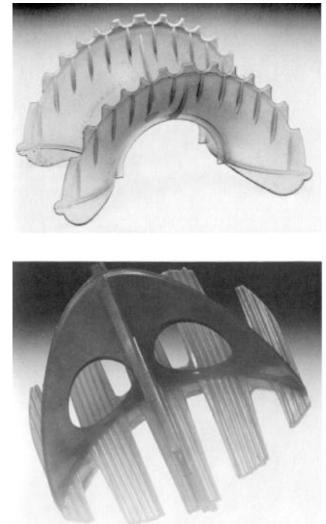


Ceramic and metal Raschig-ring

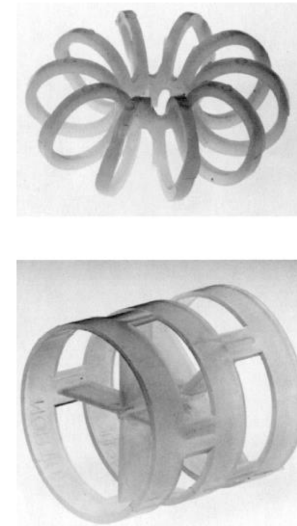


Ceramic packing (Berl and Intalox saddle)

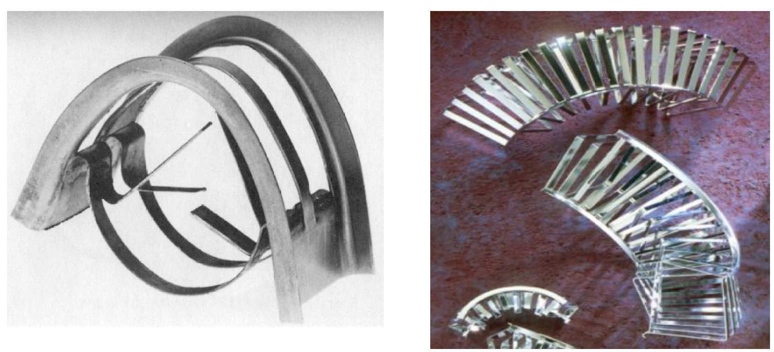
PALL-rings (conventional and HY-PAK)



SUPER INTALOX saddle and MASPAC packing

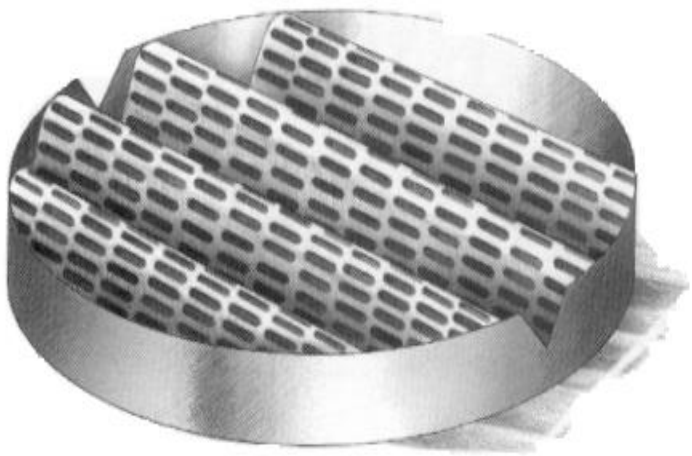


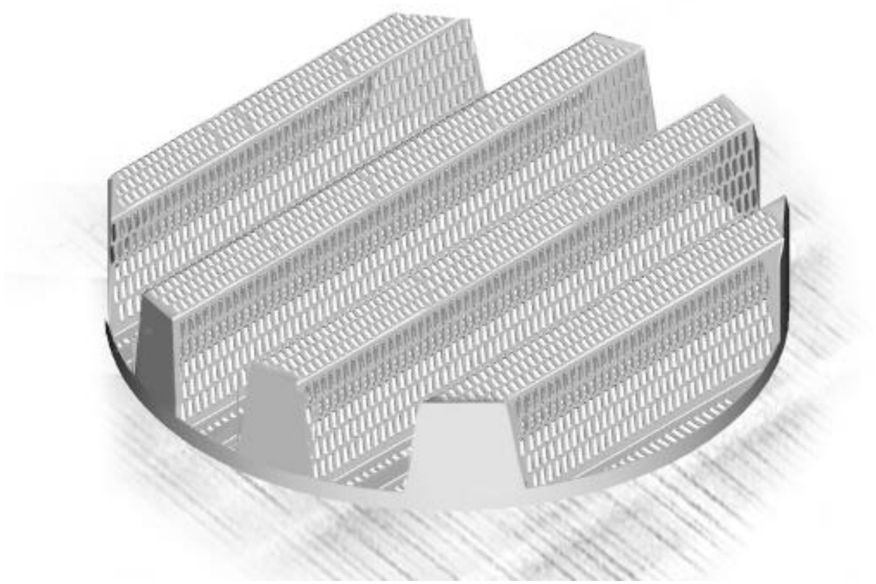
TELLERETT packing and PALL ring



IMTP and FLEXIMAX packing

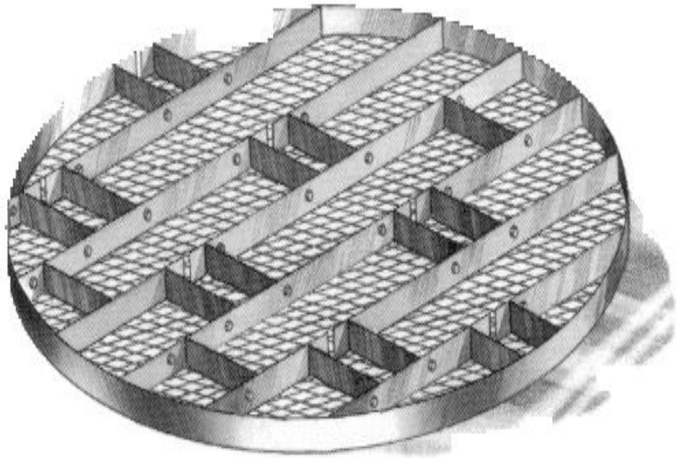
Packing supports

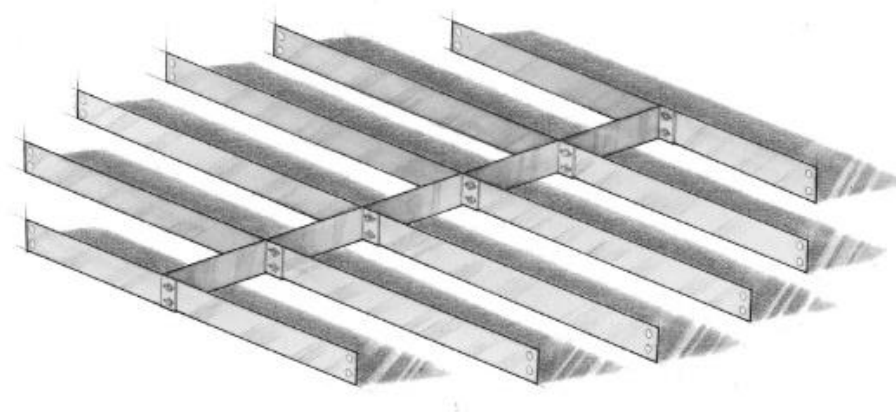




- **Objective**
  - to support the packing layer
  - to ensure the unobstructed gas and liquid flow

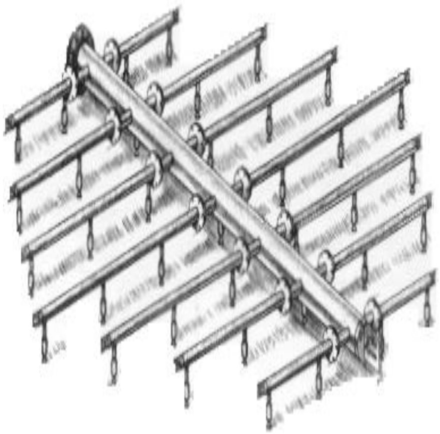
Packing overlayers

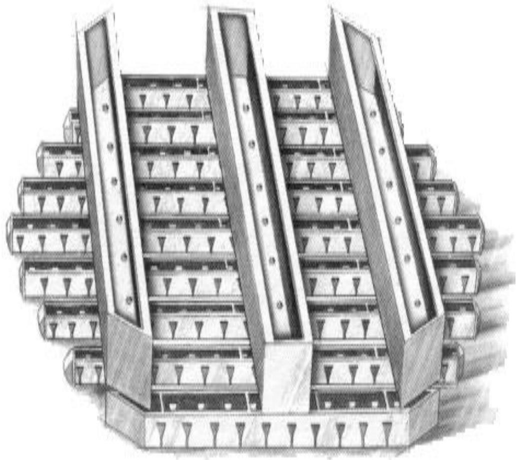


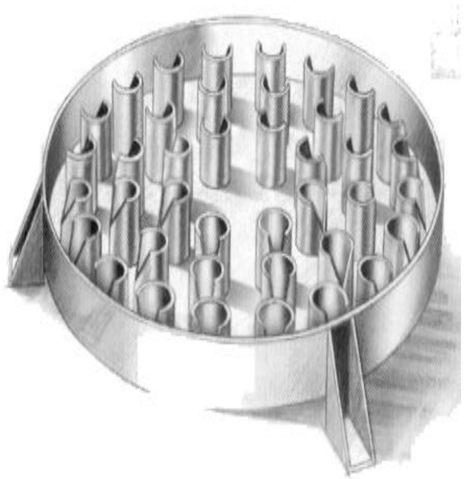


Specific weight:
100-150 kg/m^2

Liquid distributors



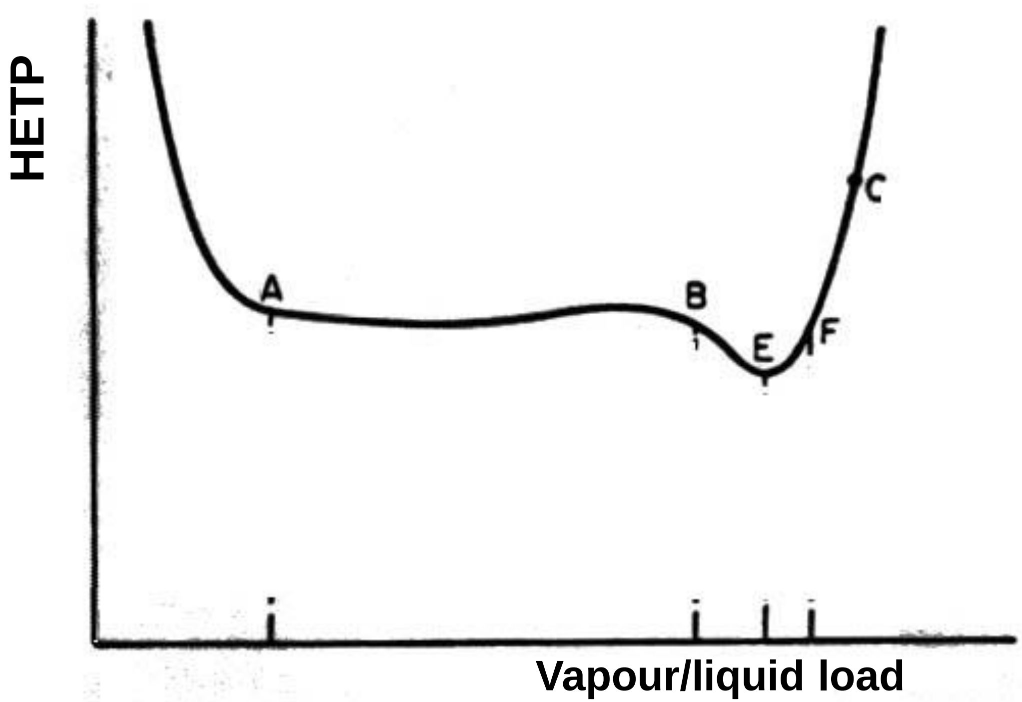




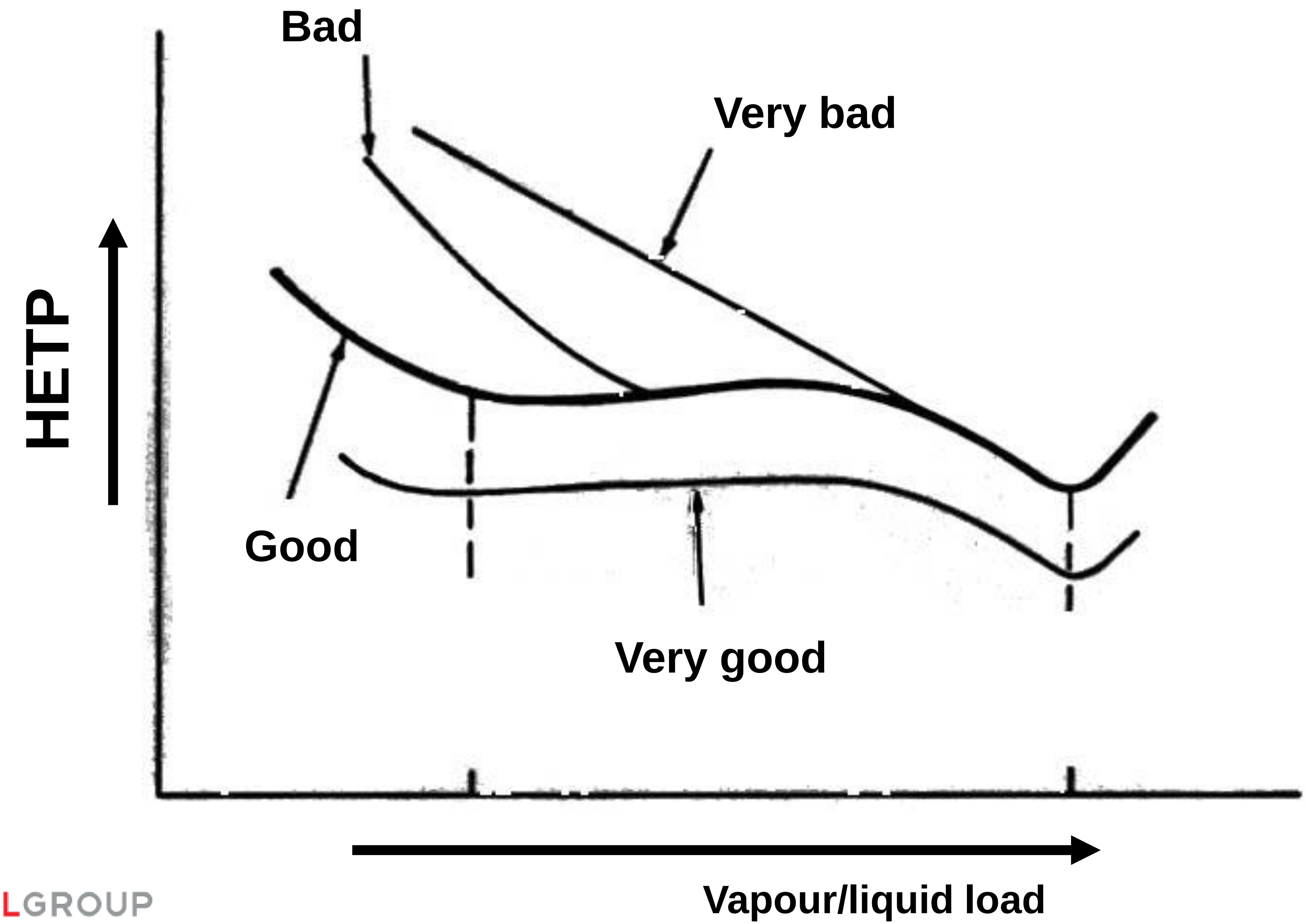
Packing type	Recommended distribution points (minimum)		
	60 point/m^2	85 point/m^2	130 point/m^2
Wire mesh			BX and CY type
FLEXIPACK and FLEXIPACK HC structured packing	205Y and greater	1.6Y and 1.4Y/350Y	1Y and smaller
INTALOX structured packing	1.5T and greater	1T and smaller	
IMTP random packing	25 and greater	15	
CMR random packing	1.5 and greater	1	

Packing efficiency

- **Means of efficiency improvement**
  - packing surface increase (m^2/m^3)
  - improvement of vapour and liquid distribution
  - improvement of wetting
- **Random packing efficiency characteristics**
  - HTU: Height of transfer unit
  - HETP: Height equivalent to a theoretical plate



Effect of liquid distribution quality on efficiency



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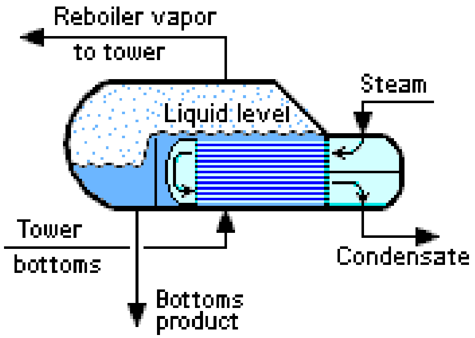
Benefits - drawbacks

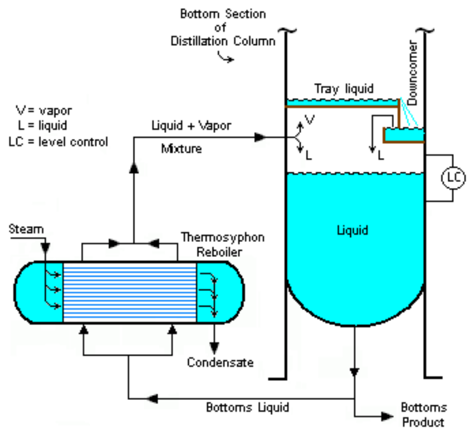
Type	Benefit	Drawback
Structured packing	Lower pressure drop High vapour capacity High efficiency Low liquid entrainment in case of easily foaming materials Easy construction	Sensitivity to contamination Sensitivity to corrosion Lower mechanical stability Not applicable in case of high liquid loads Not applicable at high pressures
High efficiency tray	High liquid capacity Medium sensitivity to contamination Mechanical stability Low axial mixing	Medium liquid entrainment Not applicable in case of foaming substances Lower efficiency than structured packing Harder construction High pressure drop
Random packing	Medium pressure drop Low liquid entrainment Can be manufactured of corrosion resistant materials Low sensitivity to contamination	Lower efficiency Harder to remove
Grid	Low pressure drop Very low sensitivity to contamination High liquid and vapour capacity	Very low efficiency

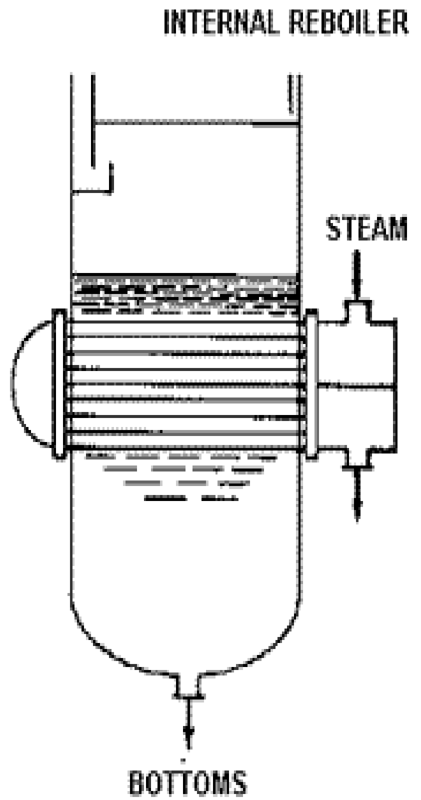
Reboilers

Kettle type reboiler

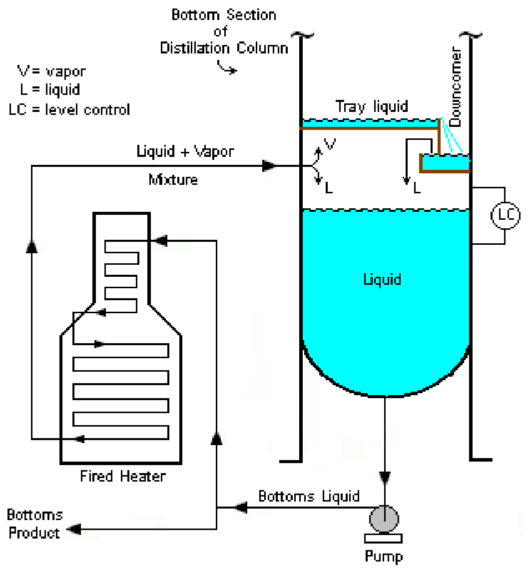


Thermosyphon reboiler (horizontal)

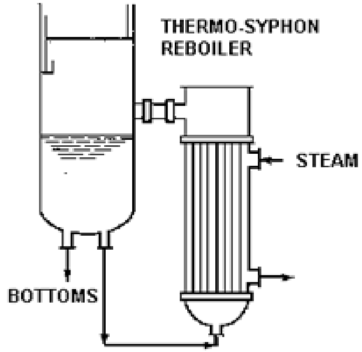




Fired heater type reboiler



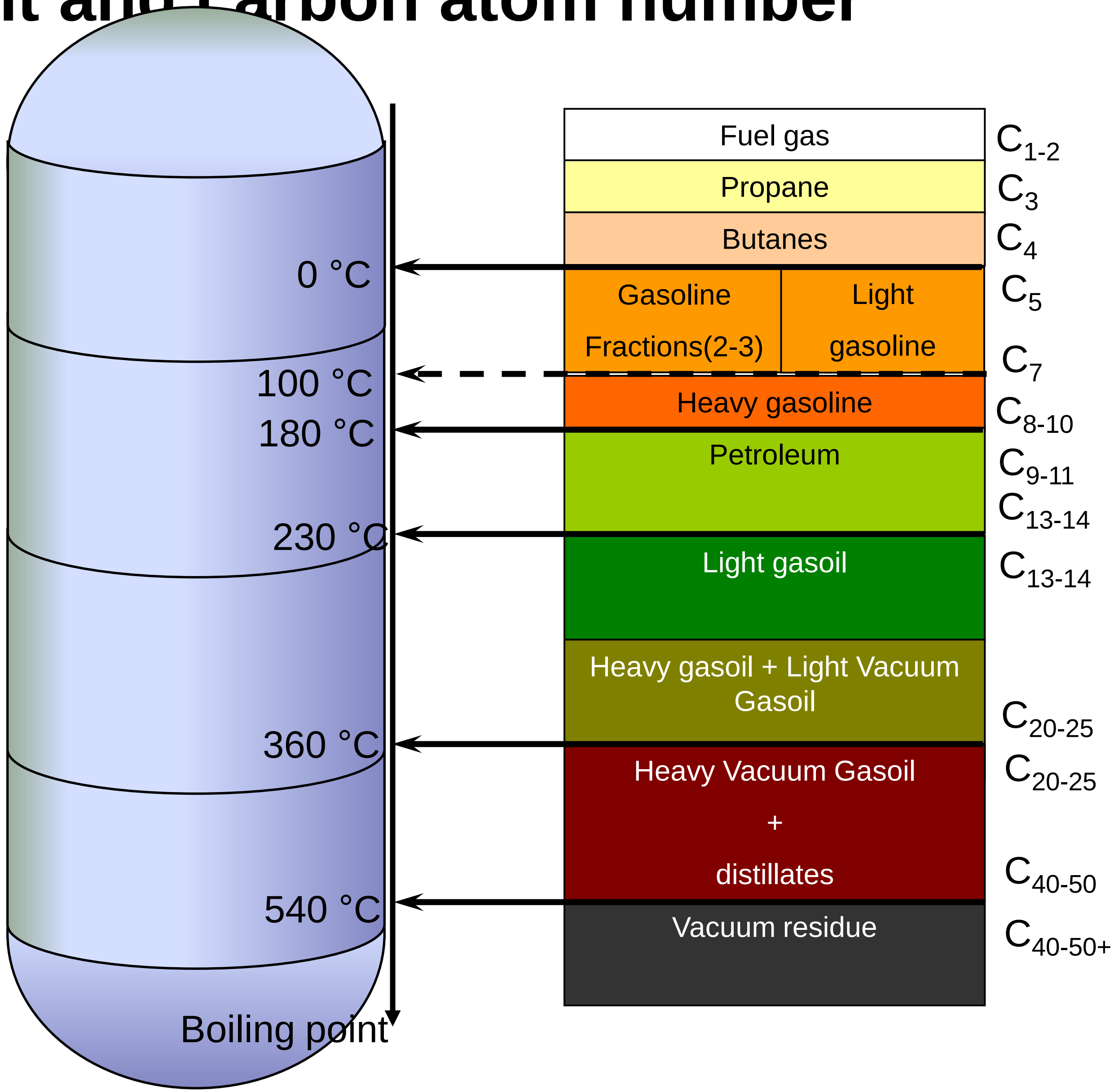
Thermosyphon reboiler (vertical)



Agenda

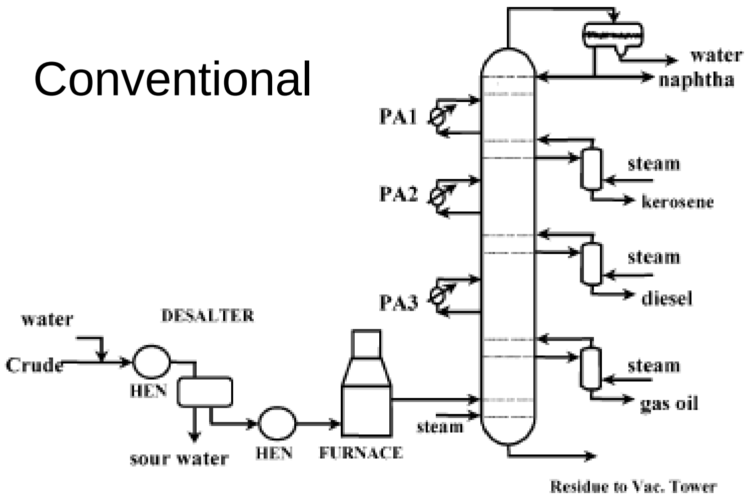
- Introduction
- Distillation
- **Crude oil distillation**

Distribution of crude oil fractions according to boiling point and carbon atom number

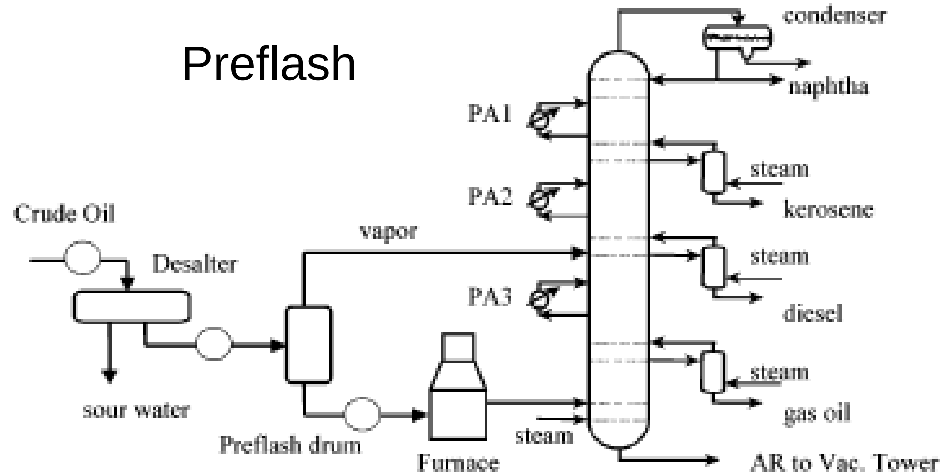


Crude oil distillation

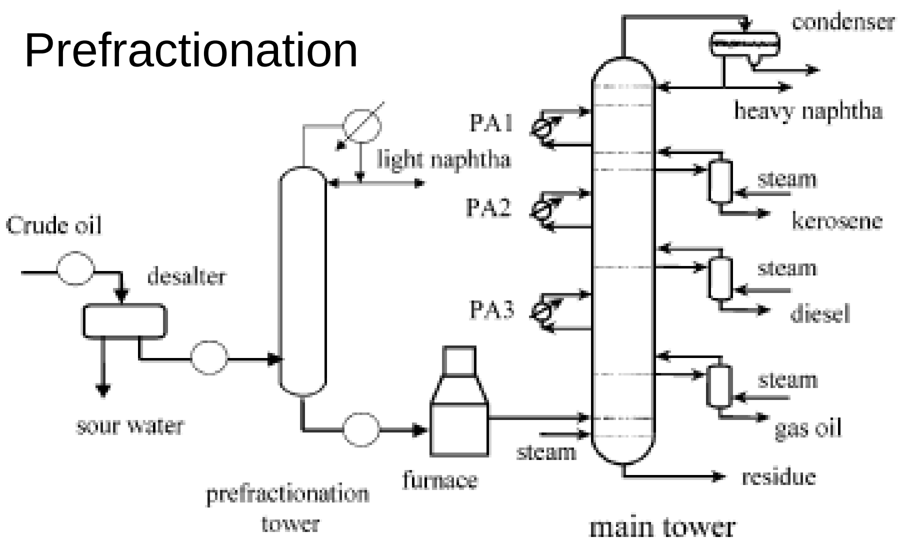
Conventional



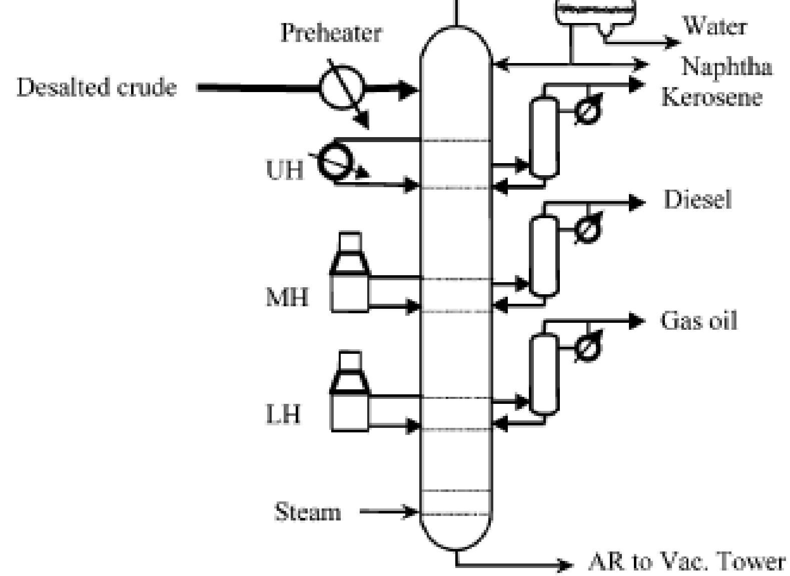
Preflash



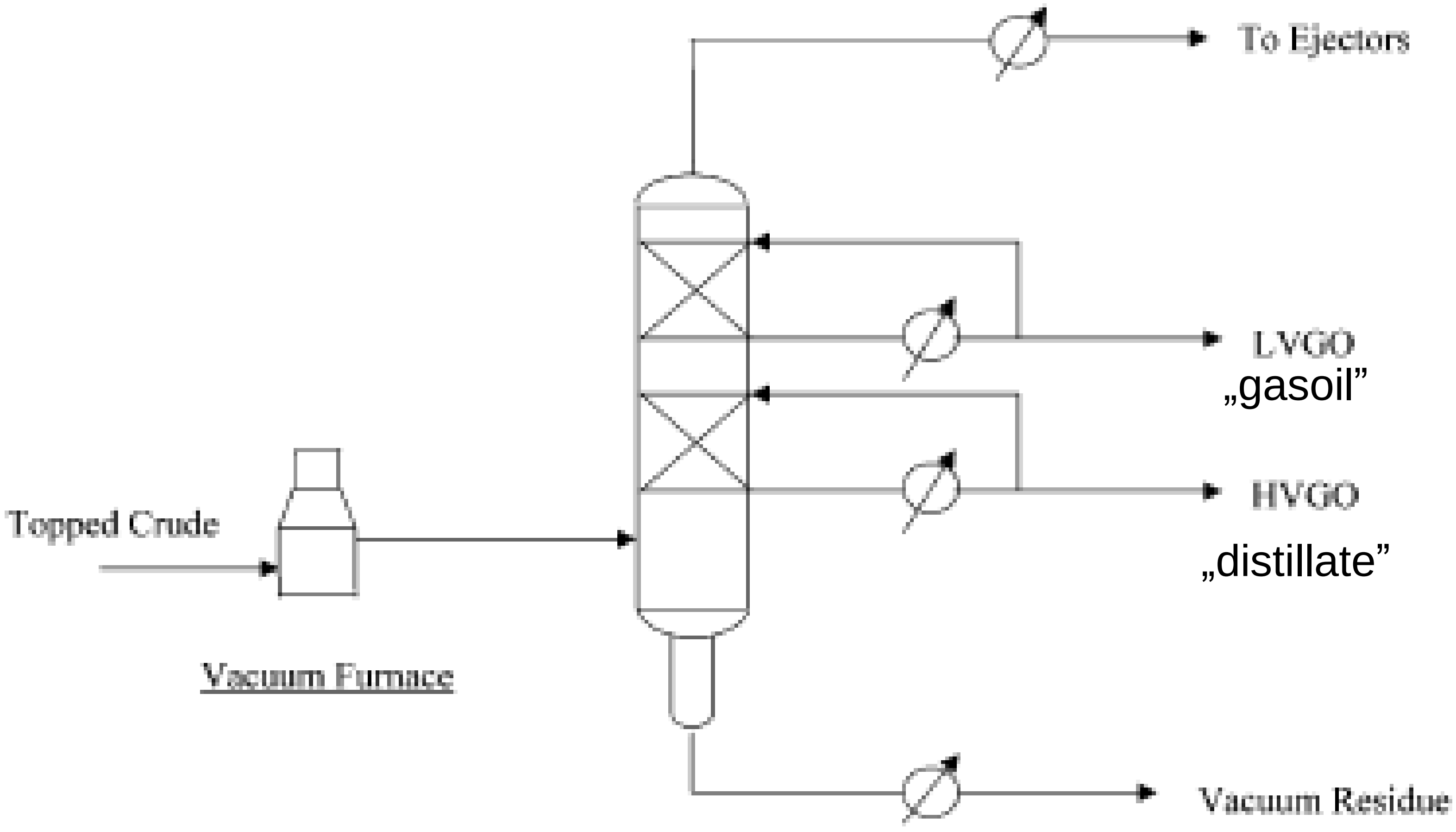
Prefractionation



Stripping



Vacuum distillation



Crude oil distillation units at Danube Refinery

CDU-1

CDU-2

CDU-3

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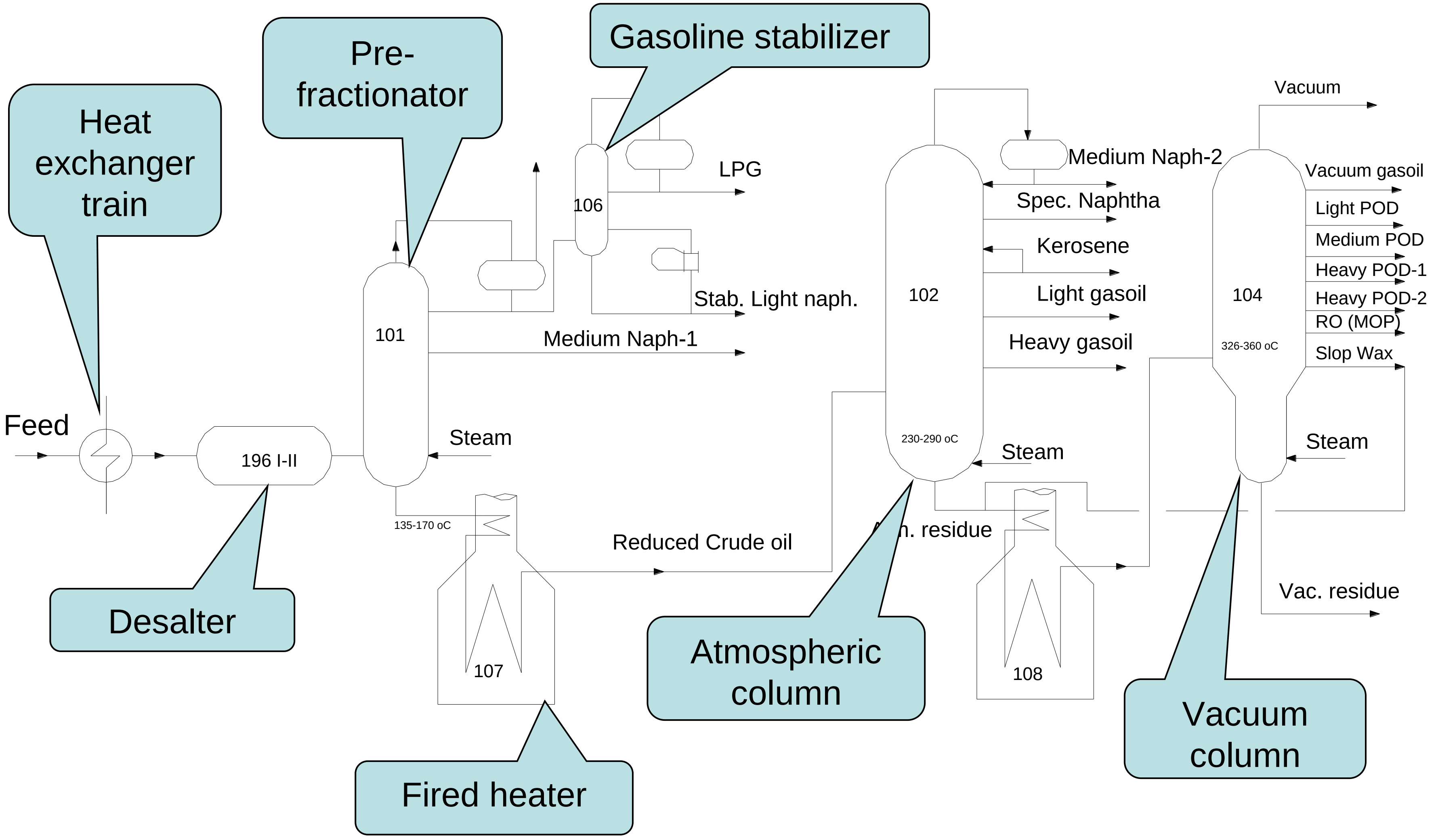
Main sections of a CDU unit



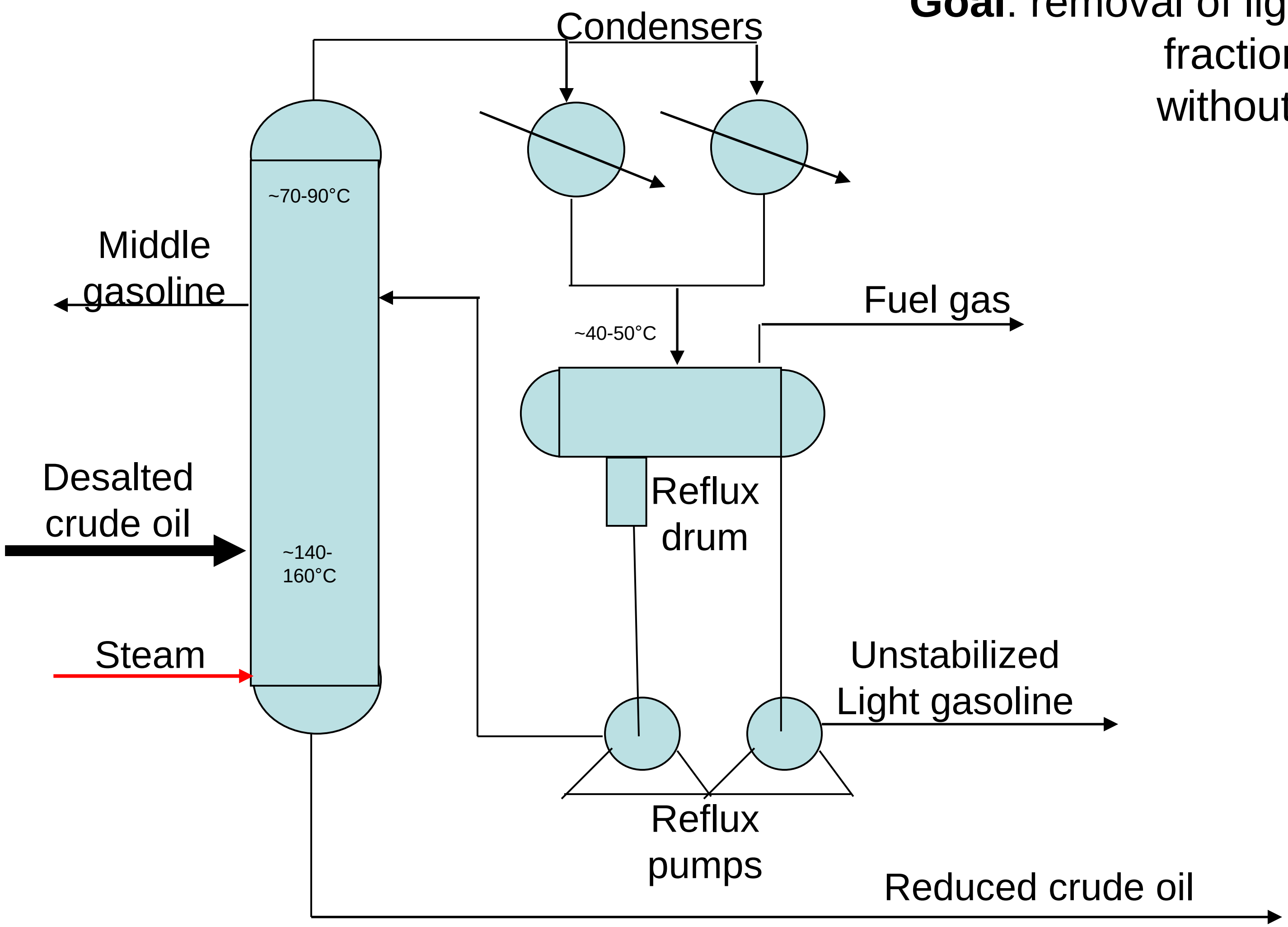
Heat exchanger train

- Upstream of the desalter the crude oil is heated up to 130-140 °C
- Downstream of the desalter the crude oil is further heated up to 200-210 °C
- While the crude oil is heated up, the products and circulation refluxes are cooled down

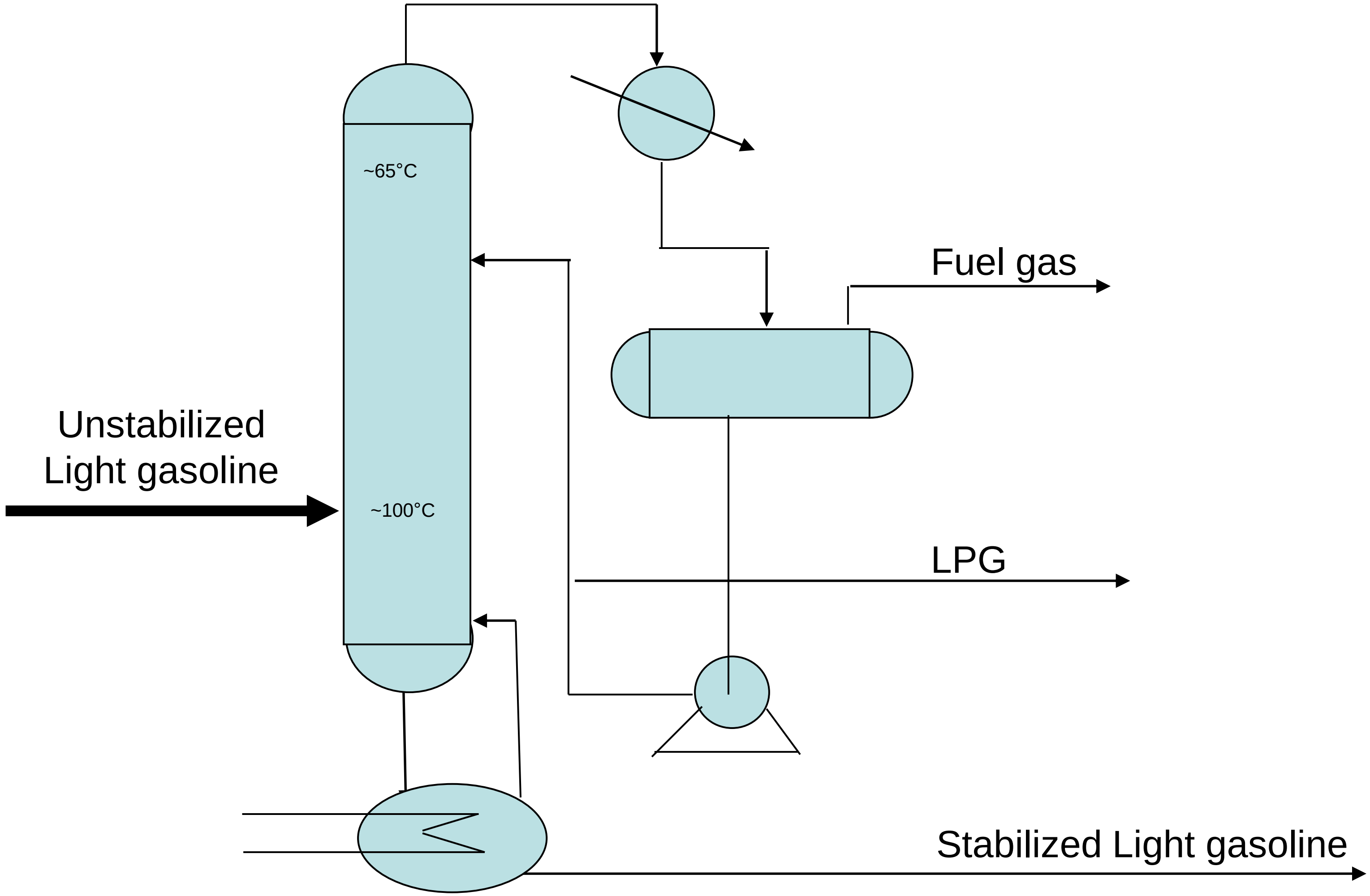
- The good heat transfer (clean exchanger surfaces) is important from energy efficiency viewpoint

Prefractionator

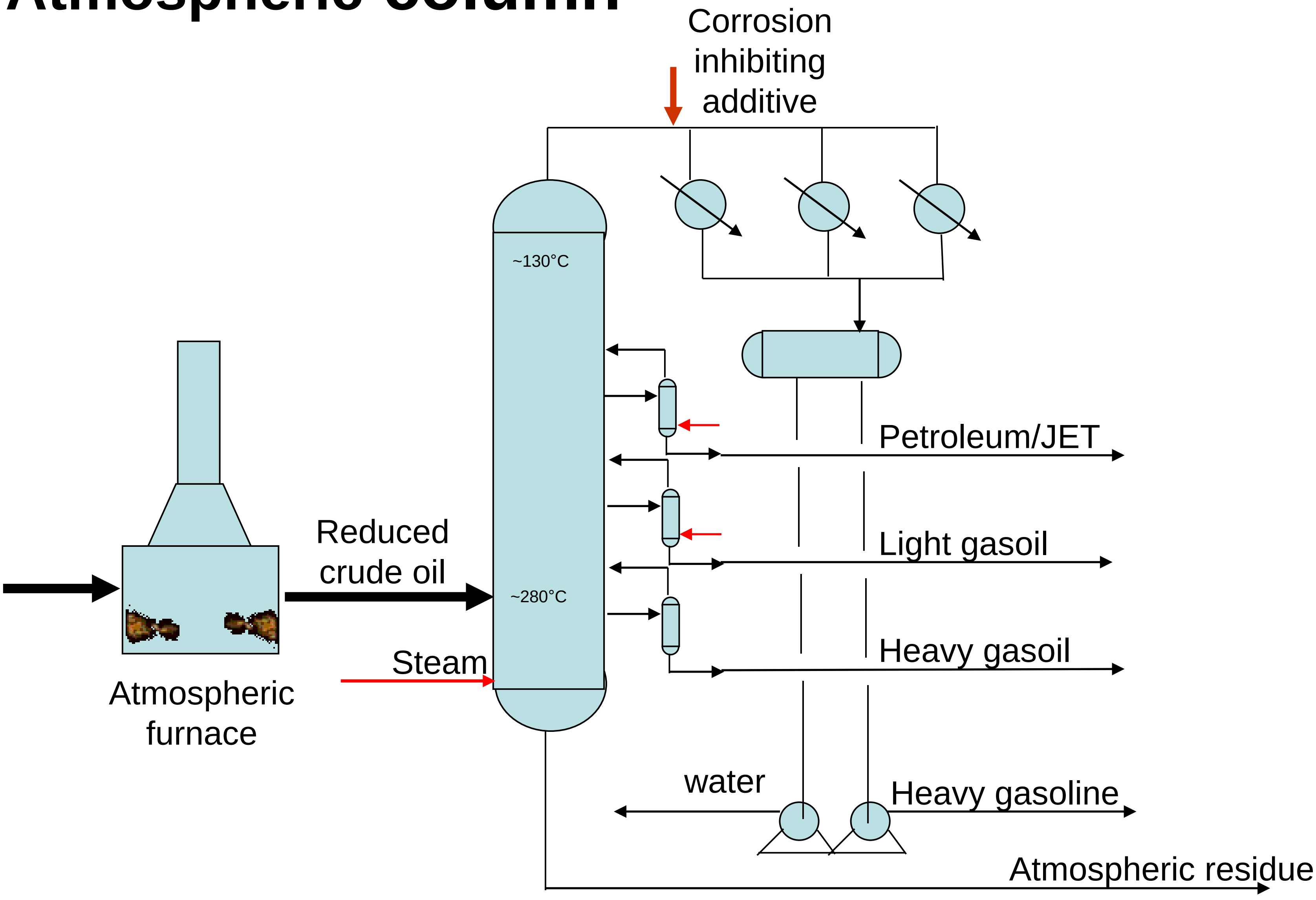
Goal: removal of lighter hydrocarbon fractions from crude oil, without direct heat input



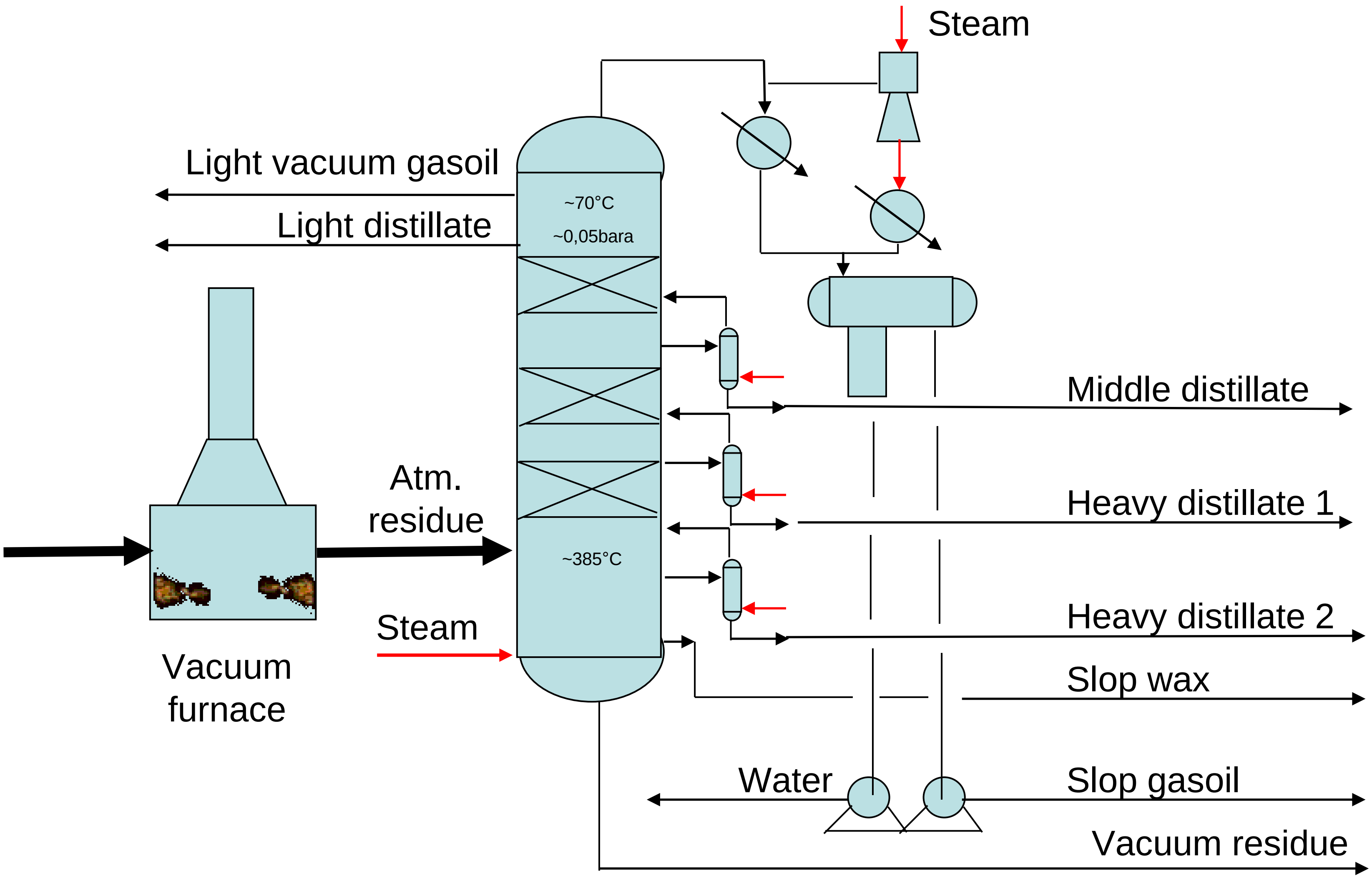
Light gasoline stabilzer



Atmospheric column



Vacuum column



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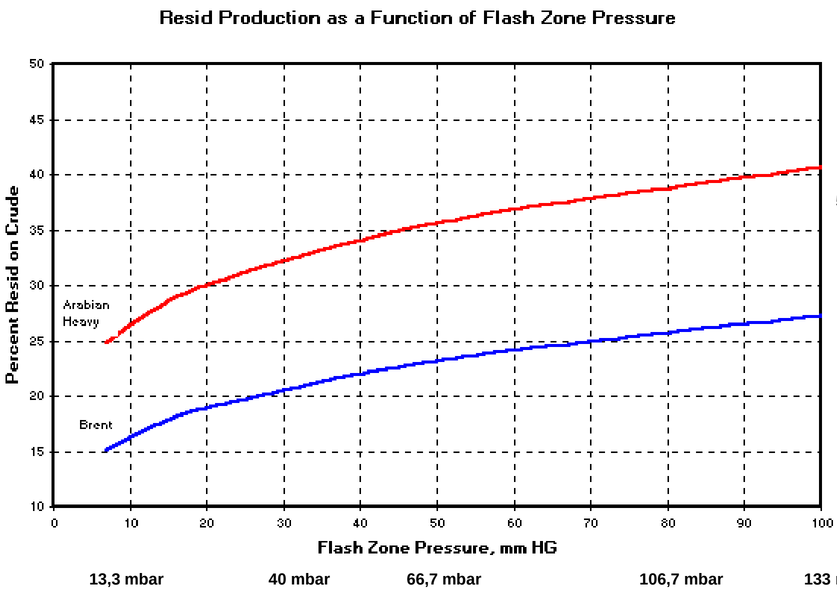
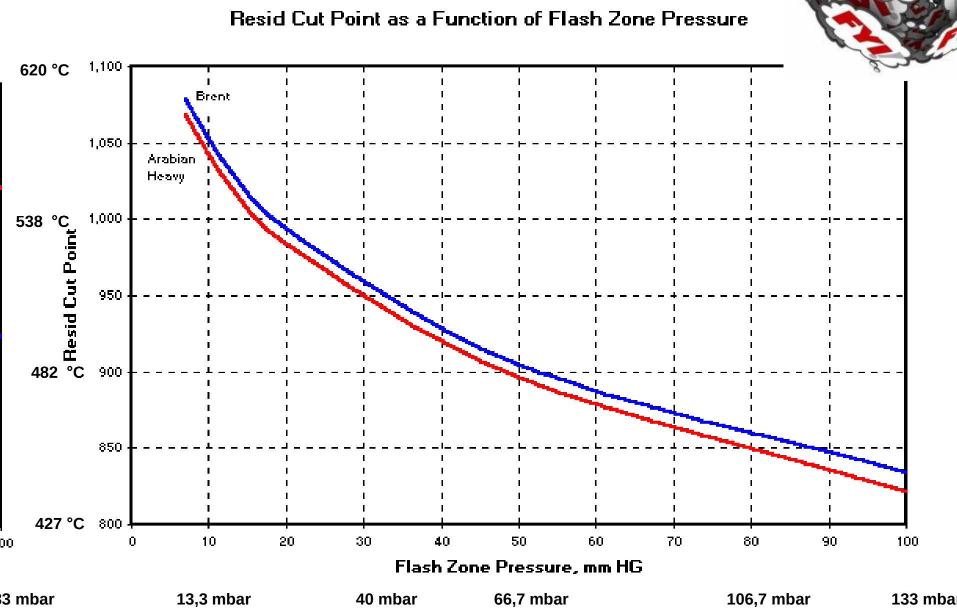
Heavy vacuum gasoil (HVGO) = all distillates together

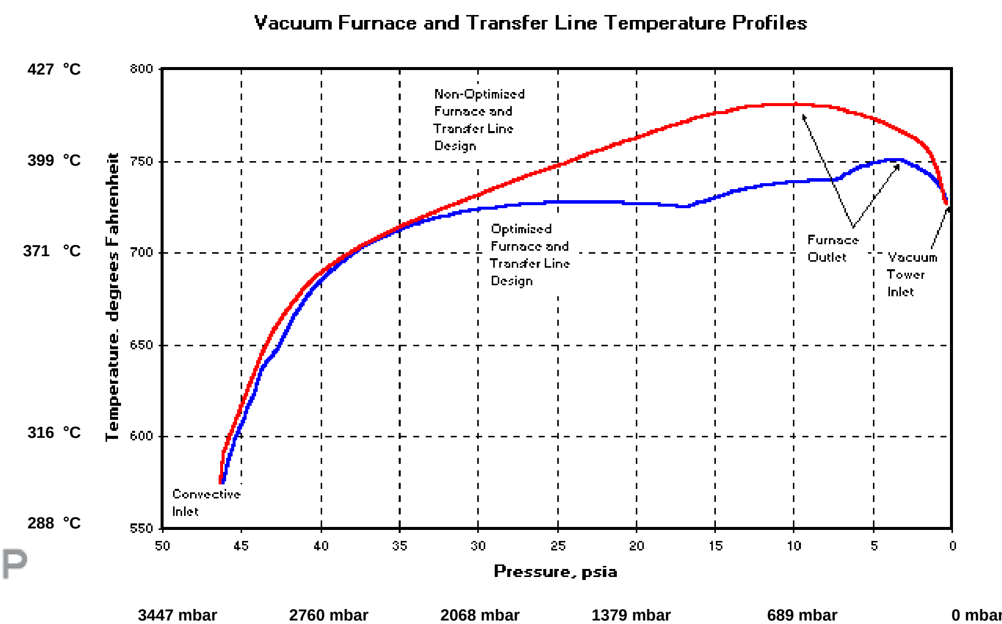
Deep-cut operation

- Goal of deep-cut operation is to maximize the „Distillate” yield an the contrary of vacuum residue
- Definition of deep-cut operation is if the cutpoint of „Distillate” and vacuum residue is higher than 565 °C.
- Conditions of realisation:
  - Low pressure (<50 mbar)
  - Low pressure drop (packings)
  - High fired heater exit temperature (400°C <)
  - Sufficient amount of washing fluid

Deep-cut operation







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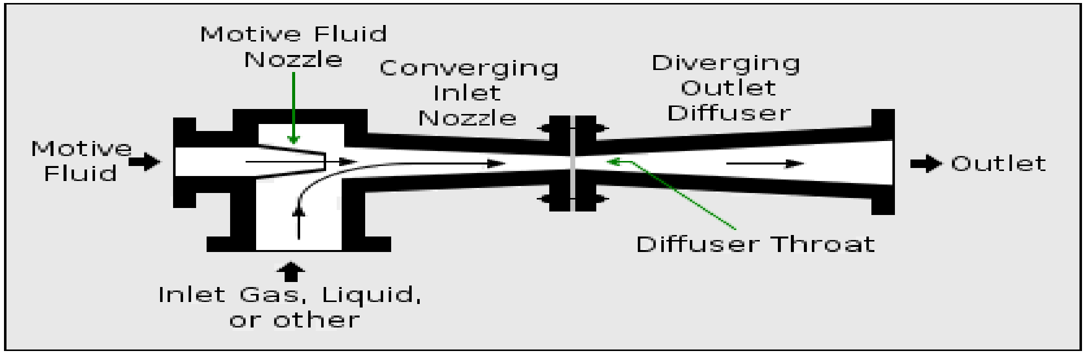
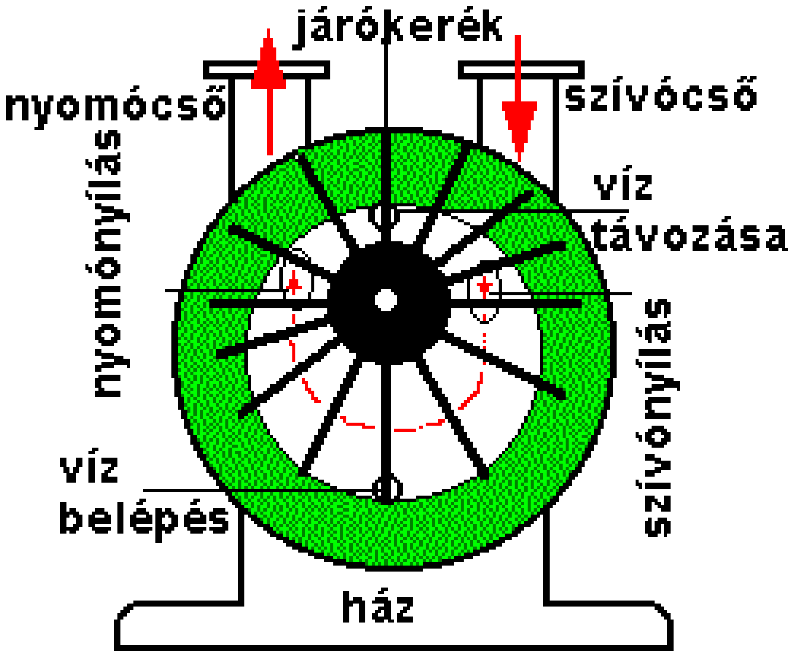
Steam ejector



- The theory is that the speed (with that the moving energy) of the steam entering the converging nozzle will increase due to converging. The increased moving energy is balanced by decreased pressure. The pressure in the space around the nozzle will decrease so gas will be sucked into the nozzle from the surrounding space. In the diverging diffuser the moving energy will decrease and the pressure will increase again.
- Steam ejectors are capable to produce vacuum, even deep vacuum in case of cascading the ejectors. They are cheap, roboust, without moving parts. Attainable vacuum is:
  - 1 stage: 810 Hgmm – 30 Hgmm
  - 2 stage: 130 Hgmm - 3 Hgmm
  - 3 stage: 25 Hgmm - 0.8 Hgmm

Water ring vacuum pumps



- In the laying tube shaped house there is an eccentrically positioned, star shaped rotating vane system. The tube is filled up to ~1/3 with liquid (usually water). The liquid shall not absorb the gas and shall not react with the gas sucked. During operation, water will form a ring due to the centrifugal power. Due to the eccentric position, the chamber volumes between the vanes will alter. Where the chamber volume is increasing vacuum will appear. The inlet nozzle is positioned in this area.

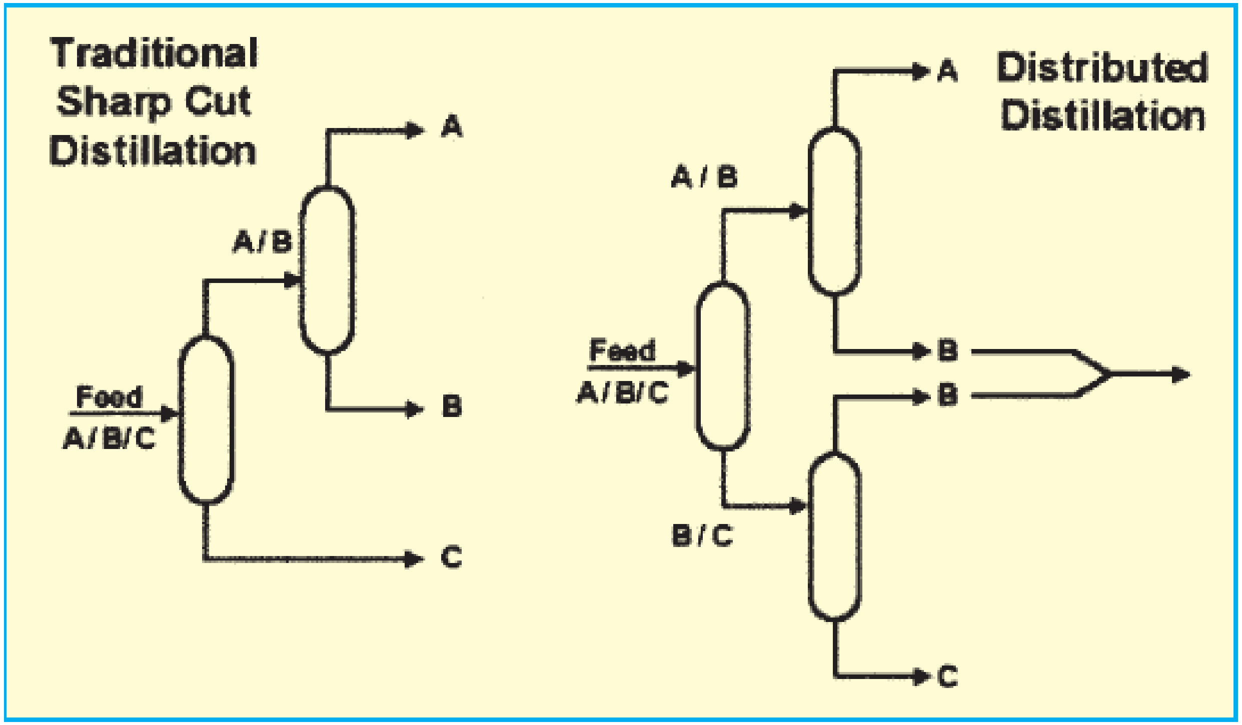
On the other side of the rotor the chamber volumes decrease, the pressure increase. There is the outlet nozzle. The water also functions as a cooling media for the comprimed gas and lubricates the gland. In order to obtain a low vacuum cool water is needed (the vapour pressure of the water will limit the vacuum generation).

Fired heaters – fuel gas and/or fuel oil

- Side burners

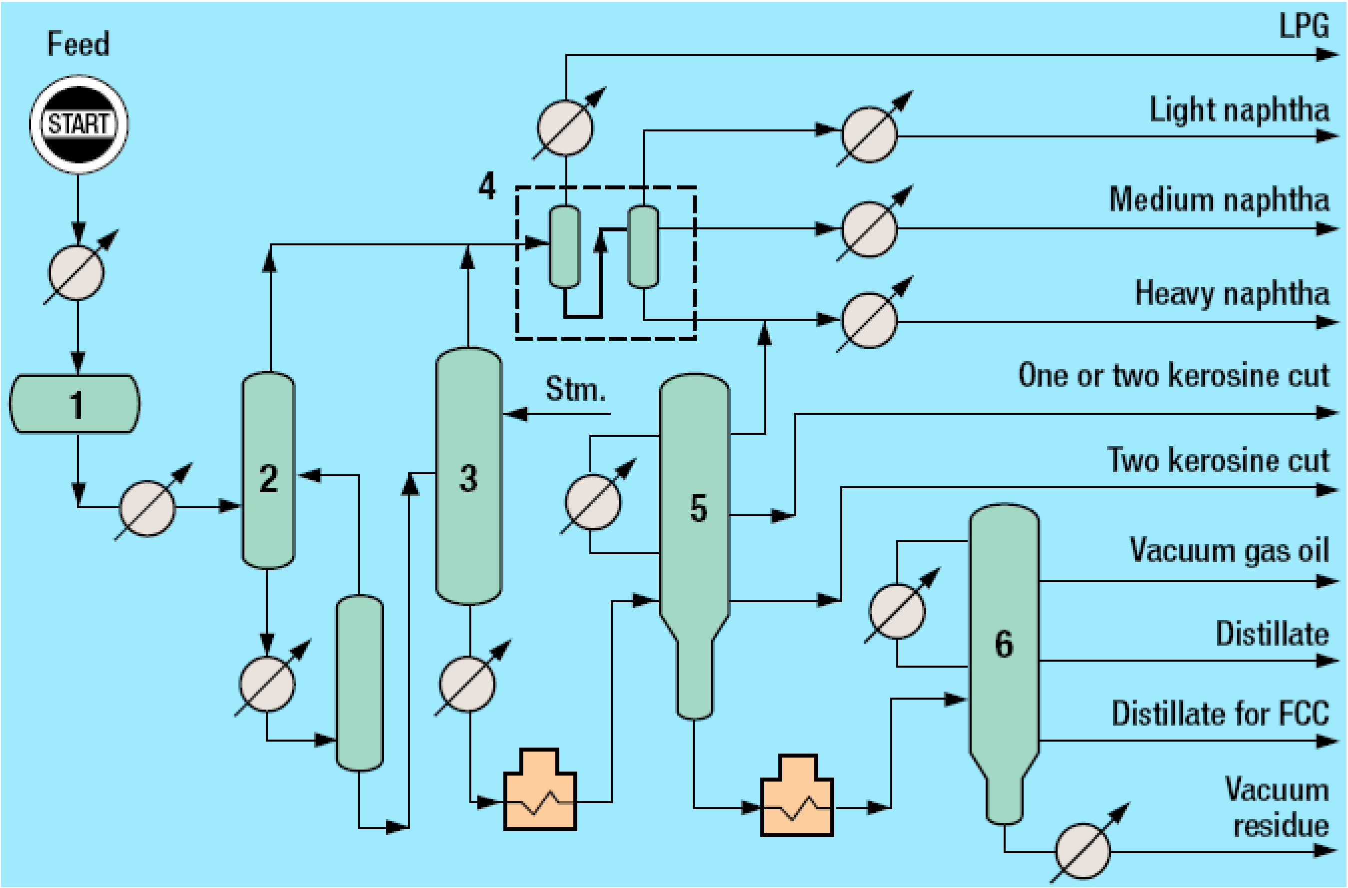
- Bottom burners

Distributed distillation



- The theory of distributed distillation is to minimize the number of sharp cuts. In the traditional sequence, the separation is done according to the relative volatility of the key components. *Separation of components A, B and C in two columns will not utilize the distribution of B in the first column.*
- During the distributed sequence, in the first column components A and C will be separated definitely, reducing the energy demand of the column. Component B will be separated as in column number two and three, as top/bottom component.

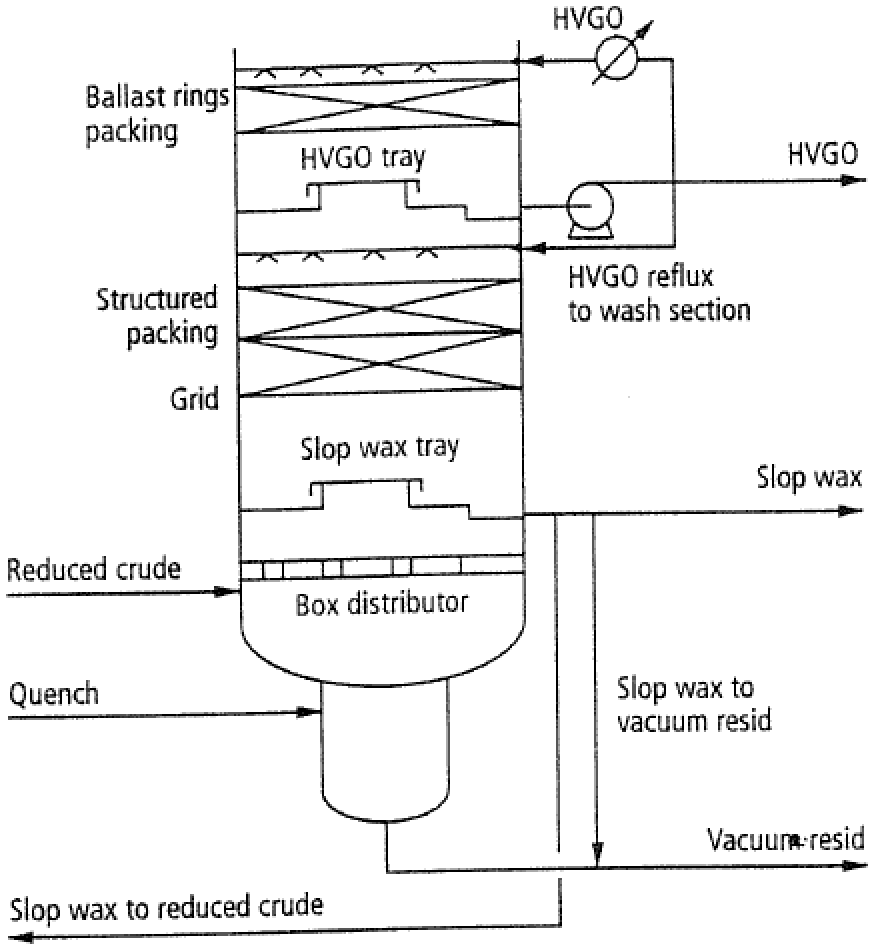
Crude separation by distributed distillation

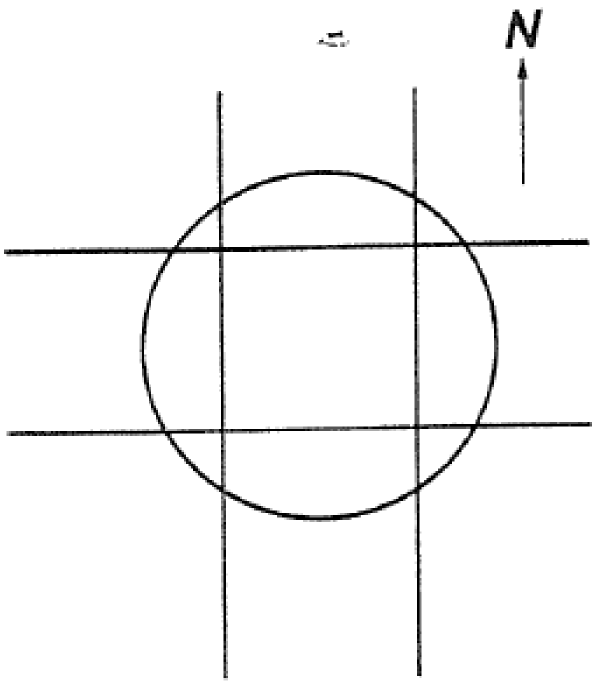


Licensor:
Technip

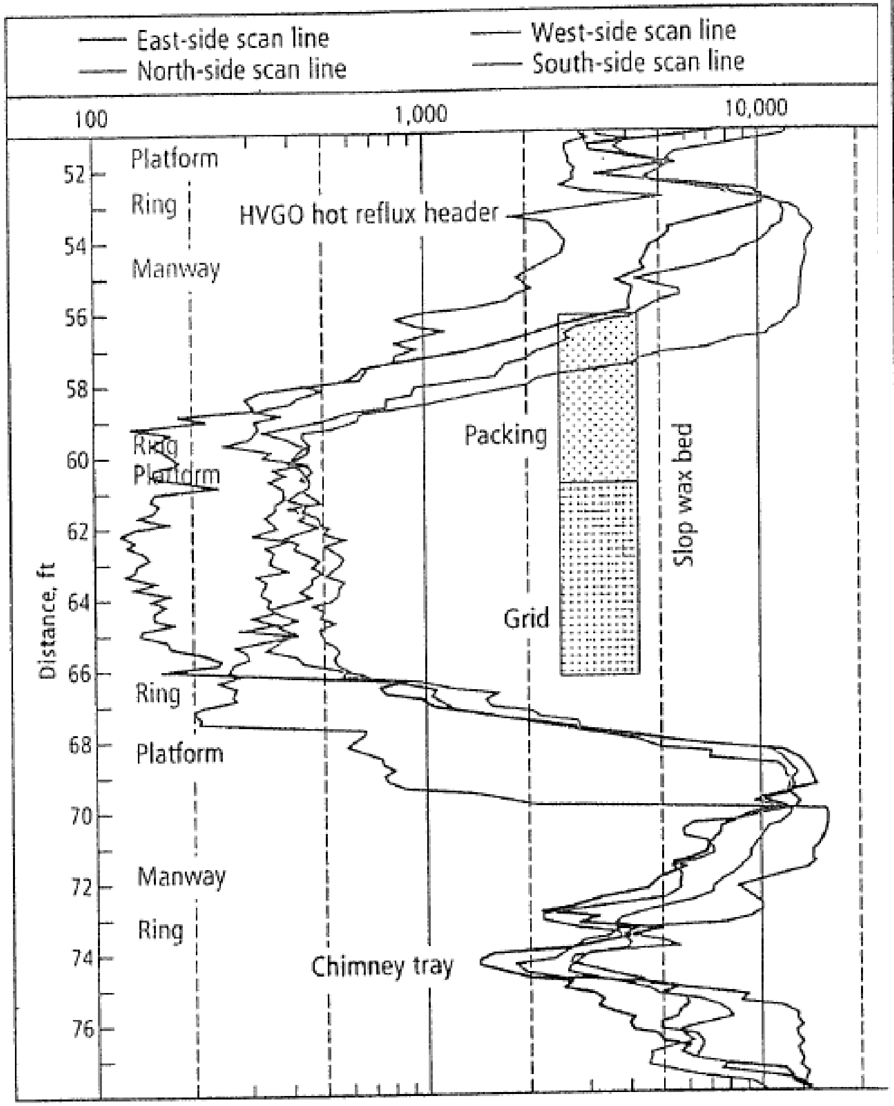
The Technip process was optimized for the following scheme: **three gasoline, one/two petroleum, two atmospheric gasoil, one LVGO, two HVGO and vacuum residue cuts.**

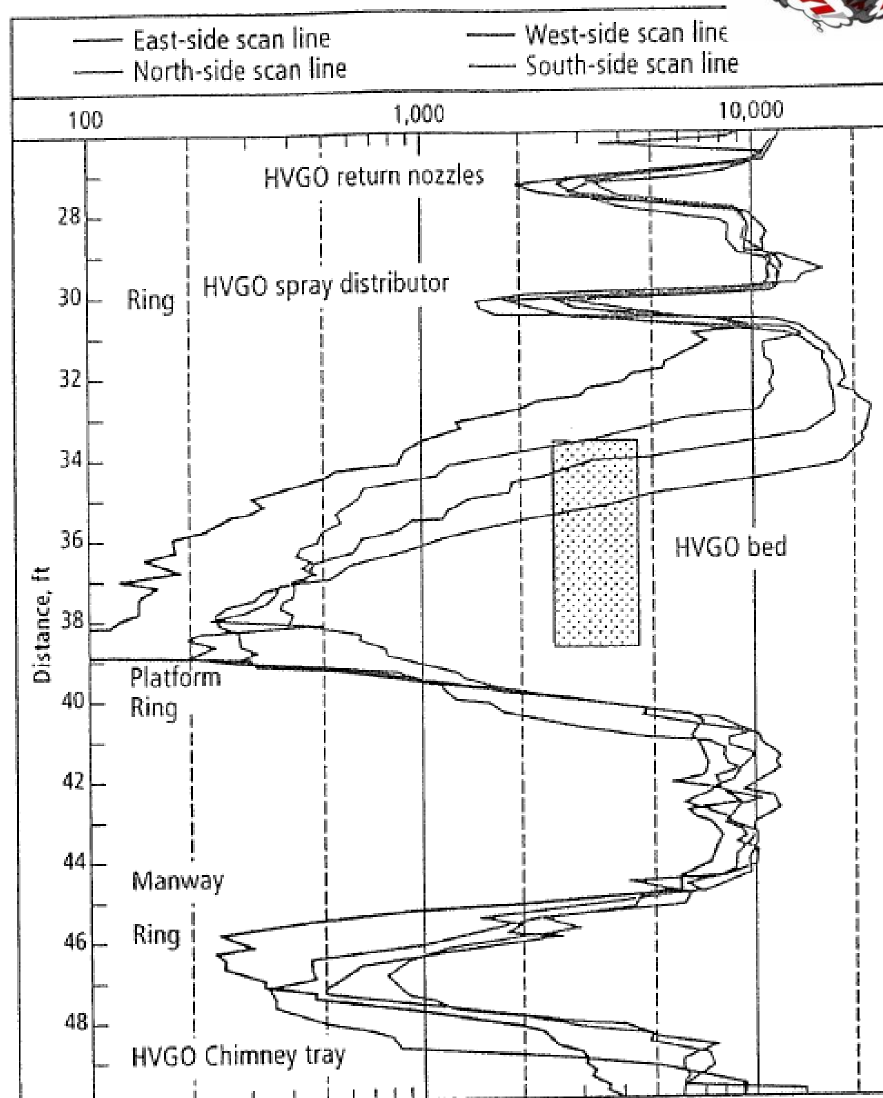
Column operation examination - Gamma scanning





Gamma scanning






Thank you for your kind attention!