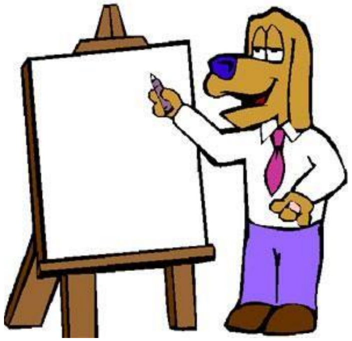
CH industrial technologies

Extraction, Aromatic production,extractive distillation, Supercritical extraction

Klára Kubovicsné Stocz
Oktober 2023

Agenda



Extraction

Aromatic component production

Aromatic extraction and distillation in DR

„Advanced” separation process

Supercritical extraction

Type of Extraction

Extraction: a process in which one or more components are dissolved from solid or liquid phase by using of selective solvent(extratant).

- solid – liquid extraction
  diffusion extraction
- liquid – liquid extraction
  solvent extraction
- supercritical extraction
  solid(or liquid)-gas extraction

Solid – liquid extraction

Subprocesses:

- Bringing the solvent with the solid component into contact until the solubility equilibrium is reached.
- The resulting solution is separated from the solid phase (by filtration, setting or centrifugation)
- The solution obtained by extraction can be decomposed into further components (distillation, evaporation crystallization etc.)

Factors influencing the extraction:

- **temperature**(as high as possible, increasing solubility, decreasing viscosity of solution and solvent and increasing the velocity
- **Specific surface area of the grain** (to be increased by comminution: appropriate fine and uniformal size)
- **Liquid velocity** (has to increase)

Solid – liquid extraction

- **batch**
  - Extractor with mixer (removing small/tiny particles)
  - diffuzor (it is the oldest version)
- **Continuous**
  - BOLLMANN-extractor
  - ROTACELL-extractor
  - HILDEBRANDT-extractor

It is used:

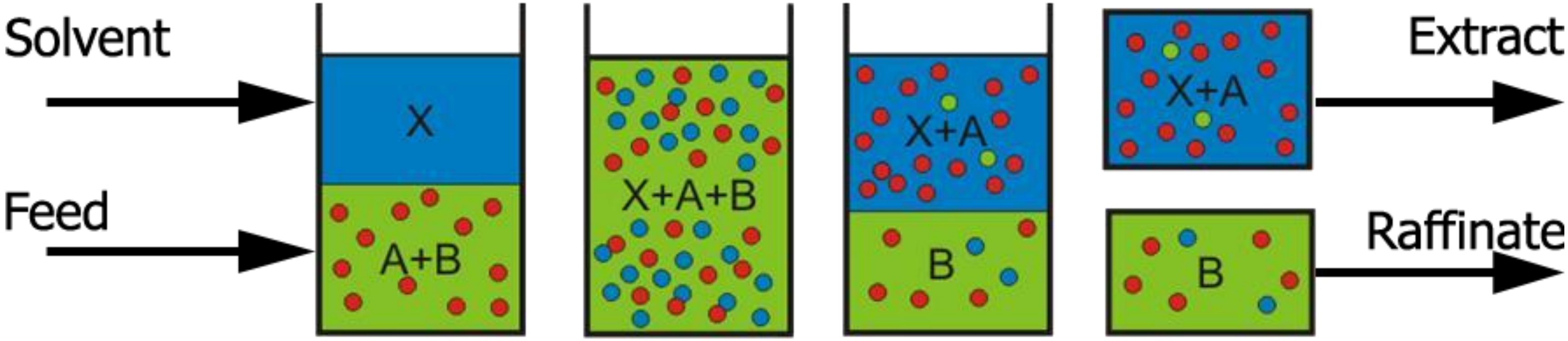
petroleum industry
pharmaceutical industry
coil processing

Liquid - liquid extraction

During Liquid-liquid extraction the components are separated on basis of differences in their relative solubility in selectively selected solvent. The extraction gives two immiscible liquid phases.

- Driving force: differnce in concentration, between the actual and equilibrium conc.
- process: mixing, sedimentation, separation

- **Extract:** solvent with dissolved components
- **Raffinate:** non-dissolved component with few amount if solvent



Liquid-liquid extraction:

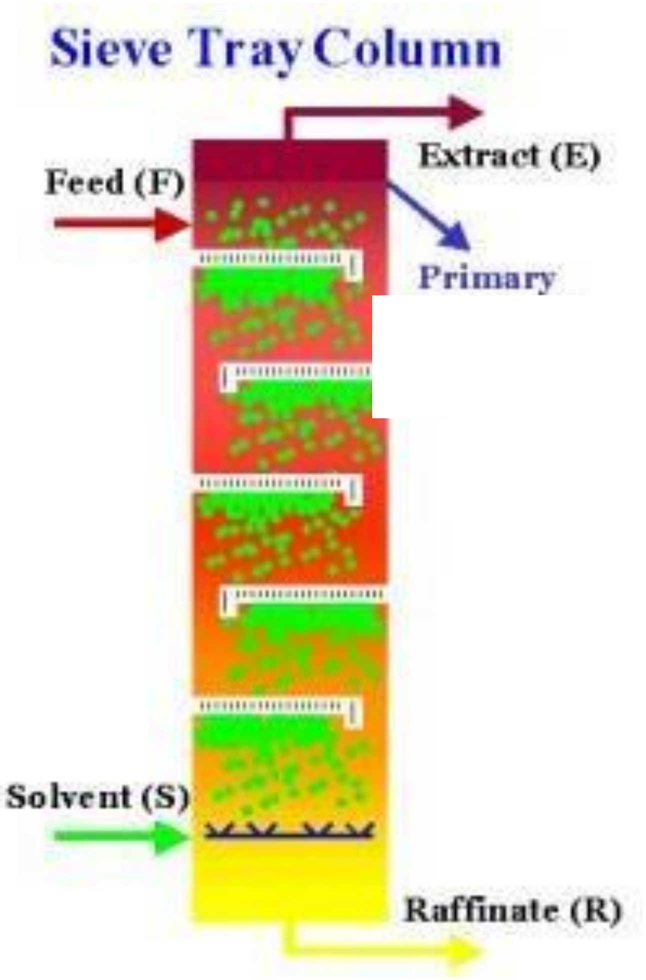
Extraction is used if:

- Extraction is more economical than distillation, when component which has high-boiling point and low concentration in the liquid is valuable.
- If the components of the liquid to be separated have a small boiling point difference
- If an azeotropic mix is formed during distillation, further separation of this mix
- If the component to extracted is sensitive to heat, at a higher temperature decomposes.

Liquid-liquid extractor

Grid tray

- capacity: 30-50 m^3/m^2-hr
- Good efficiency, no/minimal back-mixing
- More feed can cause problem
- Limited flexibility



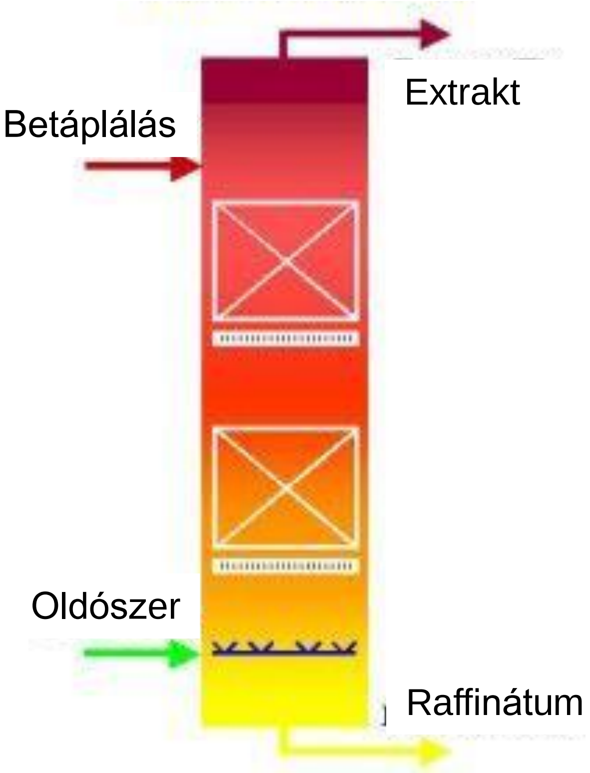
Liquid-liquid extractor

Random packing

- capacity: 20-30 m^3/m^2-hr
- Low efficiency, because of back-mixing and wetting
- Limited flexibility

Structured packing

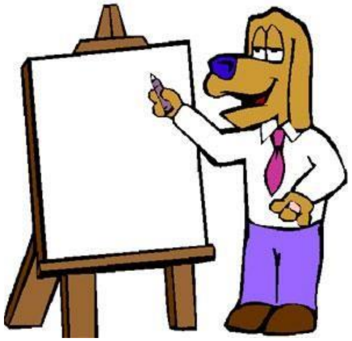
- capacity: 40-80 m^3/m^2-hr
- Low efficiency, because of back-mixing and wetting
- Limited flexibility



Extraction applications:

- Extraction of dyes from plant material and waste
- Extraction of active ingredient of herbs
- analitics: fat-oil determination
- pharmaceutical
- Oil industry
  - Aromatic extraction (aromatic production)
  - butadiene production
  - vacuum residue de-asphalting/with propane
  - vacuum product extraction (baseoil production)

Agenda



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Structure of Aromatic production (simple flowsheet)

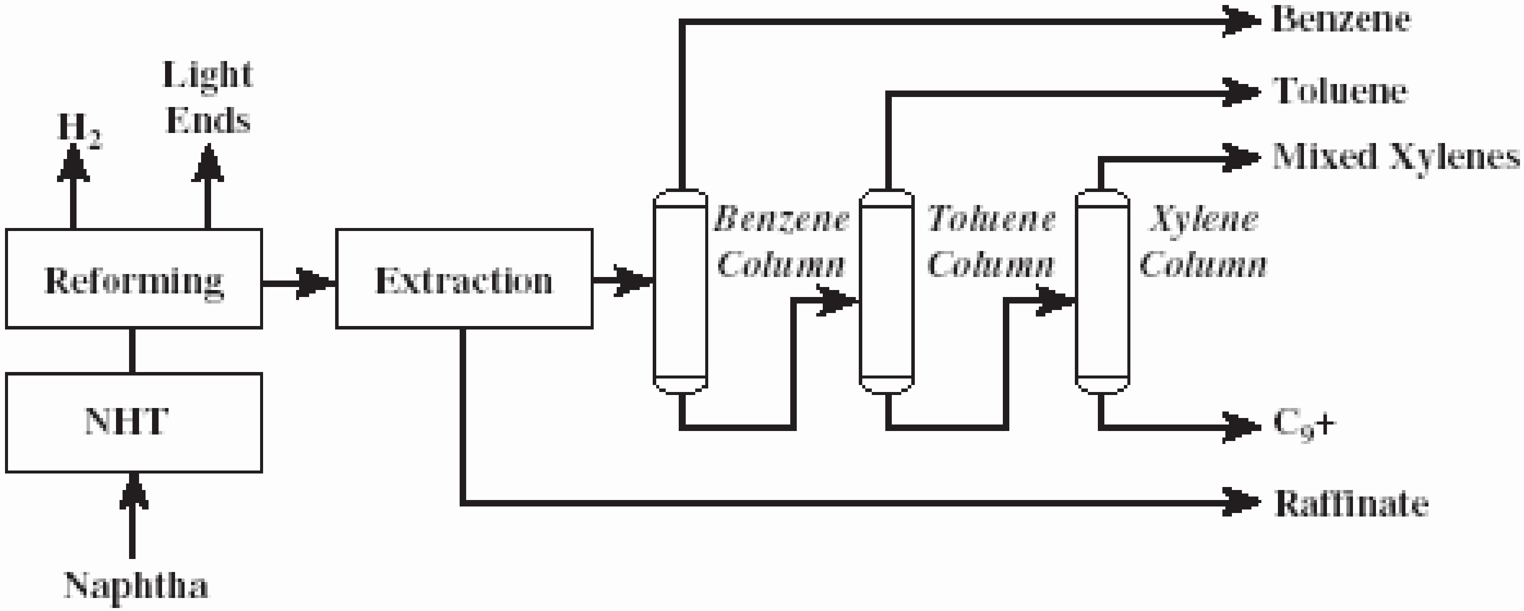


FIGURE 2.1.3 Simple aromatics complex.

Feed possibilities

Reformate

Catalytic reformer is one of the largest conversion technologies that converts low octane gasoline components into high octane reformate.

The reformate is an important feed for aromatics production and motorfuel blending component.

The reformate contains about 35-85 wt% aromatic component, which is depend on quality of feed (N+2A), used technology (semi-regenerative,CCR) and operation parameters.

Pyro naphtha

In Stream-Cracker when from naphtha and light CH (etane, propane) etilene and propilene is produced pyro naphtha with high aromatic content is also produced.

World benzene production is about 30-35% produced from pyrolysis gasoline.

The resulting C8 fraction contains 30-50 wt% of styrene, which is recovered and refhydrogenated to ethylbenzene.

BTX fraction is usually hydrogenated and distillated in SC plant before is sent to aromatic unit.

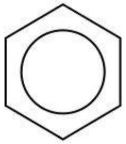
„High severity" FCC naphtha

FCC naphtha contains 50-55 %wt aromatics and 1-2 wt % benzene component, it is depend on reactor parameters. Redistillation and desulphurization of FCC naphtha is carried out in FCC unit.

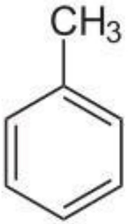
Aromatic products

Benzene and benzene derivative where hydrogen is substituted with alkyl group.

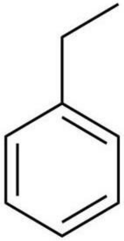
BENZENE:



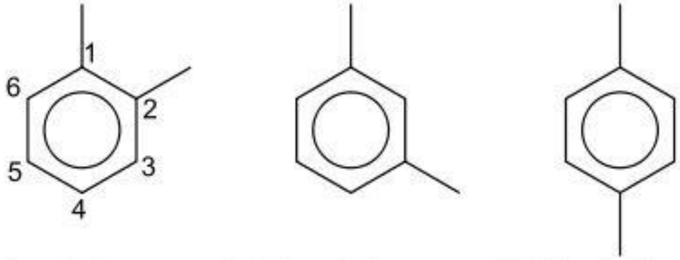
TOLUENE:



ETHYL-BENZENE:



XYLENES:



1,2-dimethylbenzene (*ortho*-xylene) 1,3-dimethylbenzene (*meta*-xylene) 1,4-dimethylbenzene (*para*-xylene)

Product qualities

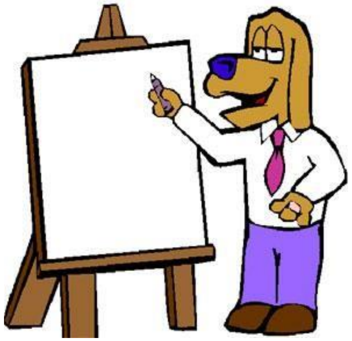
BENZENE	
Benzene content, wt. %	min. 99.90
Toluene content, mg/kg	max. 50
Non-aromatic content, wt. %	max. 0.10
S content, mg/kg	max. 1
Cl content, mg/kg	max. 1.0
Dencity @ 15°C kg/m^3	0,8820 - 0.8860
Crystal point, °C	min. 5.35
Acid wash color	max. 1
Bromide number	max. 10

TOLUOL	
Benzene content, mg/kg	max. 10
Toluene content, wt. %	min. 99.9
o,m,p-xylene, mg/kg	max. 100
Ipr-benzene content, mg/kg	max. 10
Non-aromatic content, wt. %	max. 0.08
Density @ 15°C, kg/m^3	0,869- 0.873
S content, mg/kg	max. 1
Acid wash color	max. 1
Hazen number	max. 20

Xylene Mix	
Toluene content, wt. %	max. 0.5
Ethyl benzene content, wt. %	max. 29
p+m-xylene content, wt. %	min. 55
C8 content, wt. %	min. 99
C9+ aromatics content, wt. %	max. 0.25
Non-aromatic content, wt. %	max. 0.5
Density @ 15°C, kg/m^3	0.8600 - 0.8700
Acid wash color	max. 6

O-XYLENE	
o-xylene content, wt. %	min. 98
Ipr-benzene content, wt. %	max. 0.33
Non-aromatic content, . %	max. 0.5
Styrene, wt. %	max. 0.01
Density @ 15°C, kg/m^3	0.8820 - 0.8850
Hazen number	max. 20

Agenda



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„Advanced” separation

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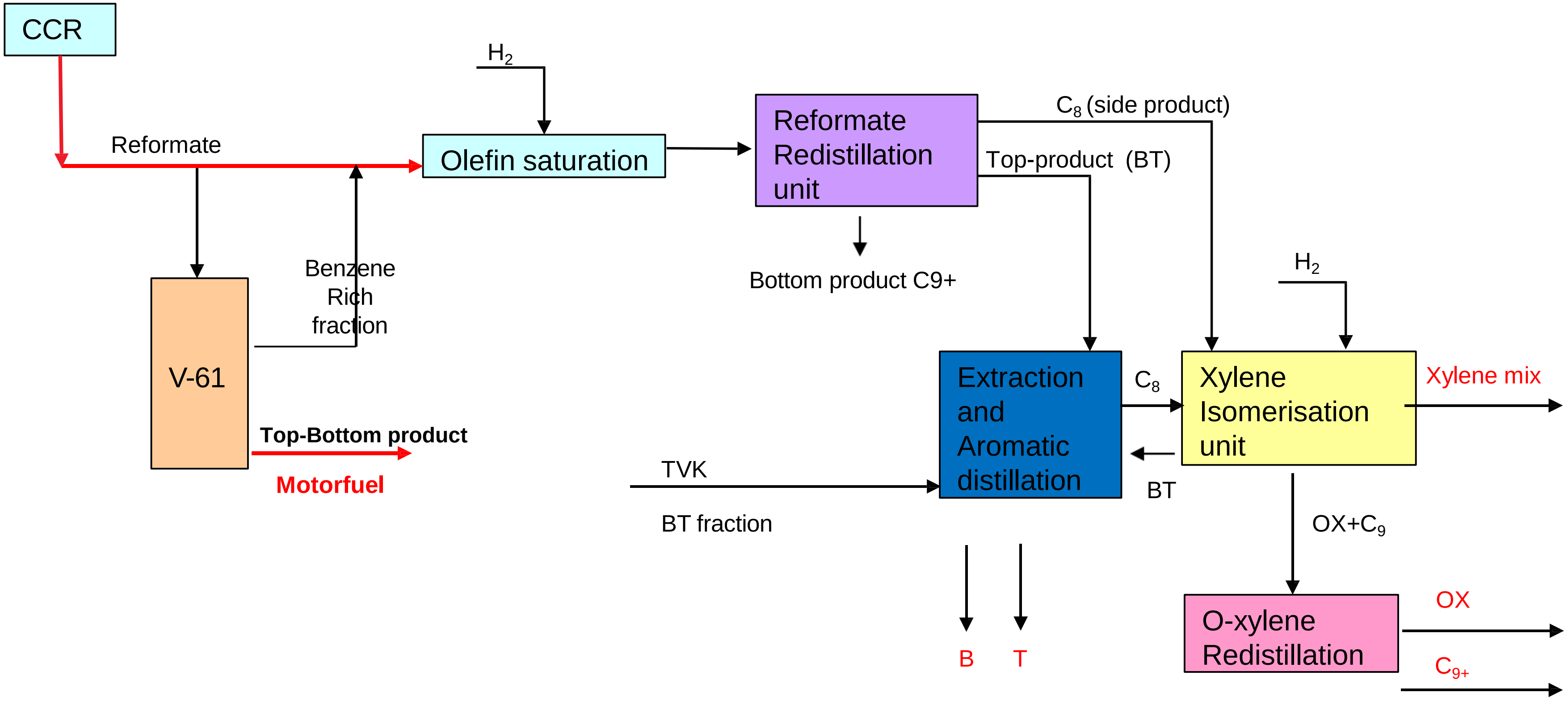
Aromatic production in Danube Refinery

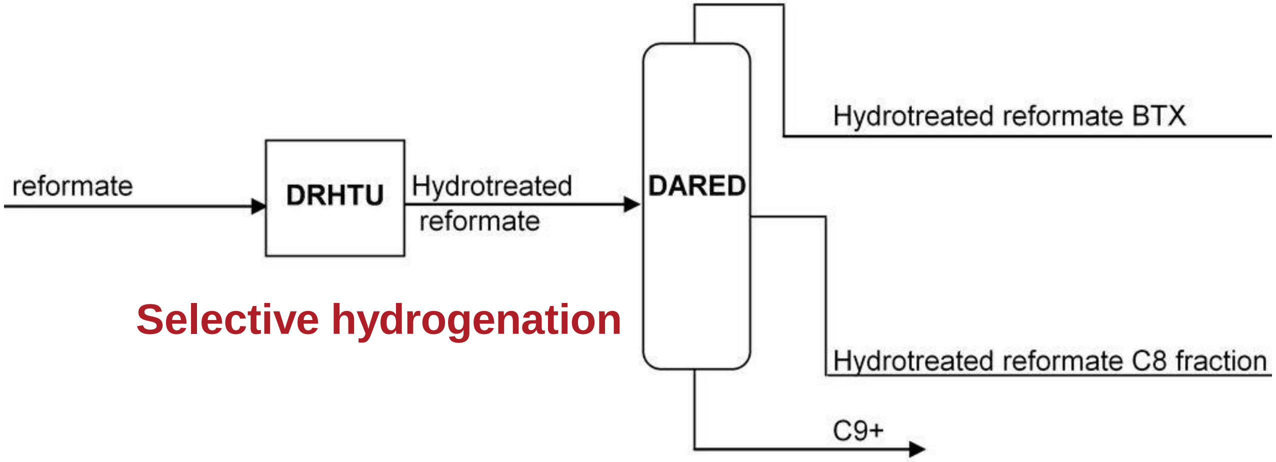


One application of the reformate is a gasoline blending component. Alternative uses include the production of high purity benzene, touene and ortho-xylene/xylene blends.

When used as a blending component in motor oil, a significant amount of benzene must be distilled off so that benzene content of the motoroil is below 1 vol%.

BTX Separation

BTXfraction can be separeted from reformate after olefine component removal.



Selective hydrogenation

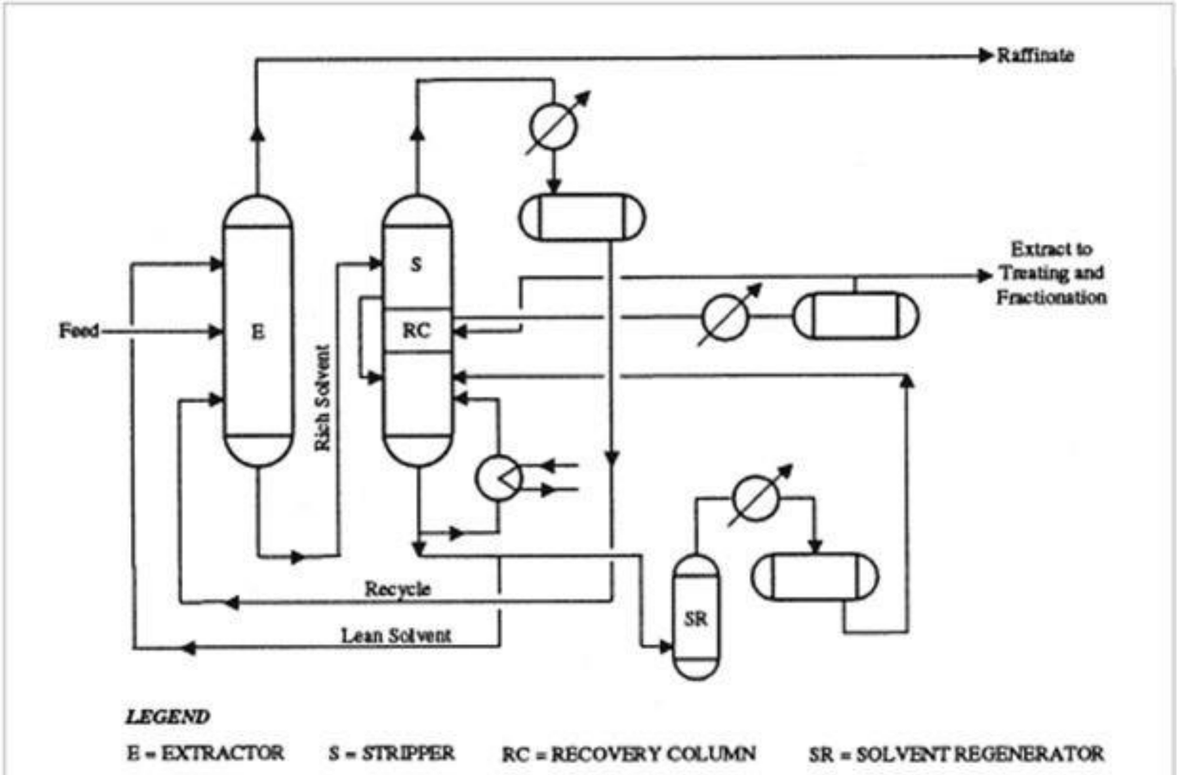
BTX fraction

BTX fraction is further processed in Aromatic Extraction Plant, where it is separated from the non-aromatic content by extraction.

C9+ fraction is used as a motorfuel blending or diesel component blending component.

C8 fraction – which non-aromatics content is good –can be load to Xylene Isomerisation unit without extraction.

Aromatic Extraction
Liquid-liquid extraction



Forrás: UOP LLC.)

Due to the difference in density,the feedstock and the solvent flow in the liquid phase countercurrently in the extractor. The solvent selectively dissolved the aromatic components.

Technological lisensors:
UOP, Lurgi, Lyondell, Axens, solvents: (Szulfolan, Glicols, NMP, Dimethil-szulfoxid, ...)

Requirements for Aromatic extraction solvents:

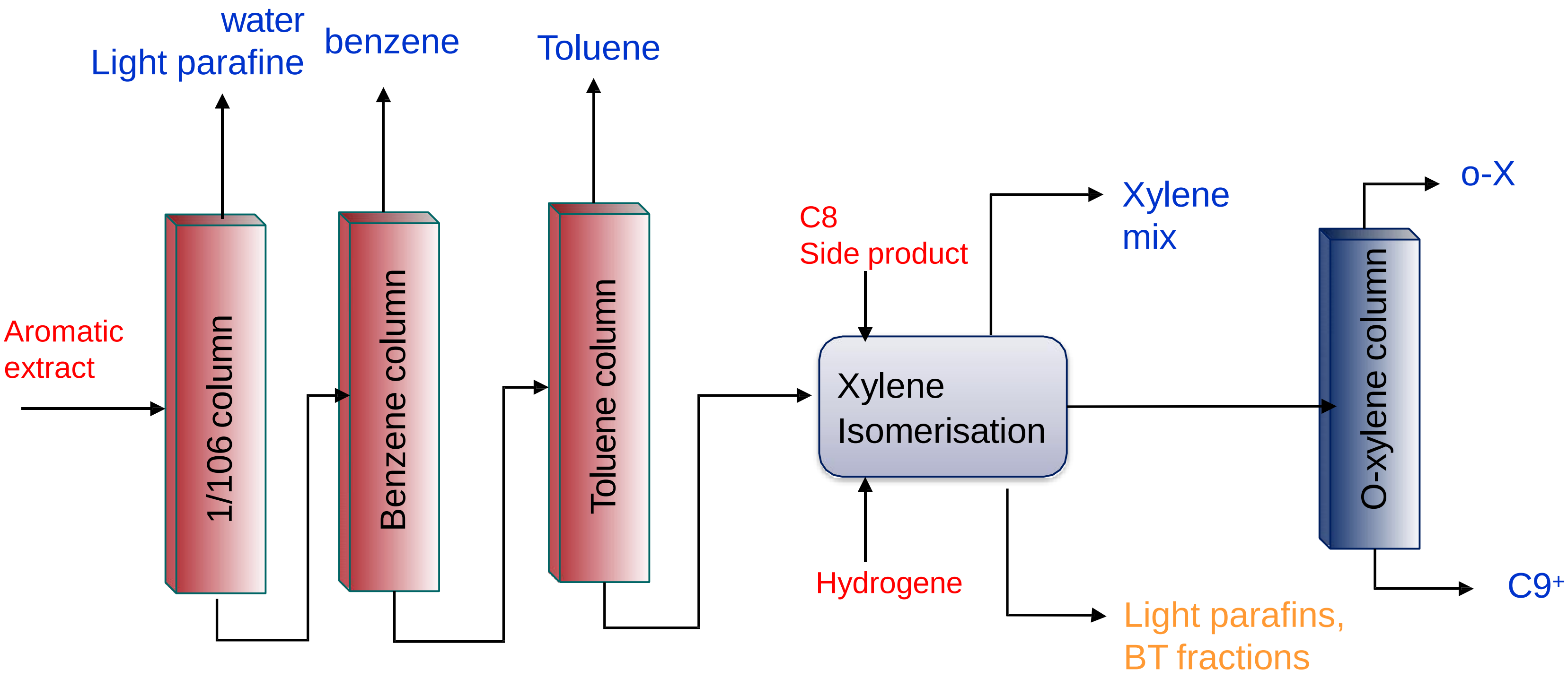
- Thermal stability
- chemical stability
- low toxicity
- low corrisivity
- availability
- Moderate cost
- Sufficiently low crystallization temperature
- Boiling point is much higher than boiling point of o-xylene(Tb≈ 140 °C)
- specific gravity(SG) higher than 1, or close to 1.1
- Viscosity at room temperature may be high, but at operating temperature less than 2,5 mPas

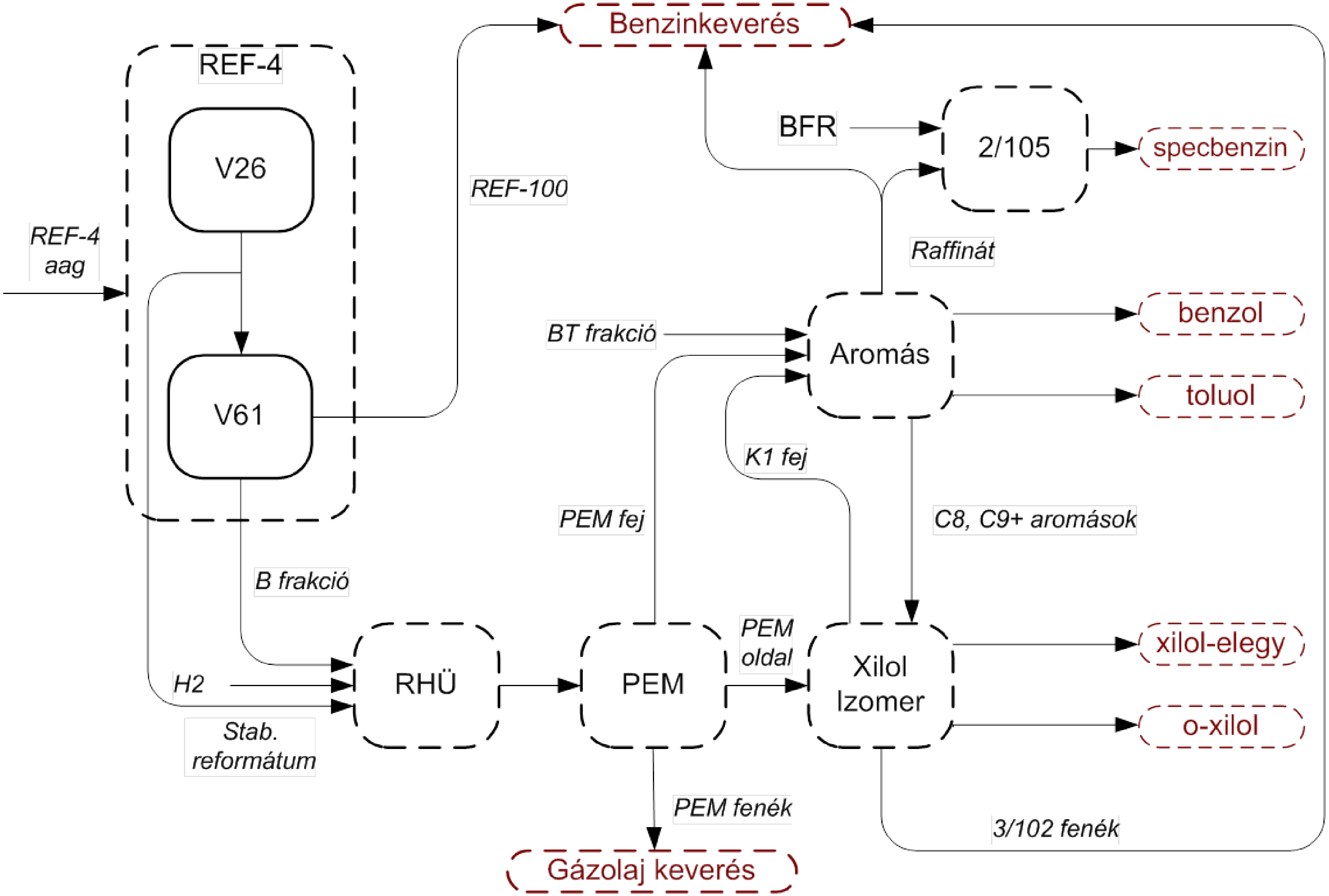
Structural composition of solvent:

- Short hydrocarbon ring and polaric group (thus soluble in water and selectively in aromatics).

Aromatic distillation in Danube Refinery

Aromatic extract is separated in distillation columns into different aromatic products (benzene, toluene, Xylene, and C9)
At Xylene Isomerisation unit amount of o-xylene product can be increased (as commertial demand) that o-xylene is distilled from equilibrium mix and residue is load back to reactor.





Benzinkeverés

REF-4

V26

V61

REF-4 aag

REF-100

BFR

2/105

specbenzin

Raffinát

BT frakció

Aromás

benzol

toluol

K1 fej

PEM fej

C8, C9+ aromások

B frakció

H2

Stab. reformátum

RHÜ

PEM

PEM oldal

Xilol Izomer

xilol-elegy

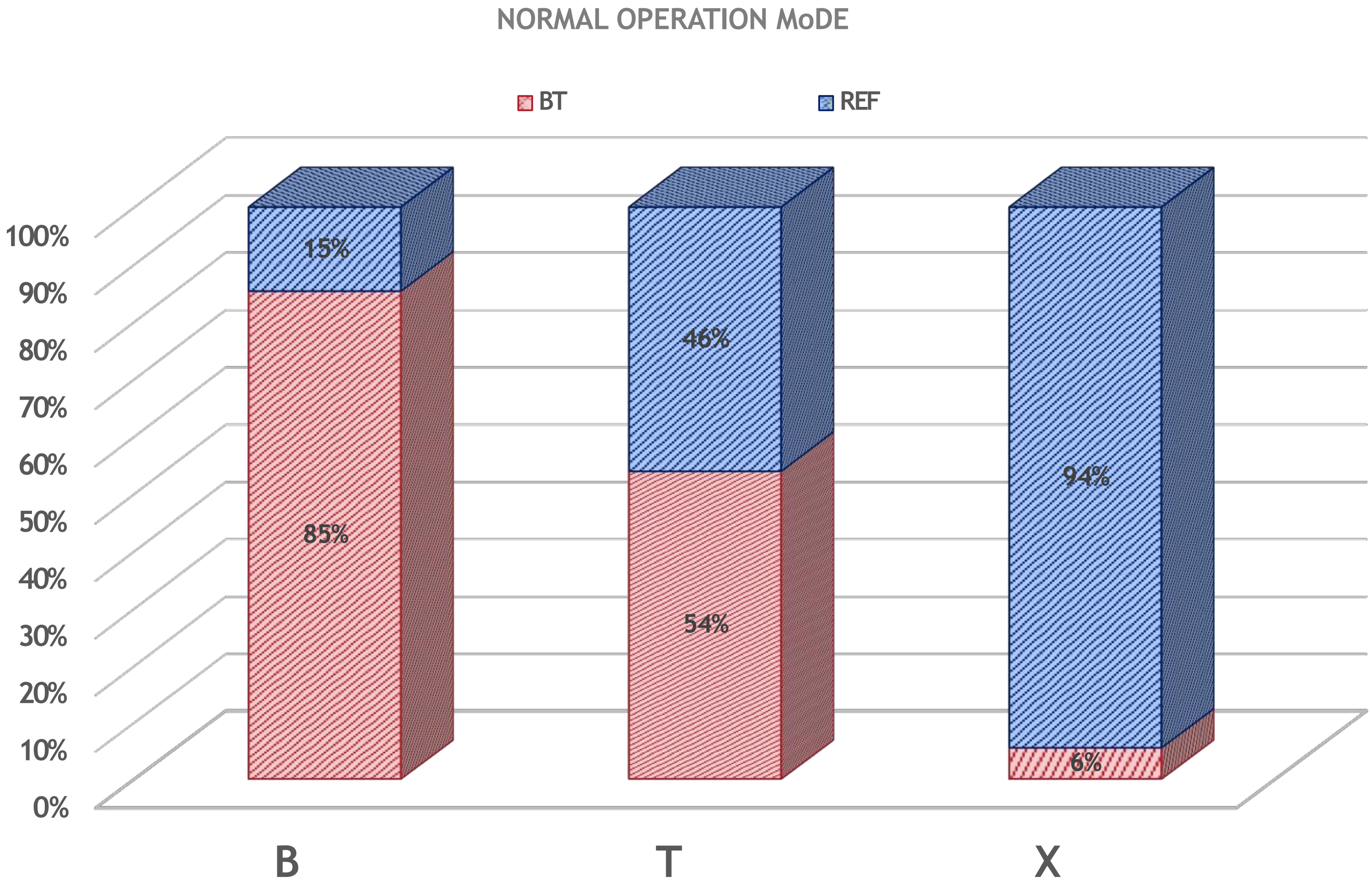
o-xilol

PEM fenék

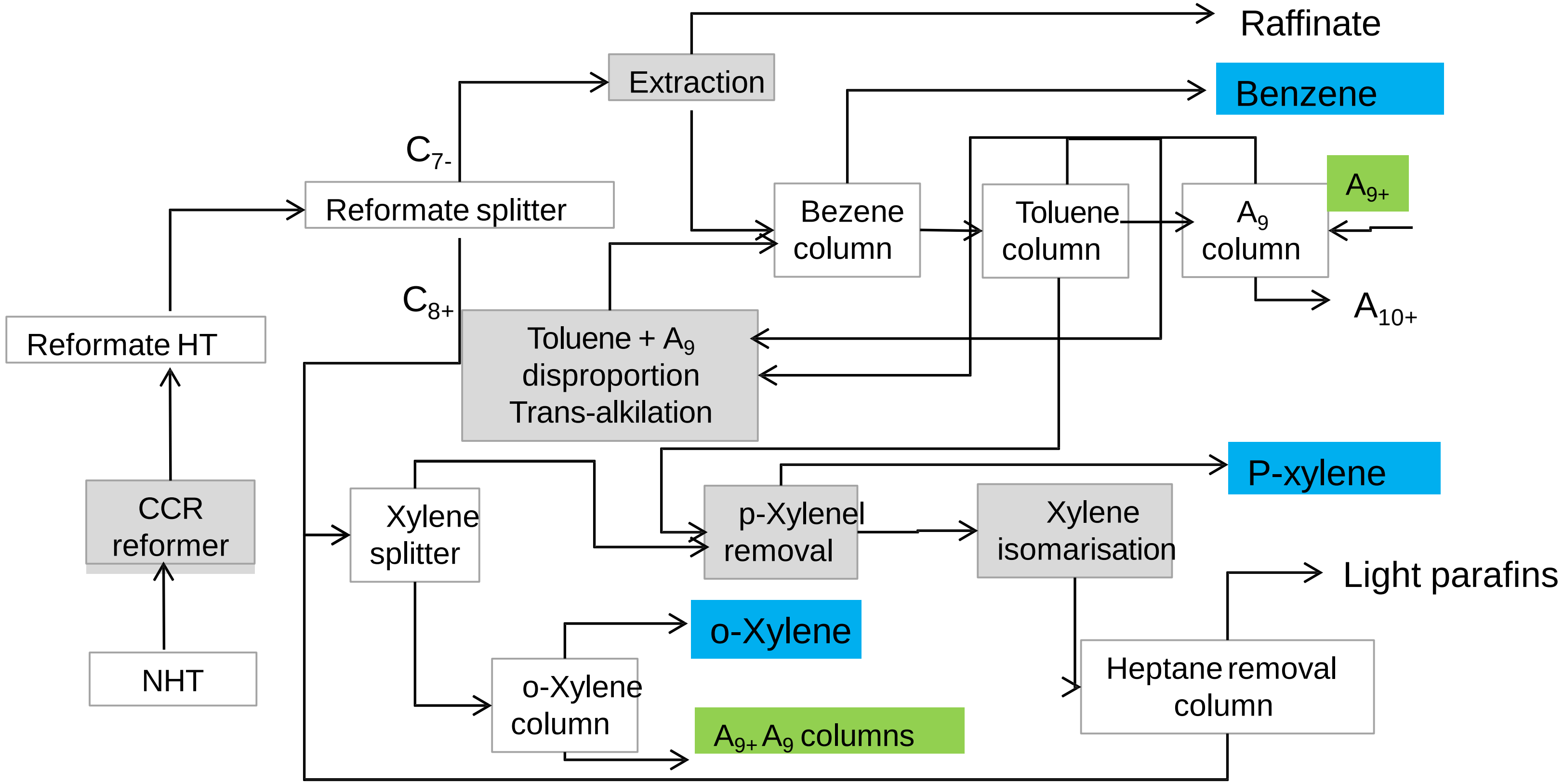
3/102 fenék

Gázolaj keverés

Benzene, toluene and xylenes distribution at Steam cracker (SC_BT) and at Reformer(REF) products



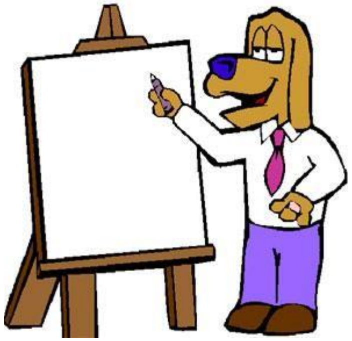
Integrated Aromatic production structure



Optimized configuration goal: maximum benzene and p-xylene production

- ☐ *CCR Reformer high aromatic content naphtha production*
- ☐ Extraction unit: benzene and toluene production
- ☐ *p*-xylene removal with continouos absorption technology
- ☐ *Xylene isomerisation: xylene isomerisation,ethyl-benzene transformation*
- ☐ Toluene and heavy aromatic components convert to xylene and benzene

Agenda



- Extraction
- Aromatic component production
- Aromatic extraction and distillation in DR
- ***„Advanced" separation***
- Supercritical extraction

Azeotrop distillation

If the relative volatility between the key components is very low then the energy demand of the distillation is process is very high which means operation cost is also.

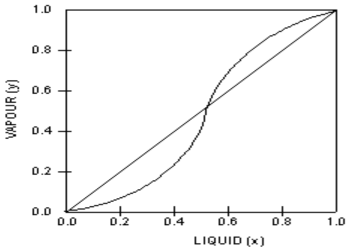
In these cases a solvent with high boiling point is given to mix which forms azeotrop mix with one of the components.

The aim is to artificially increase relative volatility.

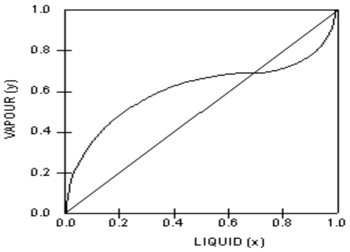
Minimum boiling point azeotrop:
- Top product: azeotrop mix
- Bottom product: Component/mix with high boiling point

Maximum boiling point azeotrop:
- Top product: Component/mix with low boiling point
- Bottom product: azeotrop mix

Minimum boiling terner azeotrop:
- Top product: terner azeotrop
- Bottom product: Component/mix with high boiling point



Maximum Boiling Point



Minimum Boiling Point

Extraktiv distillation

If the relative volatility between the key components is very low then the energy demand of the distillation is process is very high which means operation cost is also.

In these cases a solvent with high affinity to one of the key componnets is given to mix (no-forms azeotrop).

The aim is to artificially increase relative volatility. This method is used at extractive distillation process.

The **requirements for the solvent is that <u>the bond between the solvent and the solute is not too strong</u>**, because in this case the cost of solvent regeneration may be higher than theoriginal distillation cost.

<u>Extractiv distillation:</u> in the distillation column in contrast to the steam which move up a solvent flows downwards that dissolves the components selectively, thereby increasing their relative volatility.

Possibility of feed position:

- **Into Rektification zone:** when extracted component is removed as bottom product
- **Into Stripping zone:** when extracted component is removed as top product

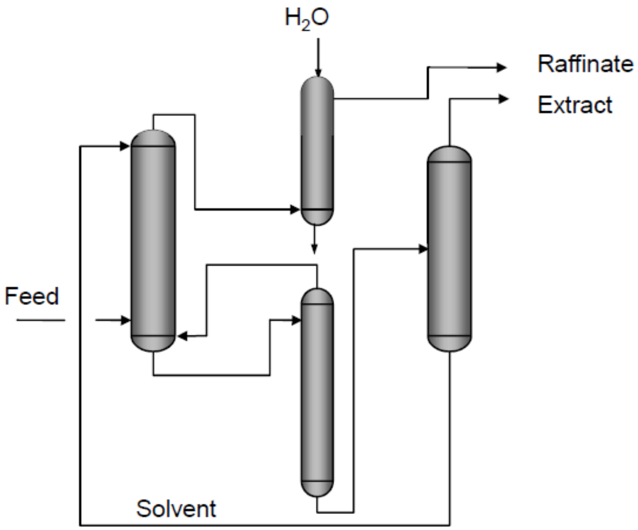
Aromatic separation with extraktív distillation

Technology: 2 distillation column:

- Extraktív distillation column (EDC)
- solvent removal column (SRC)
- Special solvent (Tentative-100)

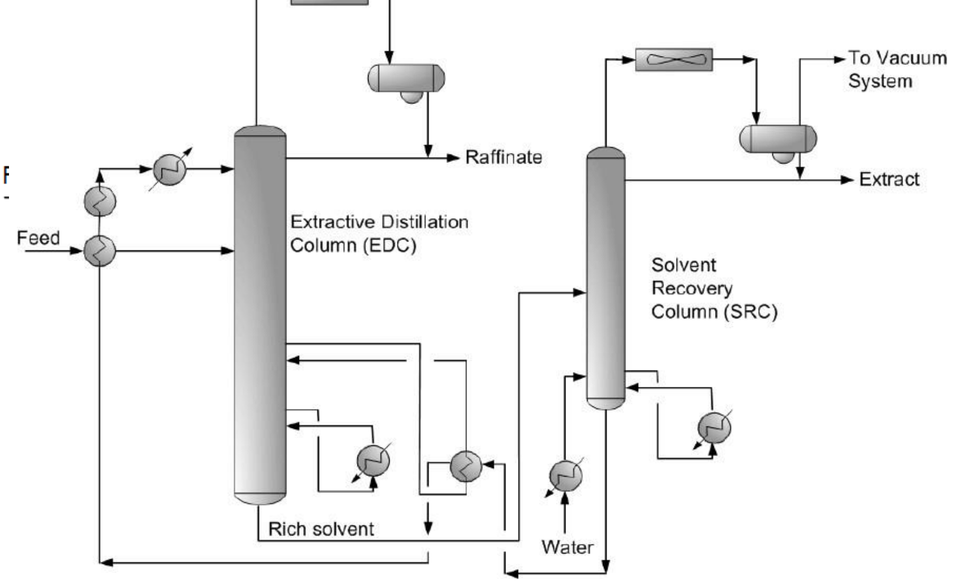
Advantage:

- CAPEX is lower about 30-40%, lower room requirements
- Lower energy demand about 20-30 %
- Higher selectivity period (C_5-C_9)
- More Stabil operation
- Lower solvent demand

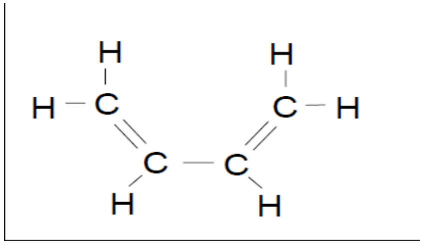


Liquid-liquid extraction

Extraktív distillation



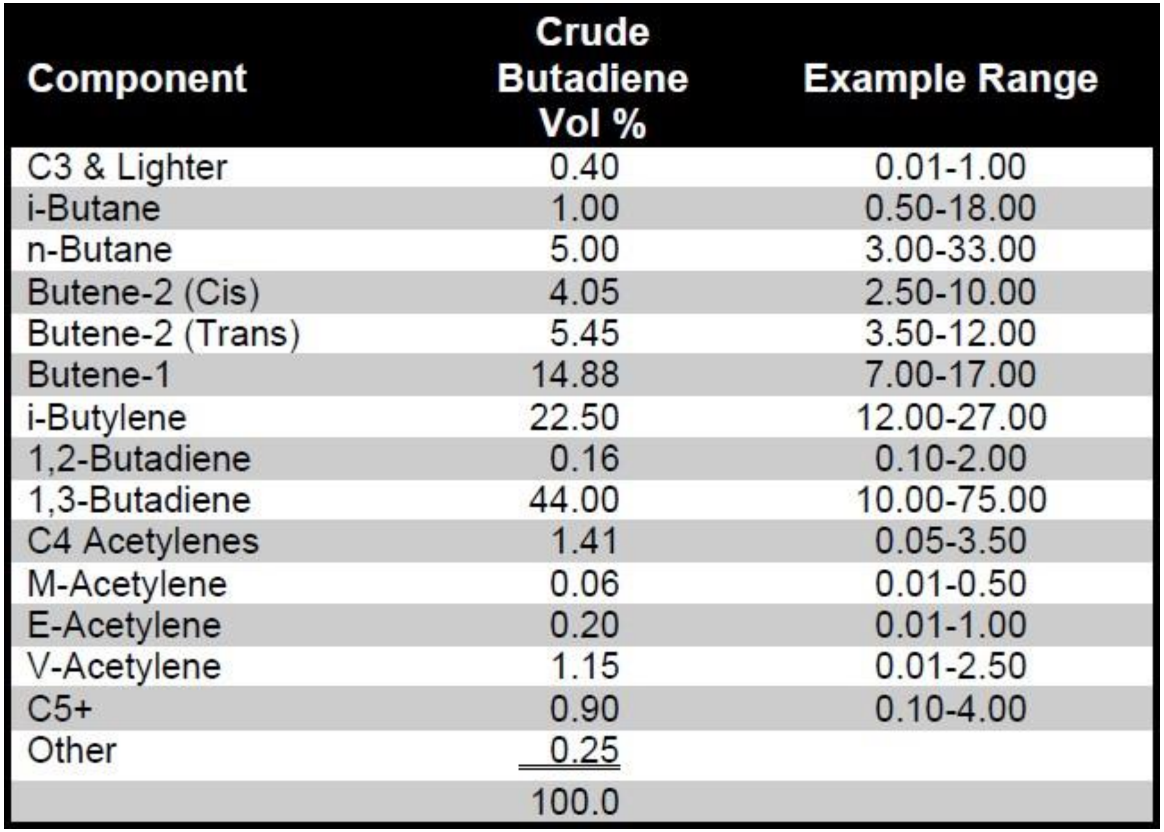
Butadiene removal with extraktiv distillation



Main part of technology:

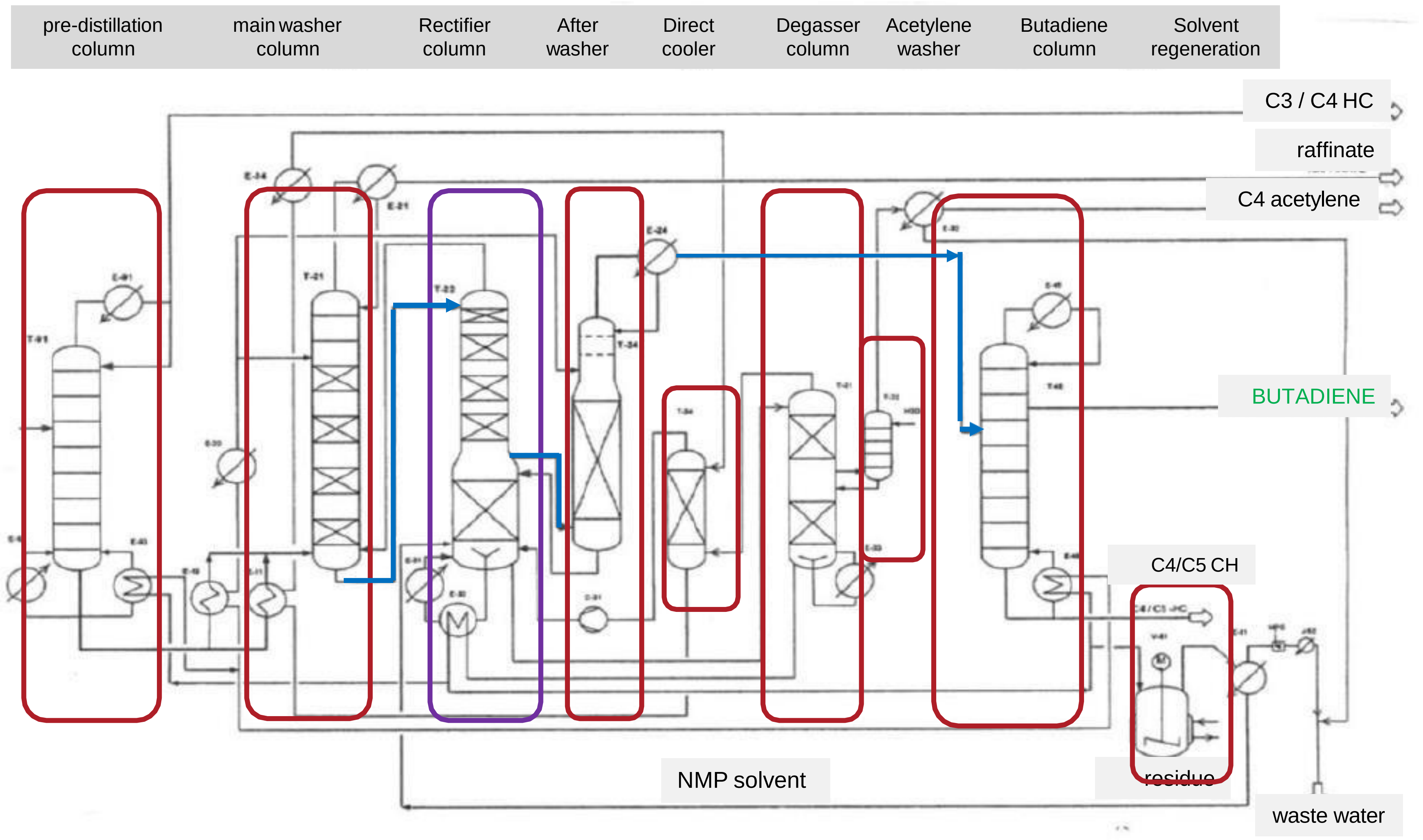
- Extraktiv distillation
- Conventional distillation
- Solvent regeneration

C4 fraction composition



Component	Crude Butadiene Vol %	Example Range
C3 & Lighter	0.40	0.01-1.00
i-Butane	1.00	0.50-18.00
n-Butane	5.00	3.00-33.00
Butene-2 (Cis)	4.05	2.50-10.00
Butene-2 (Trans)	5.45	3.50-12.00
Butene-1	14.88	7.00-17.00
i-Butylene	22.50	12.00-27.00
1,2-Butadiene	0.16	0.10-2.00
1,3-Butadiene	44.00	10.00-75.00
C4 Acetylenes	1.41	0.05-3.50
M-Acetylene	0.06	0.01-0.50
E-Acetylene	0.20	0.01-1.00
V-Acetylene	1.15	0.01-2.50
C5+	0.90	0.10-4.00
Other	0.25	
	100.0	

Simple flowsheet- Butadiene extraction



pre-distillation column

main washer column

Rectifier column

After washer

Direct cooler

Degasser column

Acetylene washer

Butadiene column

Solvent regeneration

C3 / C4 HC

raffinate

C4 acetylene

BUTADIENE

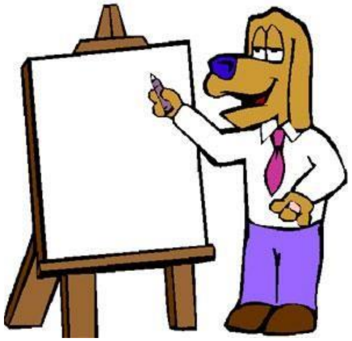
C4/C5 CH

residue

NMP solvent

waste water

Agenda



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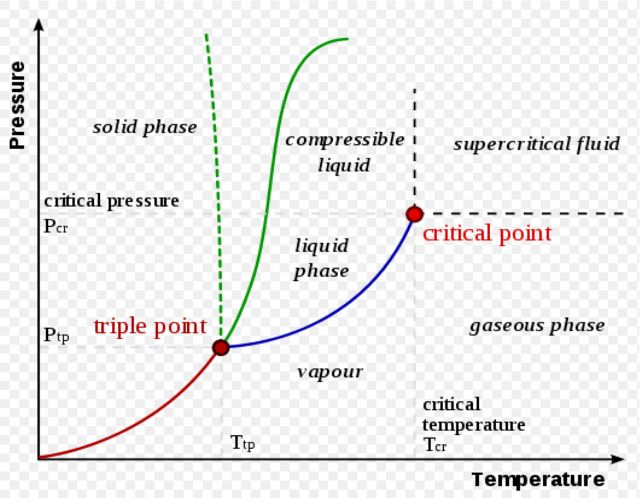
Supercritical extraction



Triple point: that T and p, where three termodinamical state meet

Critical point: density of liquid = saturated steam density

(p_{cr}, T_{cr})

If the material heated **above its critical temperature** is compressed at a **pressure higher than the critical pressure** the materal remaimns hoogeneous and a **fluid state** is formed. It is a transition **state between a liquid and vapour** in which **properties of material are similar to those liquid properties.**

.

The advantage of this state - which is close to the critical point - is that a small changes in pressure means high changes in density. It is useful at extraction.

While density is important at solubility of fluidum, so modifying the pressure can modify solubility of the solvent in a wide range.

Supercritical extraction (SFE)

- During **supercritical fluid extraction (SFE)** soluble components are extracted from solid or liquid materials with **supercritical or (the other named) fluid solvent**
- By varying the pressure and temperature, the solubility of **the extractant can be varied evenly and over a wide range,** so that selective dissolution and selective separation ca be achived.
- The solute is usually separated from the solvent at the end of operation by pressure reduction or other method (absorption, adsorption)
- Unlike traditional extraction processes, the product is free of the organic solvents that are harmful to health, so it is more valuable.
- During the extraction and sepration the inert atmosphere provides protection against oxidative damage.
- The operating cost of SFE technology is low but the investment cost is high due to the high pressure which is applied.
- Th disadvantages of supercritical solvents is that their solubility is mostly lower than that of organic solvents

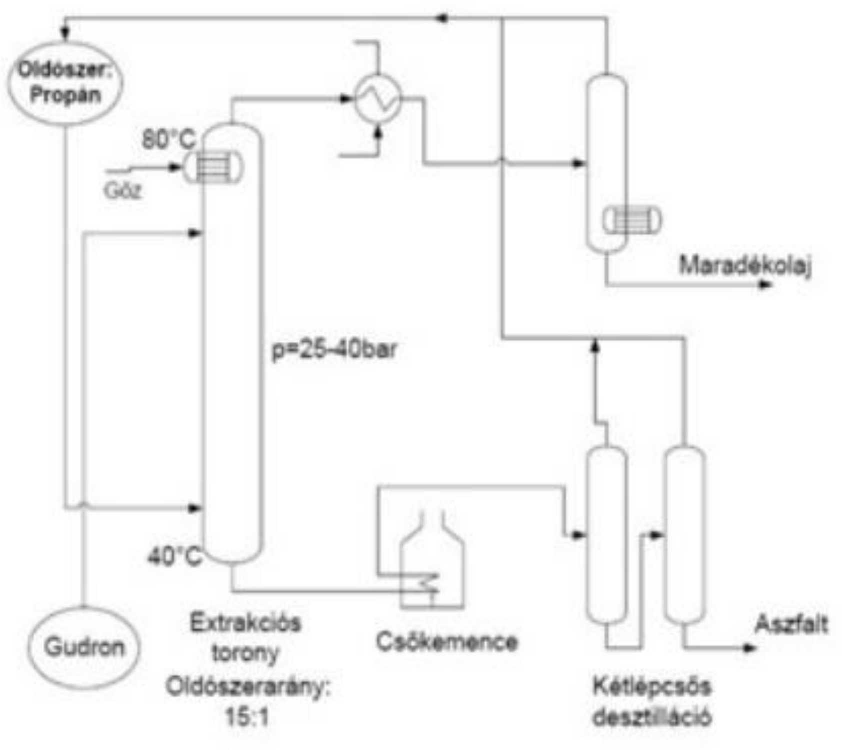
Application area of supercritical extraction

- Food applications
  - coffein, extraction from green wet coffee beans
  - nicotine removal from tobacco
  - Spice extract (pl. cinnamon, ginger, vanilin)
  - Extraction of herbal active ingredient (chamomile)
- Cosmetics industry
  - Fatty, oily and natural dyes
- Environmental applications
  - Cleaning of the contaminated soil (pl. policyclic aromatic hydrocarbons, polychorinated biphenyls…..oil contaminants)
- Oil industry

  vacuum residue extraction with C3 / C4 / C5 solvent

Asphalt removal with propane

AIm: High molecular weight, resins component is removed with solvent from Lube oil part with high boiling point and high viscosity in the gudron



Technology:

- **Gudron with appropriate temperature** is fed into extracion column middle part, and a lower density **liquid propane** into lower third part.
- In the extractors, liquid propane is the continuous (dispersing) phase andgudron is the dispersed phase
- Density of the sdispersed, lower propane-containing bituminous phase is higher than that of propane-rich lower density continuous phase, so it moves downard in the extraction tower.
- The oil components soluble in liquid propane, along with most of the part propane, leave at the top of the extraction column as residual propane oil or Bright Stock base.
- The higher gravity bitumen leaves the column at bottom with smaller part of propane.
- Propane-free residual oil or Bright Stock is pumped into tank-farm

Thanks!