

NETFLIX

EXTRACTION
OFFICIAL TRAILER



Theory of extraction

- ▶ Extraction: *solving* a predefined (valuable or undesired) components *selectively* from a solid, liquid or gas mixture by the means of a solvent
- ▶ The extraction will not directly yield pure components, the solvent must be regenerated

Main tasks during extraction:

- ▶ *intense contact and mixing* of the raw mixture and the solvent
- ▶ *sufficient contact time* in order to allow the material transport of the desired component between the phases
- ▶ *separation of the two phases* produced during extraction (raffinate and extract)



Extraction **types** in a refinery

- ▶ liquid – liquid extraction: aromatic extraction
- ▶ supercritical extraction: asphaltenes extraction
- ▶ gas – liquid extraction: sour gas/fuel gas desulphurisation

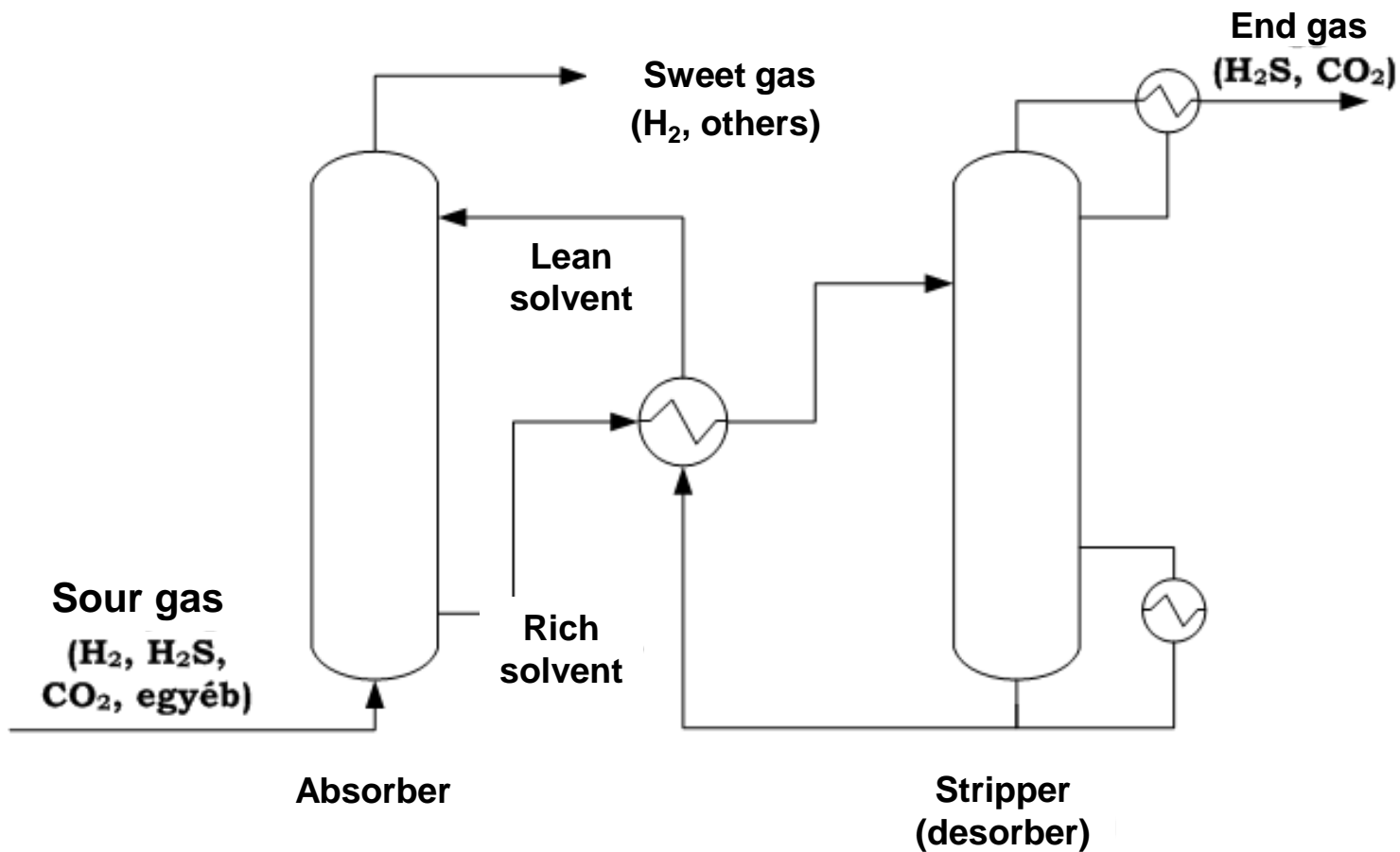
Hydrogen-sulphide removal from refinery gases

Sources of light gases

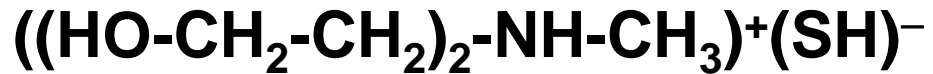
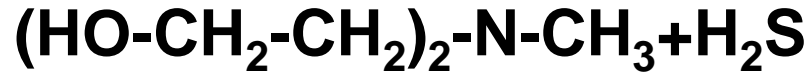
- **Low H₂S content** – fuel gas
 - Crude oil – primary distillation
 - Originally present in the crude oil
 - LPG fractionation
 - Reforming
 - ...
- **High H₂S content** – H₂ rich gases
 - Hydrotreaters – blowdown gas
 - FCC – sour gas

Important

Hydrogen-sulphide removal from high hydrogen concentration gases



The reaction (MDEA)



Most frequently used absorbents

Absorbent	MEA	DEA	MDEA
Molecular weight	61	105	119
Concentration (vol%)	15	30	50
Minimum H ₂ S load ($n_{\text{H}_2\text{S}}/n_{\text{amine}}$)	0,05	0,02	0,01
Maximum H ₂ S load ($n_{\text{H}_2\text{S}}/n_{\text{amine}}$)	0,6	0,6	0,5
Capacity (H ₂ S/dm ³)	1,77	2,18	2,77

MEA: mono-ethanol-amine

DEA: di-ethanol-amine

MDEA: methyl-di-ethanol-amine

Liquid – liquid extraction

- ▶ The components of the raw mixture are separated by contacting the mixture with a non miscible solvent
- ▶ **The method of extraction**
 - ▶ liquid transfer from one liquid phase to the other one
 - ▶ the end of the process: **dynamic equilibrium** (concentration)
 - ▶ **driving force**: concentration difference between the actual vs. equilibrium concentration
 - ▶ process steps: mixing, settling, separation



Liquid – liquid extraction

L-L extraction: potential applications

- L-L extraction is more economic than the distillation, if **the liquid mixture boiling range is high and the valuable component is present at low concentrations.**
- If the **boiling point difference** of the liquid components to be separated is **small**
- Further separation of the **azeotrope mixture**, formed during distillation or rectification
- If the component to be separated is **sensitive to heat**, or it disintegrate at higher temperatures

Requirement towards the solvent

- To be **selective**
- To have low volatility
- To be cheap and regenerable
- Not to be solved in the liquid mixture
- Not to be corrosive nor toxic

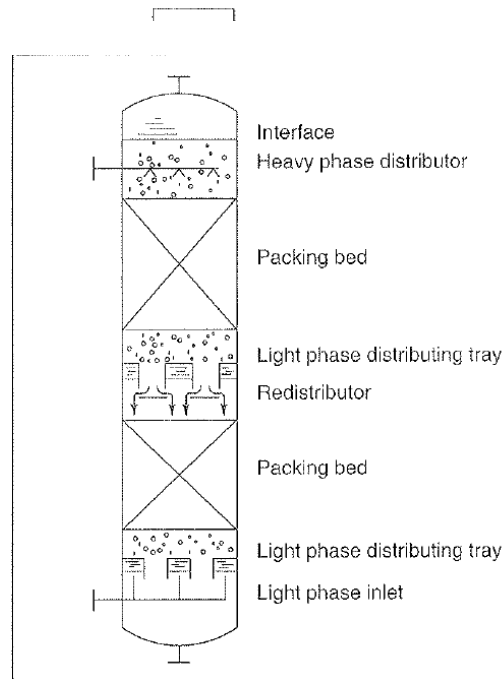
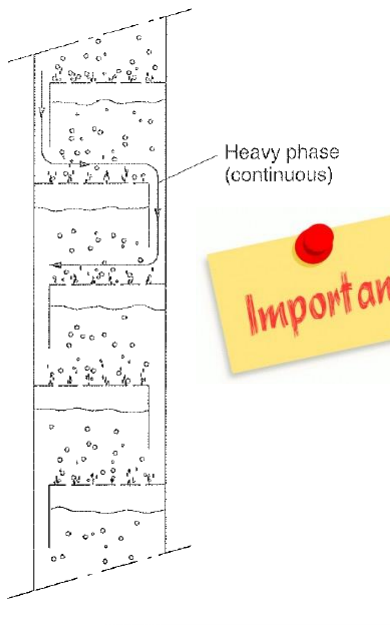
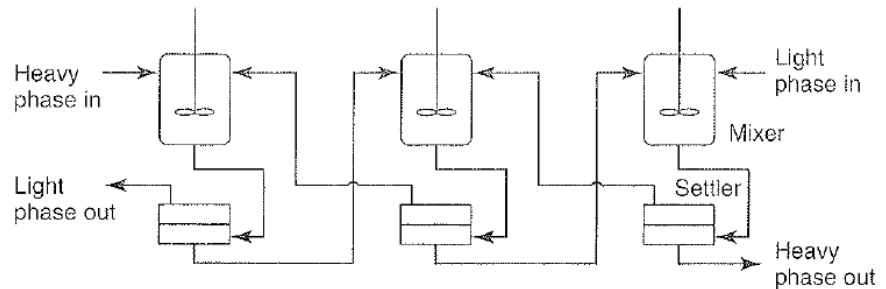
Liquid – liquid extraction

Layout

- batch: mixing and separation in the same device
- continuous: raw mixture input at one side, solvent on the other

Equipment

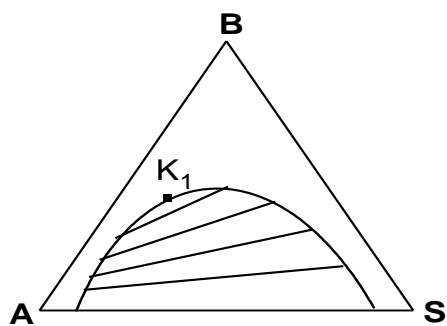
- Sieve trayed column
- Packed column
- Stirred column



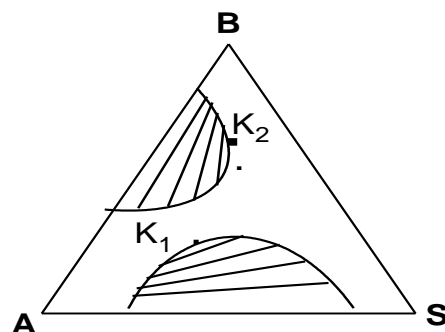
Liquid – liquid extraction equilibrium

If you mix two different liquid at under given temperature and pressure

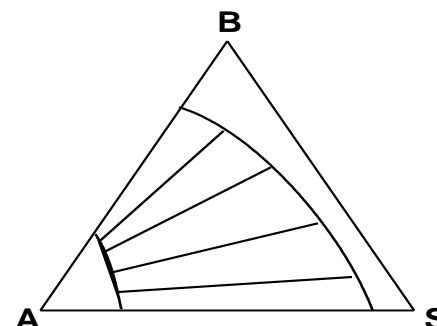
- they may mix perfectly,
- they may limitedly mix
- they do not mix and will form two separate phases



One critical mixing point



Two critical mixing points



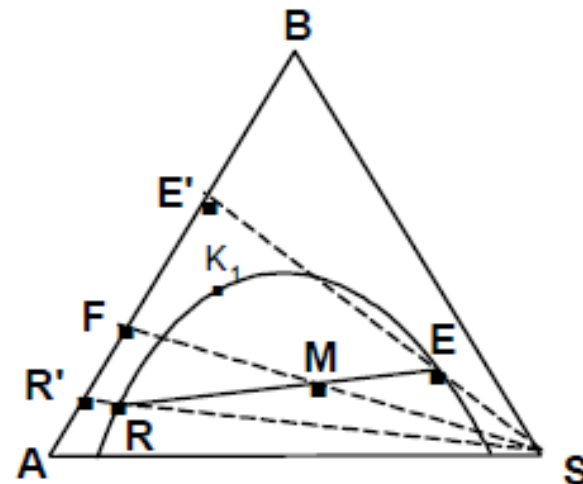
No critical mixing point

- Limited mixing territory – area below the curve (heterogeneous phase)
- Unlimited mixing territory – area above curve (homogeneous phase)
- Binodes – straight lines interconnecting compositions of two phases in equilibrium
- K – critical mixing points



One step L–L extraction

A , B are unlimitedly intermixing two liquids. After adding S solvent (S is mixing with A limitedly) the next diagram is produced. If you know F composition (of A and B), quantity of S and the binode, the composition of M (actual working point) can be received. If the quantity of S is adequate, than two phases will be formed: E extract and R raffinate.

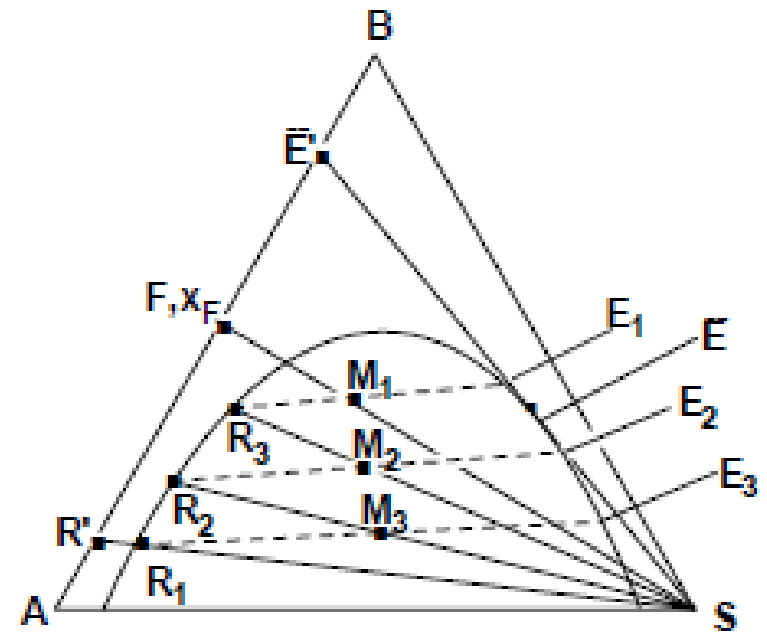
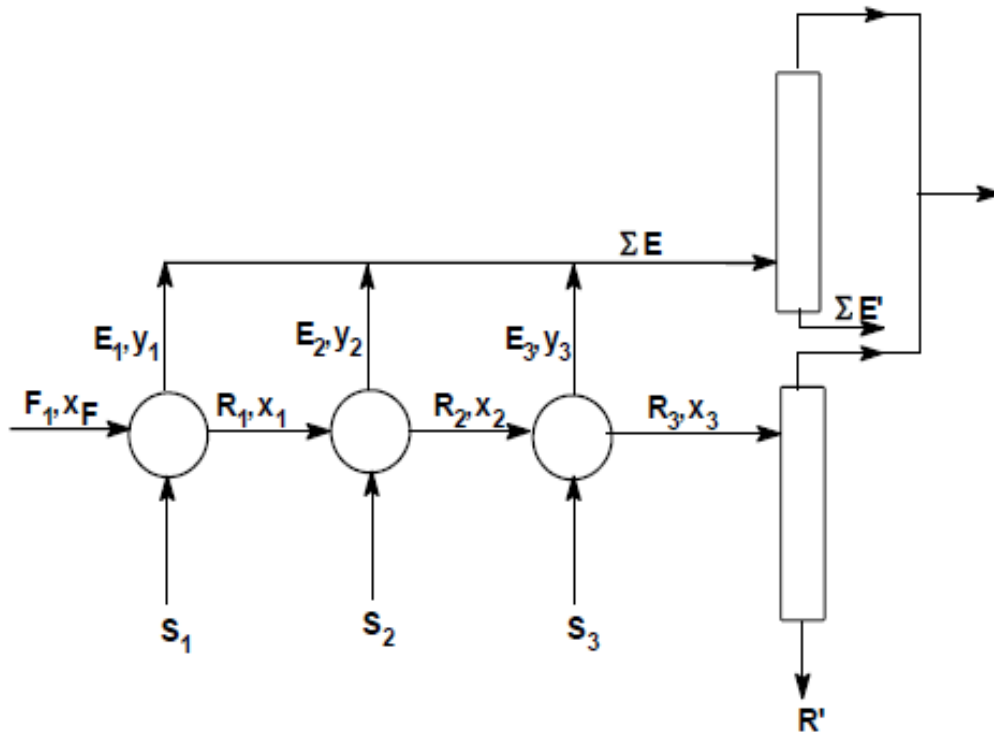


After separating the two phases and removing the solvent from extract and raffinate, E' és R' composition phases will be present.



Multi step L-L extraction with fresh solvent in every step

If there is significant amount of valuable component in raffinate after the first extraction step, than after phase separation the raffinate may be extracted once again. This may be executed several times



Industrial utilisation of extraction

- Pigment removal from plants
- Active agent removal from herbs
- analytics: grease-oil investigation
- Pharmaceutical industry
- Oil industry
 - aromatics extraction with TEG (tetra-ethylene-glycol)
 - asphaltene removal from vacuum residue with propane (SDA = Solvent DeAsphalting)
 - distillate extraction with NMP (N-methyl-pyrrolidone)

Aromatic production

Important

Simple aromatic production scheme

Pygas (Steam cracker naphtha)

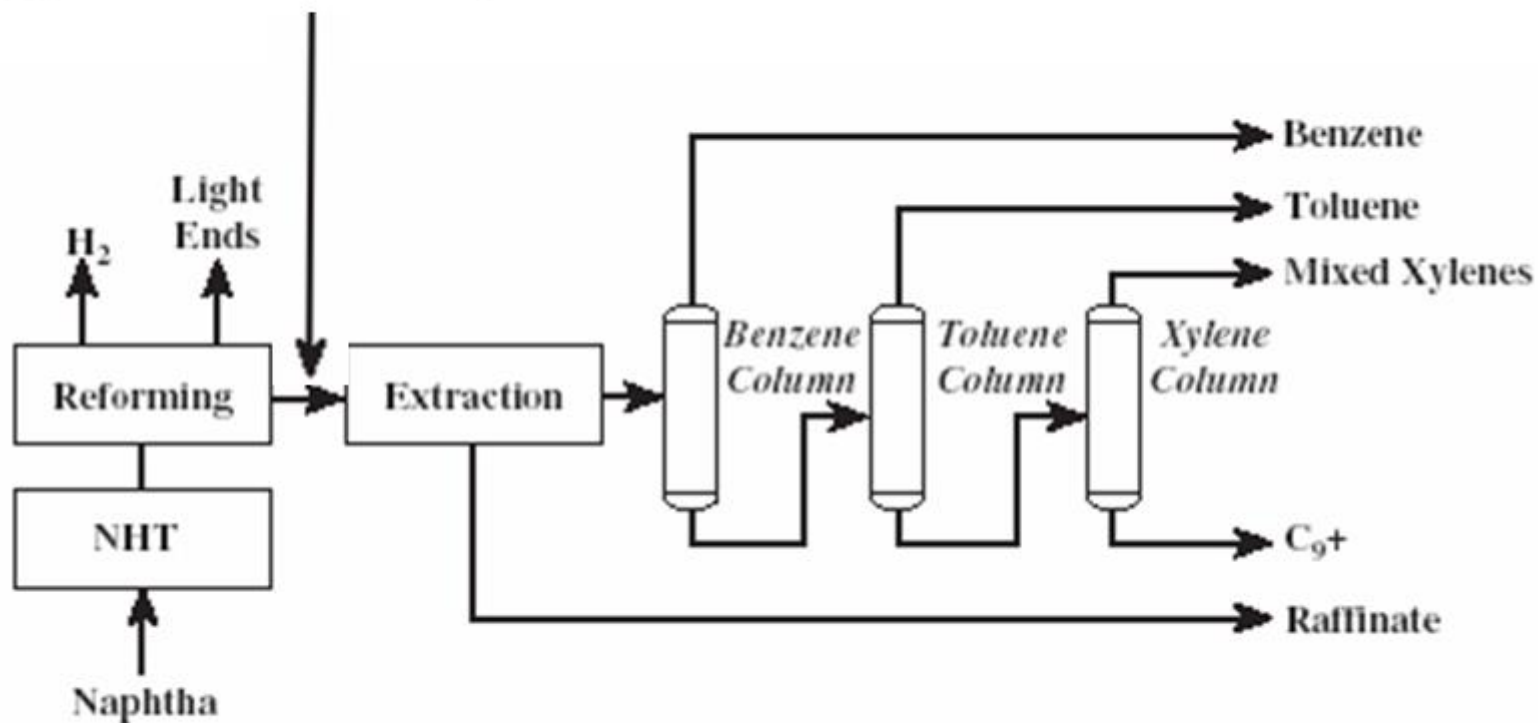
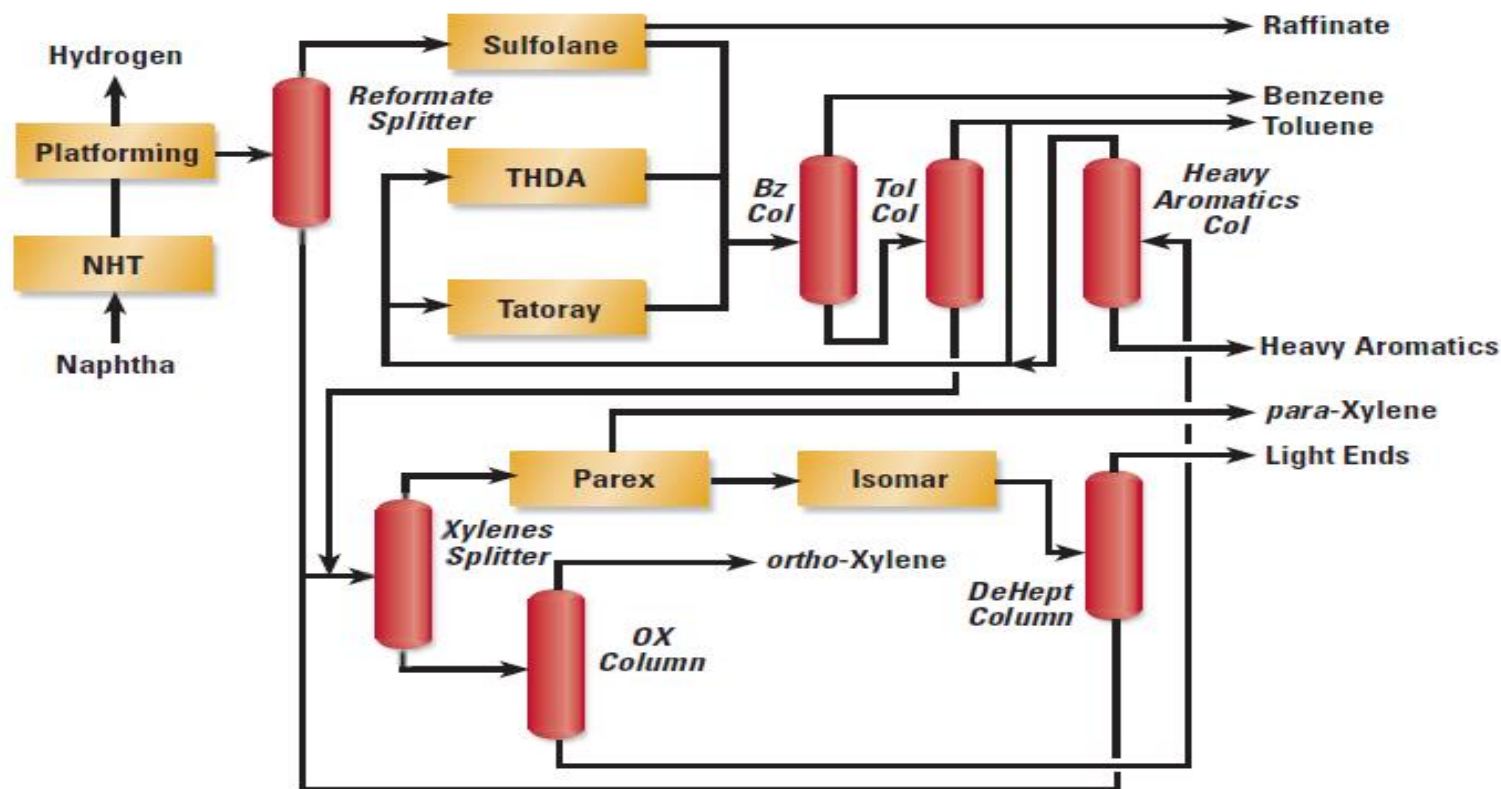


FIGURE 2.1.3 Simple aromatics complex.

Integrated aromatic production scheme – UOP



Sulfolane™ Process – removes benzene and toluene from reformate via extractive distillation

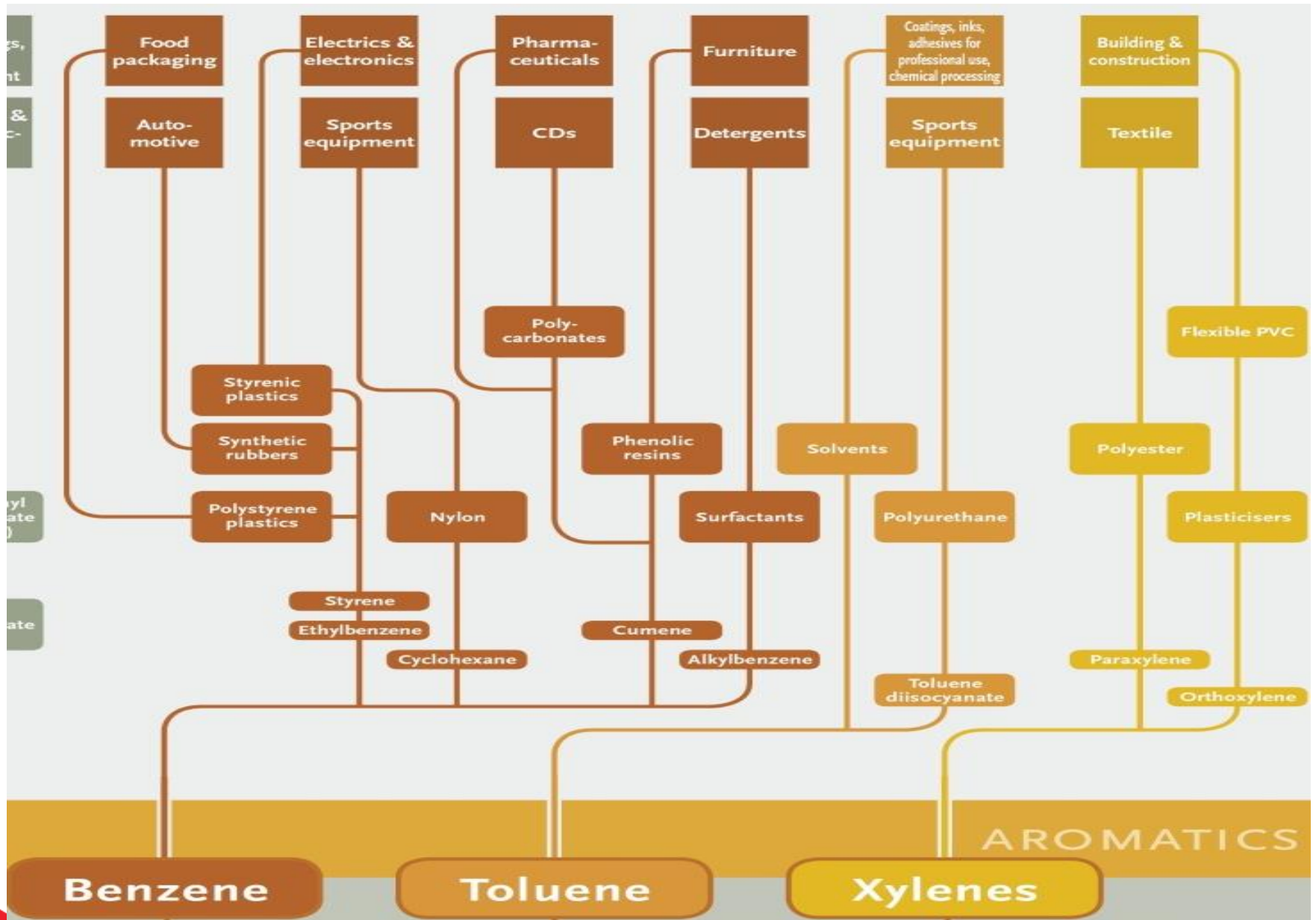
THDA™ Process – thermal hydro-dealkylation of toluene and heavier aromatics to benzene

Tatoray™ Process – toluene and C9/C10 aromatics trans-alkylation to benzene and xylenes

Parex™ Process – high purity para-xylene removal from C8 aromatic mixture

Isomar™ Process – equilibrium composition xylene mixture production

Usage of individual aromatic components



Further usage of xylene mixtures

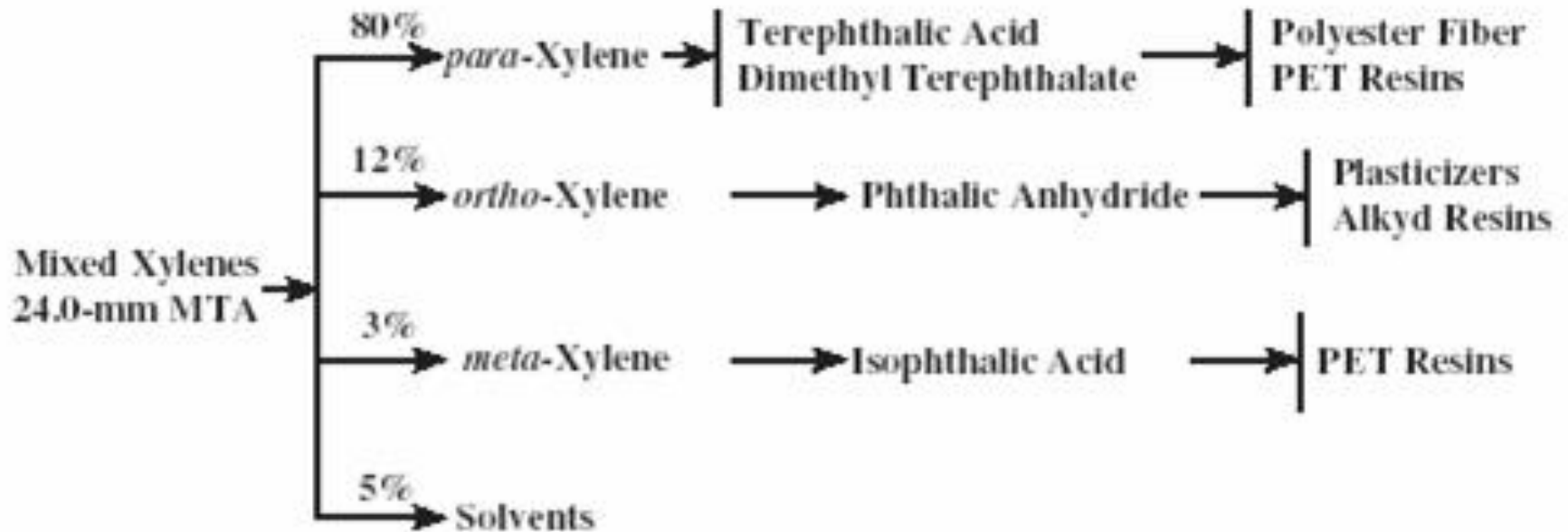


FIGURE 2.1.2 World xylenes consumption, 1999.

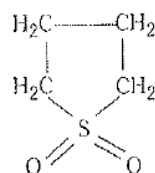
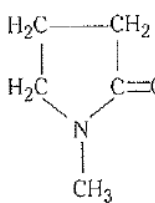
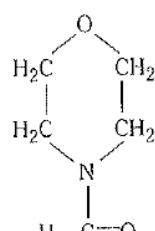
Requirements of the extracting solvent

- ▶ **High selectivity**
- ▶ **Thermal stability**
- ▶ Chemical stability
- ▶ Low toxicity
- ▶ Low corrosivity
- ▶ Good availability
- ▶ Moderate cost
- ▶ Low enough crystallisation temperature
- ▶ **Boiling point well above o-xylene boiling point** ($T_{bp} \approx 140 \text{ }^\circ\text{C}$)
- ▶ Specific gravity at least 1.1
- ▶ Viscosity at operating temperature lower than 2,5 mPas

- ▶ Solvent chemical structure
 - ▶ Small hydrocarbon ring and a polar group (this allow to solve in water and selectively in aromatics)



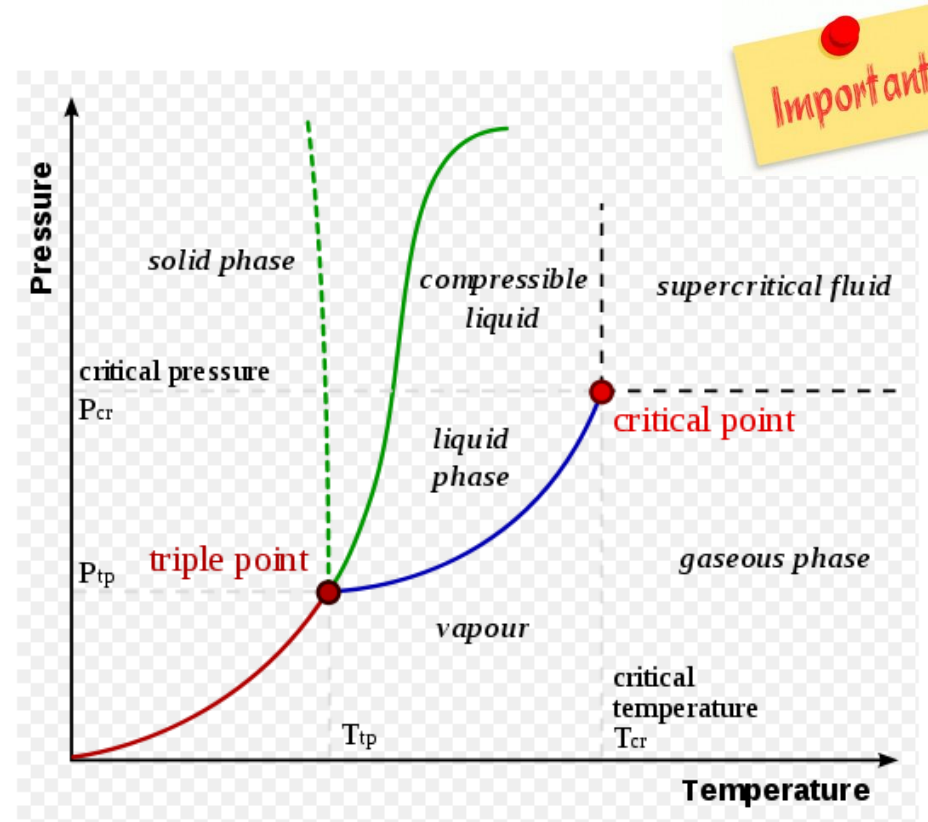
Aromatic extraction solvents

Pure solvent	Developed formula	M (kg/kmol)	T_f (°C)	T_b (760 mmHg) (°C)	ρ (kg/m ³) (at 20°C)	μ (mPa.s) 0 (°C)
Diethyleneglycol (DEG)	$H(OCH_2-CH_2)_2OH$	106.1	-8	245	1 116	35.7/20 0.97/140
Triethyleneglycol (TEG)	$H(OCH_2-CH_2)_3OH$	150.2	-7	288	1 123	49/20 0.70/140
Tetraethyleneglycol (TETRA)	$H(OCH_2-CH_2)_4OH$	194.2	-4	291 (300 mmHg)	1 125	61.9/20 1.8/150
Sulfolane		120.2	27.6	287	1 266 (at 30°C)	10.3/30 2.5/100
N-methylpyrrolidone (NMP)		99.1	-24.4	202	1 027	1.65/25 1.3/30
N-formylmorpholine (NFM)		115.1	20	244	1 150	8.13/20 0.65/150
Dimethylsulfoxide (DMSO)	$CH_3-S(=O)-CH_3$	78.1	18.5	189	1 080	1.99/25 1.6/35

Supercritical extraction

Supercritical extraction

The valuable component is dissolved from solid or liquid raw material by the means of solvent, being in supercritical state. The extracted material is separated from the solvent by depressurization (or by adsorption, absorption).



The pressure, to be applied at critical temperature in order to make occur liquefaction, is called critical pressure.

If the material, heated above its critical temperature, is pressed with higher than its critical pressure, the **material will stay homogeneous, supercritical fluid state will come into existence.** The exceptionally big advantage of this close-to-supercritical-point state is that small alteration regarding the pressure will cause great alteration in specific gravity. **Since the sp. gravity has a great effect on the solubility of the fluid, varying the pressure you may alter the solubility of the solvent in a wide range.**

Applications of supercritical extraction

➤ Food industry applications

- caffeine extraction from green coffee bean
- nicotine removal from tobacco
- spices extract (e.g. cinnamon, ginger, vanilla)
- active ingredient removal from herbs (e.g. chamomile)

➤ Environmental applications

- purification of polluted soil (e.g. polycyclic aromatic hydrocarbons, polychlorinated biphenyls, chlor-phenols, dioxins and oil pollution)
- removal of traces of insecticide from plants

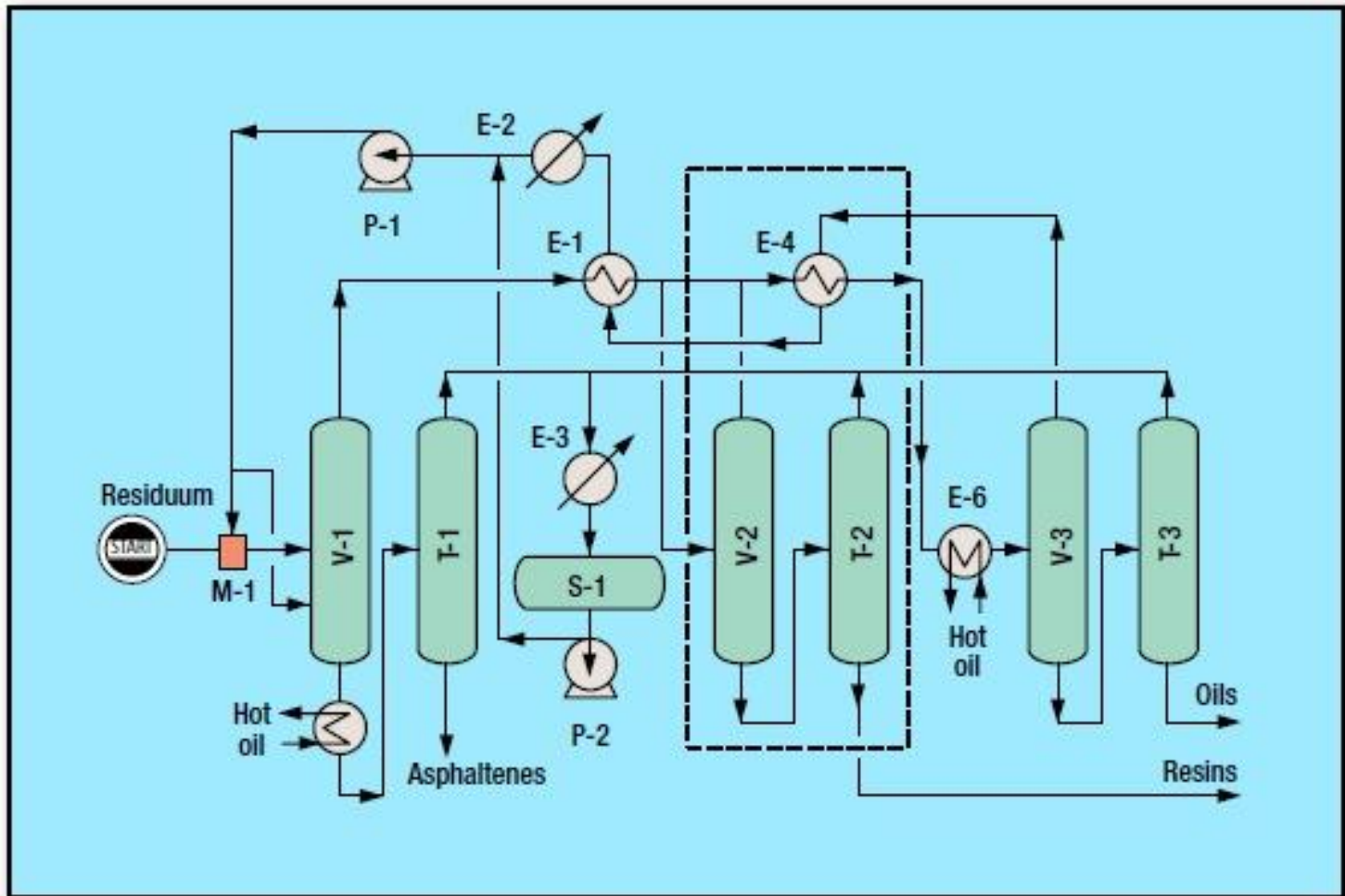
➤ Oil industry applications

- Vacuum residue extraction with C3/C4/C5 solvents

➤ Advantages:

- No Fired heaters
- No Compressor
- High degree of heat integration

ROSE deasphalting process by KBR



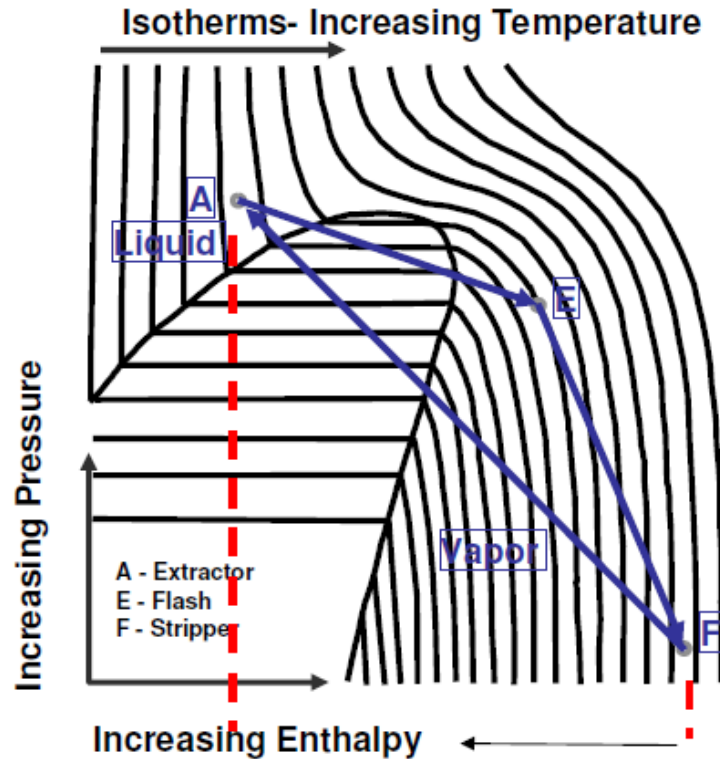
ROSE = Residuum Oil Supercritical Extraction

ROSE deasphalting process by KBR

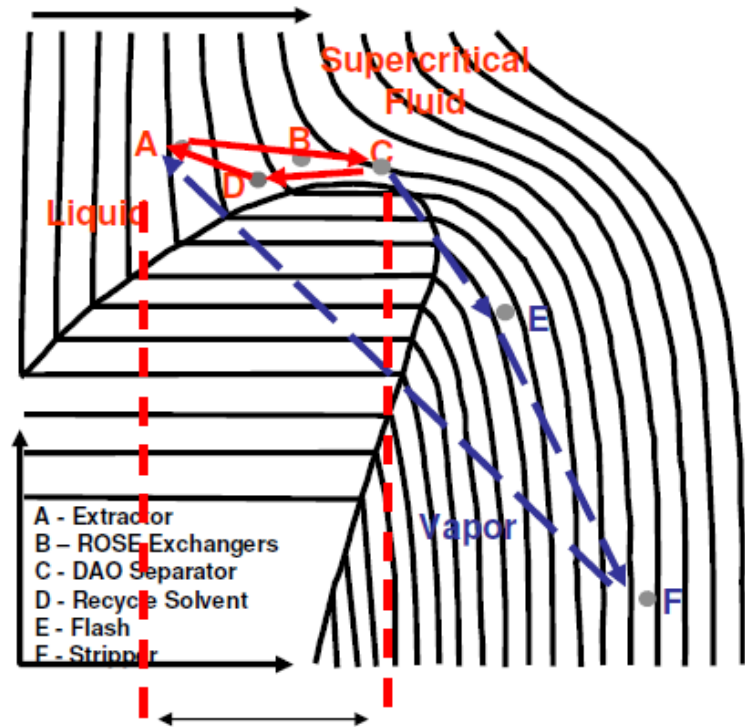
- Resid is charged through a mixer (M-1), where it is mixed with solvent before entering the asphaltene separator (V-1), which uses special ROSEMAX™ internals to achieve maximum benefit of counter current solvent flow. The solvent extracts primarily non-asphaltenic, paraffinic deasphalted oil (DAO).
- The asphaltene-rich stream leaves from the bottom of the separator and after being further heated enters the asphaltene stripper (T-1). The extracted oils and solvent flow overhead (V-1) through heat exchangers (E-1, E-4, E-6) so that the **solvent reaches conditions where it exists as a supercritical fluid in which the oil is virtually insoluble.**
- Recovered solvent leaves the DAO separator top (V-3) to be cooled by heat exchanger (E-4, E-1) and a cooler (E-2). The only solvent vaporized is a small amount dissolved in fractions withdrawn in the separators. This solvent is recovered in the DAO product stripper (T-3). The DAO is leaves from the bottom of the DAO stripper.
- Alternately an intermediate resin rich product can be produced in V2 and T2.
- **Solvents range from propane through hexane** and almost always are streams produced in refineries.

Conventional vs. supercritical SDA

Comparison of energy demand



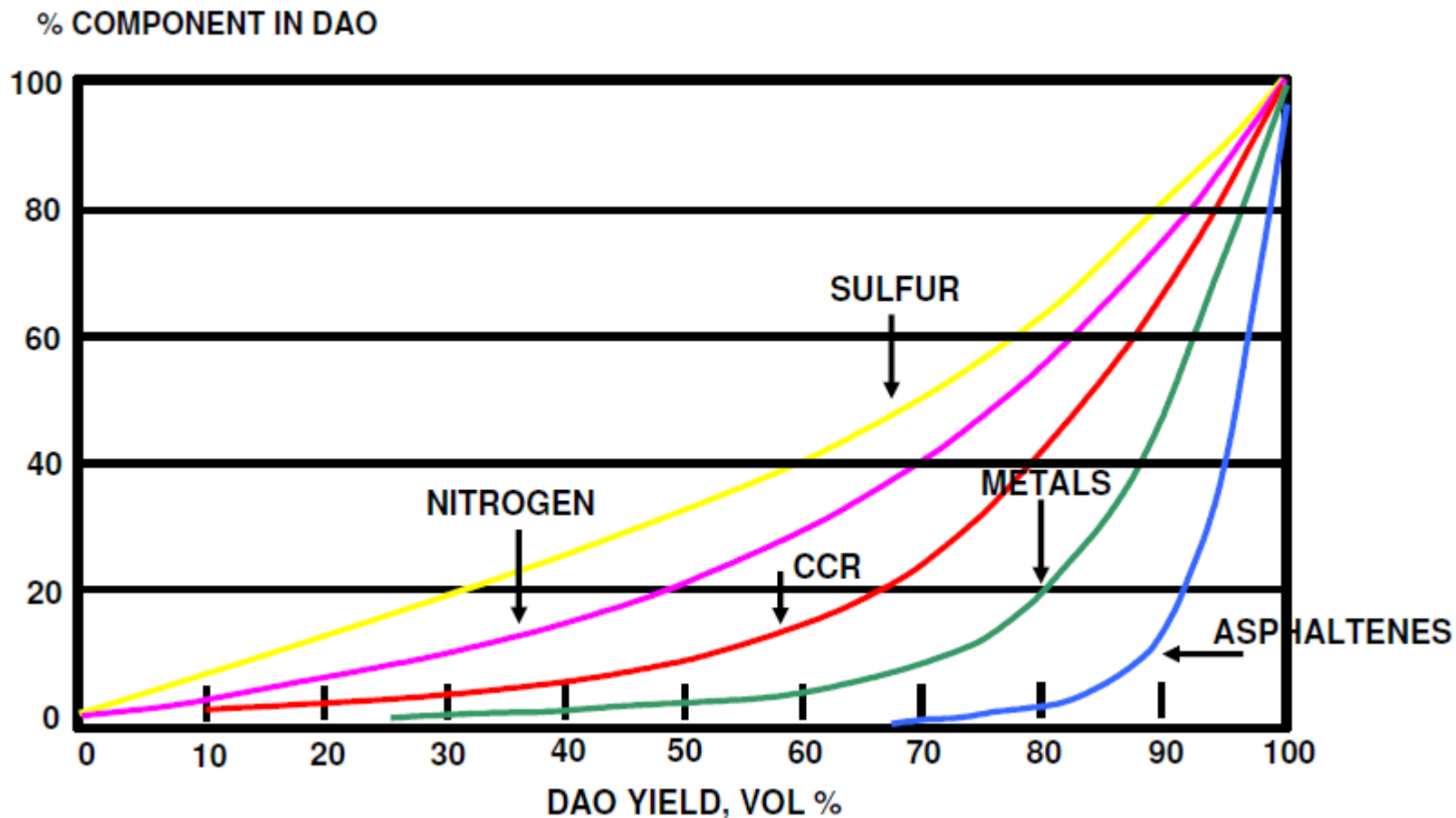
Conventional SDA:
high energy demand



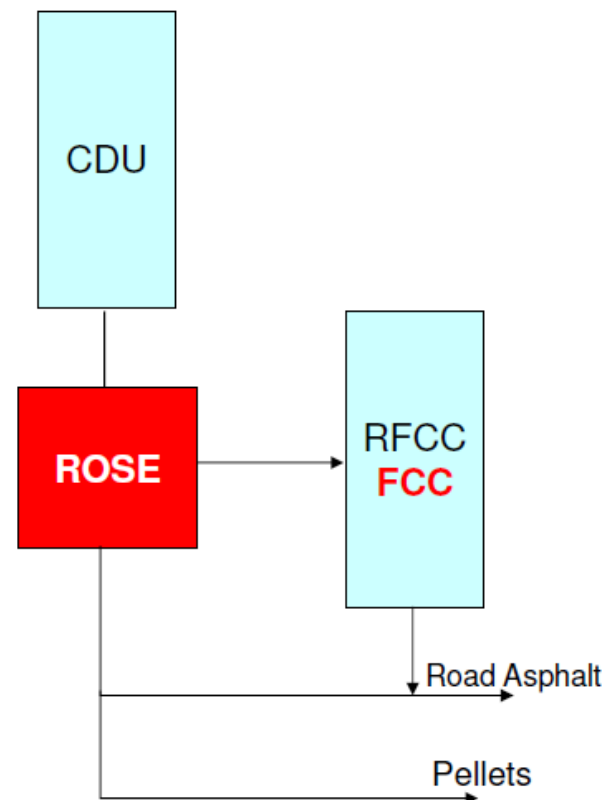
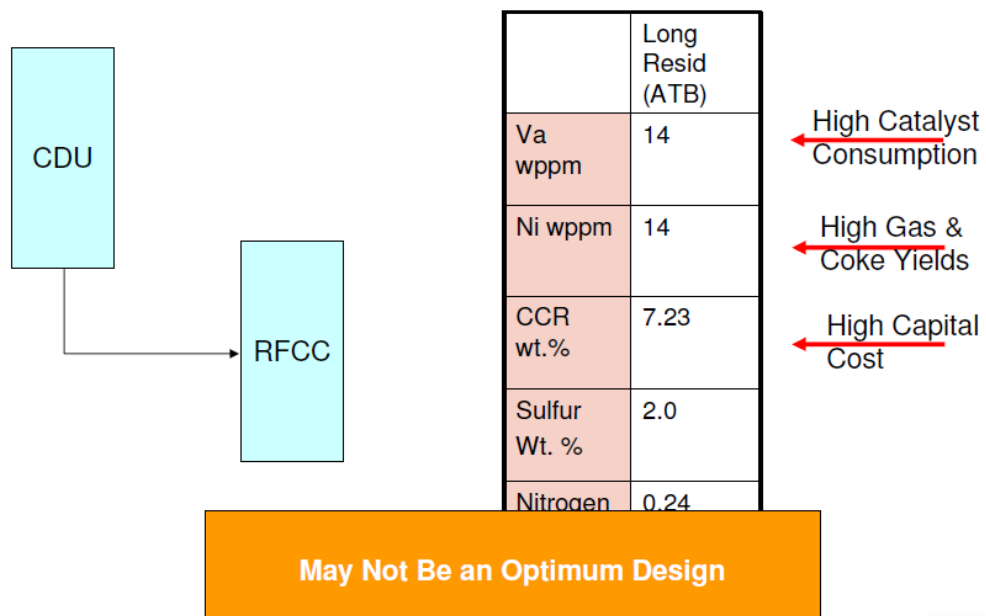
Supercritical SDA:
lower energy demand

SDA = solvent deasphalting

DAO product quality vs. yield



SDA applications (RFCC unit)

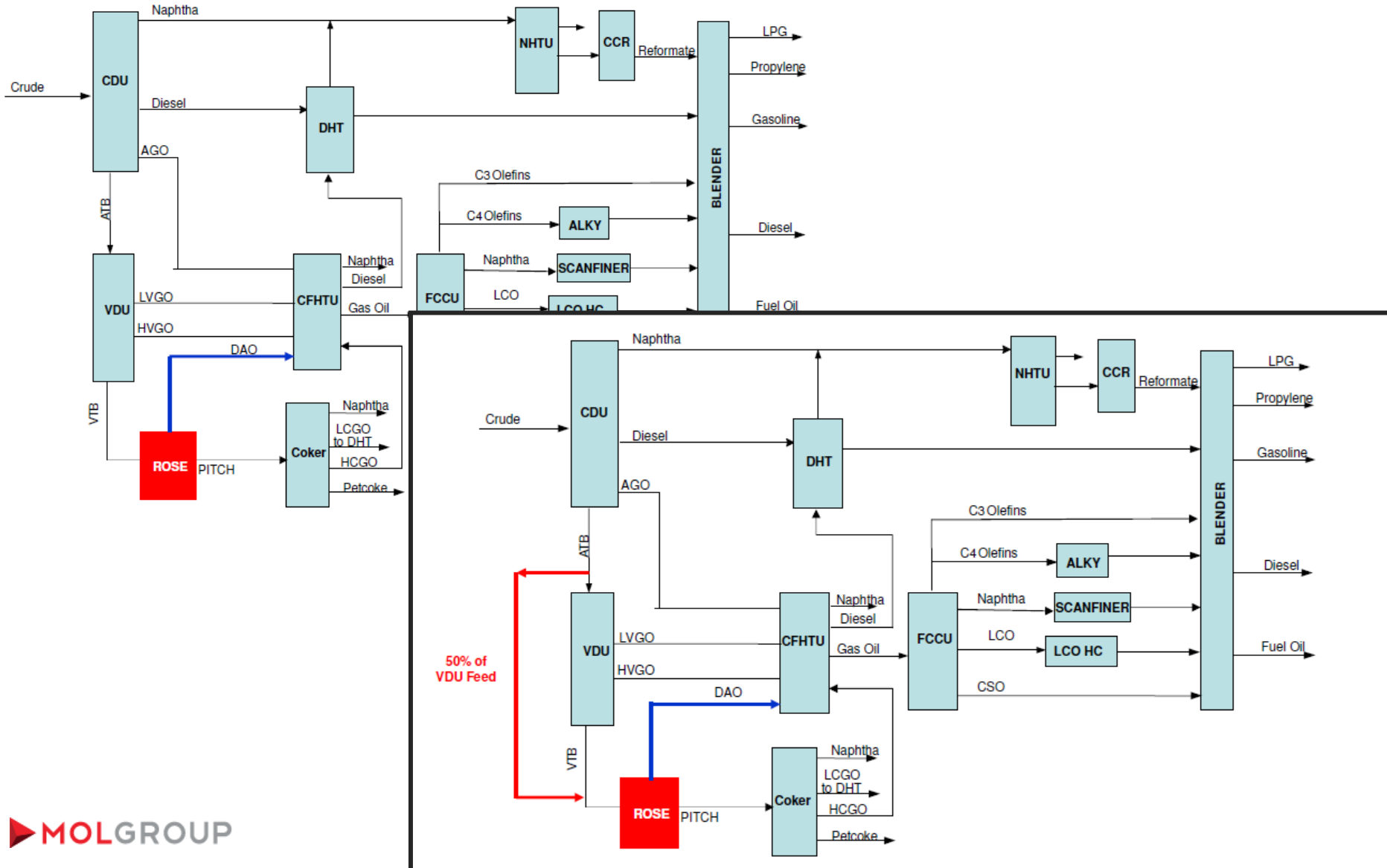


Gain:

- RFCC/FCC: lower catalyst cost, lower CAPEX, better conversion
- High quality road bitumen from the asphaltene (not verified in wide scale)
- Peletized asphaltene (cement production, IGCC, other industrial usage)

Important

Debottlenecking in case of heavier crude oil/capacity improvement



Debottlenecking in case of heavier crude oil/capacity improvement



	Base	ROSE	VDU Bypass	Fill up Units
Crude °API	31.1	31.1	31.1	31.1
MBPSD	202	202	202	303
VDU	100	100	50	100
Coker	38	18	18	27
Coke T/D	2050	1420	1420	2130
ROSE	-	38	69	89
FCC	72	90	90	135

Message: if you introduce a SDA unit to the right point of your refinery flowscheme, you may debottleneck your old vacuum unit (VDU) and/or your delayed coker. Doing so, you may increase your overall crude processing capacity significantly, which may increase your profit.

Azeotrope and extractive distillation

Azeotrope and extractive distillation

If the relative **volatility difference of the key components is low**, then the energy demand of distillation is high (and the operating cost too). In this case you may add a solvent to the mixture, which has great difference in solubility towards one of the key components. The goal is to increase the relative volatility artificially. This method may be utilised during **azeotrope and extractive distillation**.

It is required, that the bonding of solvent and extracted material shall be not great, since in this case the cost of regeneration may be higher than the original distillation cost.

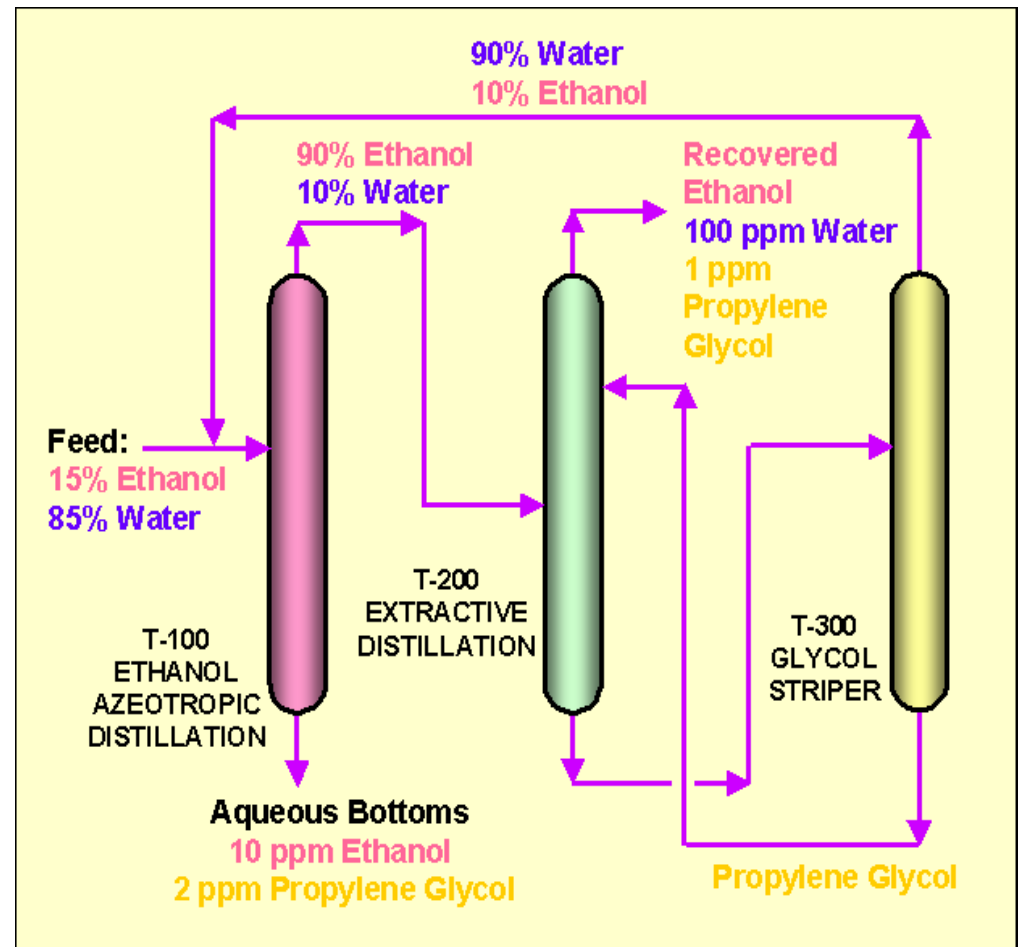
Solvent inlet possibilities

- **To the rectification zone:** if the extracted component is removed at the bottom
- **To the stripping zone:** if the extracted component is removed at the top

Water-ethanol separation by extractive distillation

The water-ethanol mixture forms minimum boiling point azeotrope (89,4 mol% , 96 wt% ethanol), which may be separated by propylene-glycol addition.

The first column is an azeotrope distillation. The top product is close to azeotropic concentration, the bottom is ~pure water. The upper part of the second column is rectification part, where the remaining azeotropic water is separated from ethanol. **The water molecules will form bondage with the added propylene-glycol, thus increasing the relative volatility of the ethanol molecules.** The top product is ~pure ethanol. In the third column the propylene-glycol is being regenerated.





Thank you for your kind attention!