Aromatic compounds

production, usage

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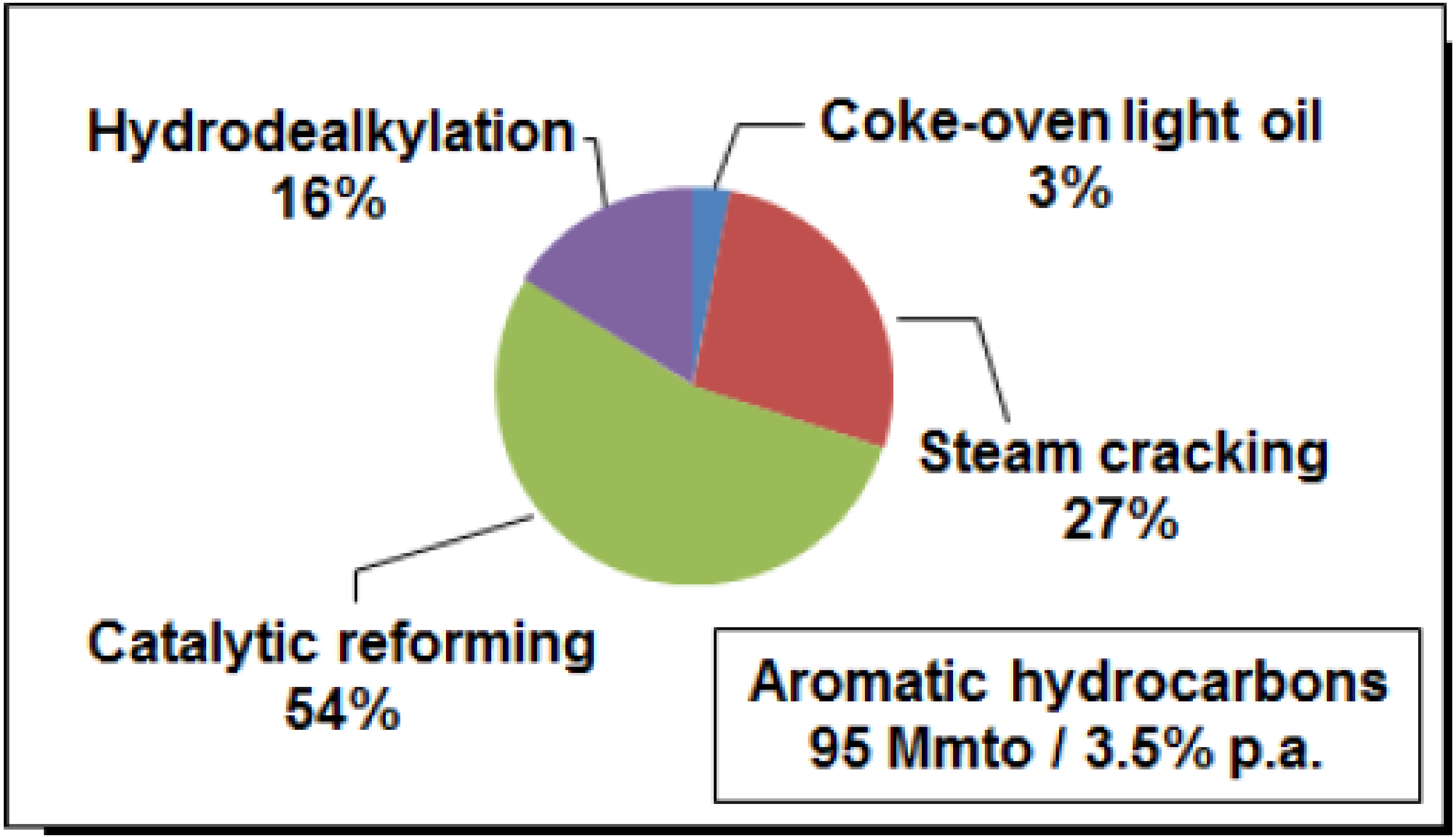
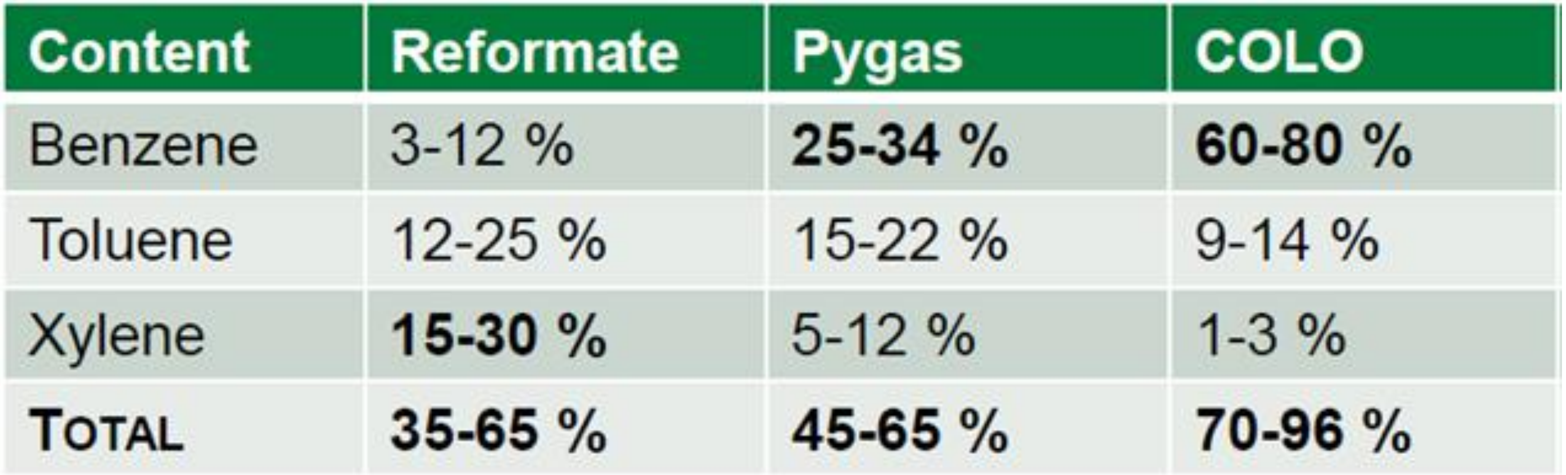
BME

Aromatic compounds – **Sources**

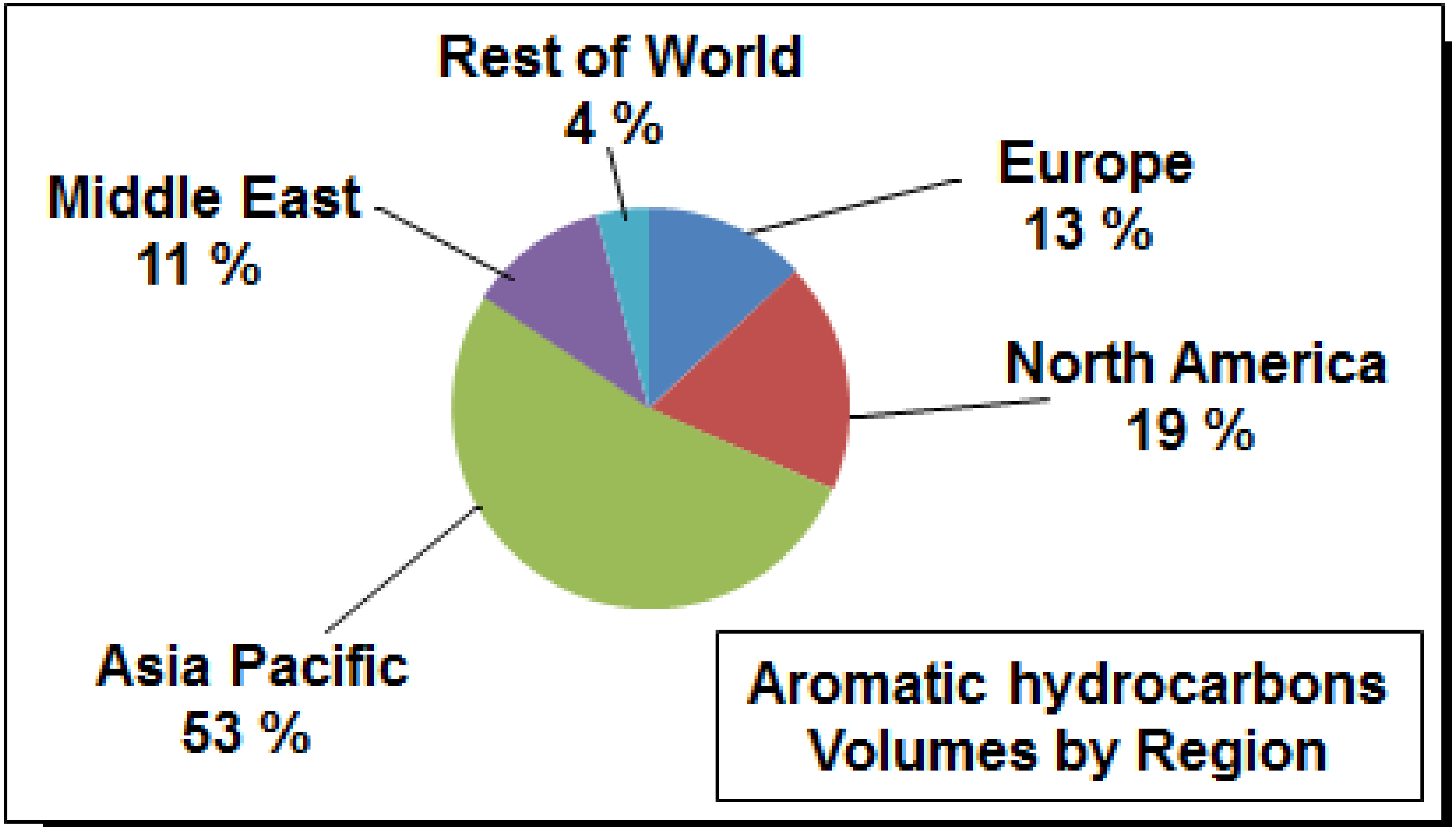


Aromatic compounds – Composition



Content	Reformate	Pygas	COLO
Benzene	3-12 %	**25-34 %**	**60-80 %**
Toluene	12-25 %	15-22 %	9-14 %
Xylene	**15-30 %**	5-12 %	1-3 %
TOTAL	**35-65 %**	**45-65 %**	**70-96 %**

Aromatic compounds – **Usage**



Aromatic hydrocarbons Volumes by Region

Benzene

History

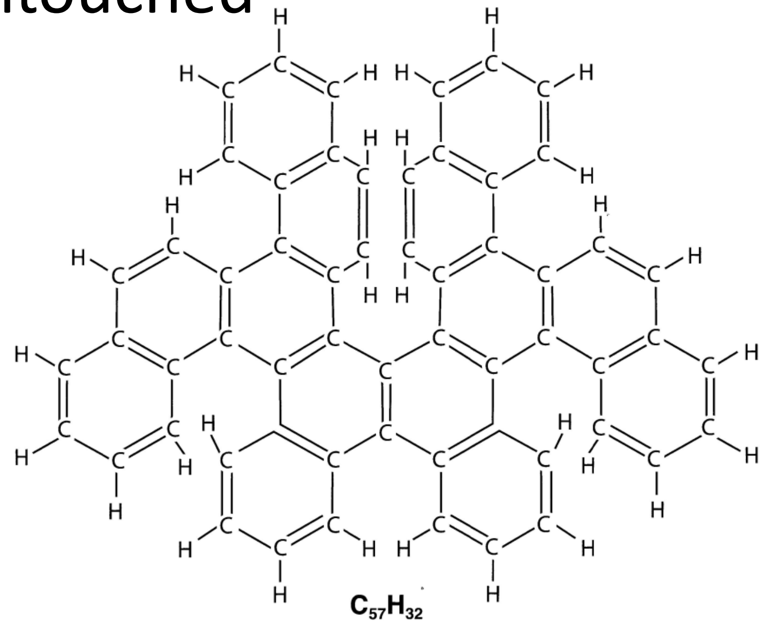
- **Michael Faraday** – 1825 – first time to be isolated, but benzene remained a „mystery” for almost a century (its behaviour and reactivity was different from any other compound with double bonds)
- **August Kekulé** – 1865 – supposed molecular structure (alternating single-double bonds, which are in continuous exchange – „Kekulé formula”)
- **Linus Pauling** – 1930’ies – quantum mechanical verification of Kekulé’s theory (common electron cloud)

Driving forces

- **XIX. century** – limited, low volume usage, mainly as solvent
- **First half of XX. century** – it was recognised that benzene has high octane number (RON 113), as a consequence there emerged an incentive to recover all the by-product benzene in the coke ovens at steel mills
- **Around WWII** – beginning of petrochemical usage, explosives production
- **Since the middle of XX. century** – rapid growth of petrochemical consumption (nylon, styrene, etc.)

Sources – **Coke production**

- Steel processing aid
- Source: coal
- Processing: destructive distillation of coal
- Thermally cracking 1 ton of coal above 1900°C, excluding air, „pure” coal (coke) remains, but the benzene rings remain partially untouched
  - 750 kg coke
  - 250 kg side products
    - Coal gas
    - Coal oil
    - Coal tar



Sources – **Coke production**

- **Coal gas**
  - It was used as municipal lighting around 1900
- **Coal tar**
  - Once it was an insulation material in the construction industry and the component of asphalt roads
- **Coal oil**
  - Liquid with ~80% aromatic content, especially
    - 60% benzene
    - 15% toluene
    - 5 % xylenes
  - Until the 1950'ies the steel industry was the primary source
  - After that the benzene demand growth was much faster than the steel industry would be capable to supply the market with its side product

Sources – Crude oil refining

- **Crude oil** – contains originally only 0,1-0,3% benzene
- **Catalytic reforming** – benzene content is 3-12%, depending on the technology and process severity
- **Fluid catalytic cracking** – 0,5-1,5%

Stream	Benzene content, %	Conditions	Contribution to benzene pool, %
Light SR naphtha	1-5	Crude oil dependent	2-5
HCK gasoline	4-5	Side product	2-5
FCC gasoline	0,5-1,5	Main gasoline component	10-15
Reformate	3-12	Feedstock boiling range, process parameters	75-80

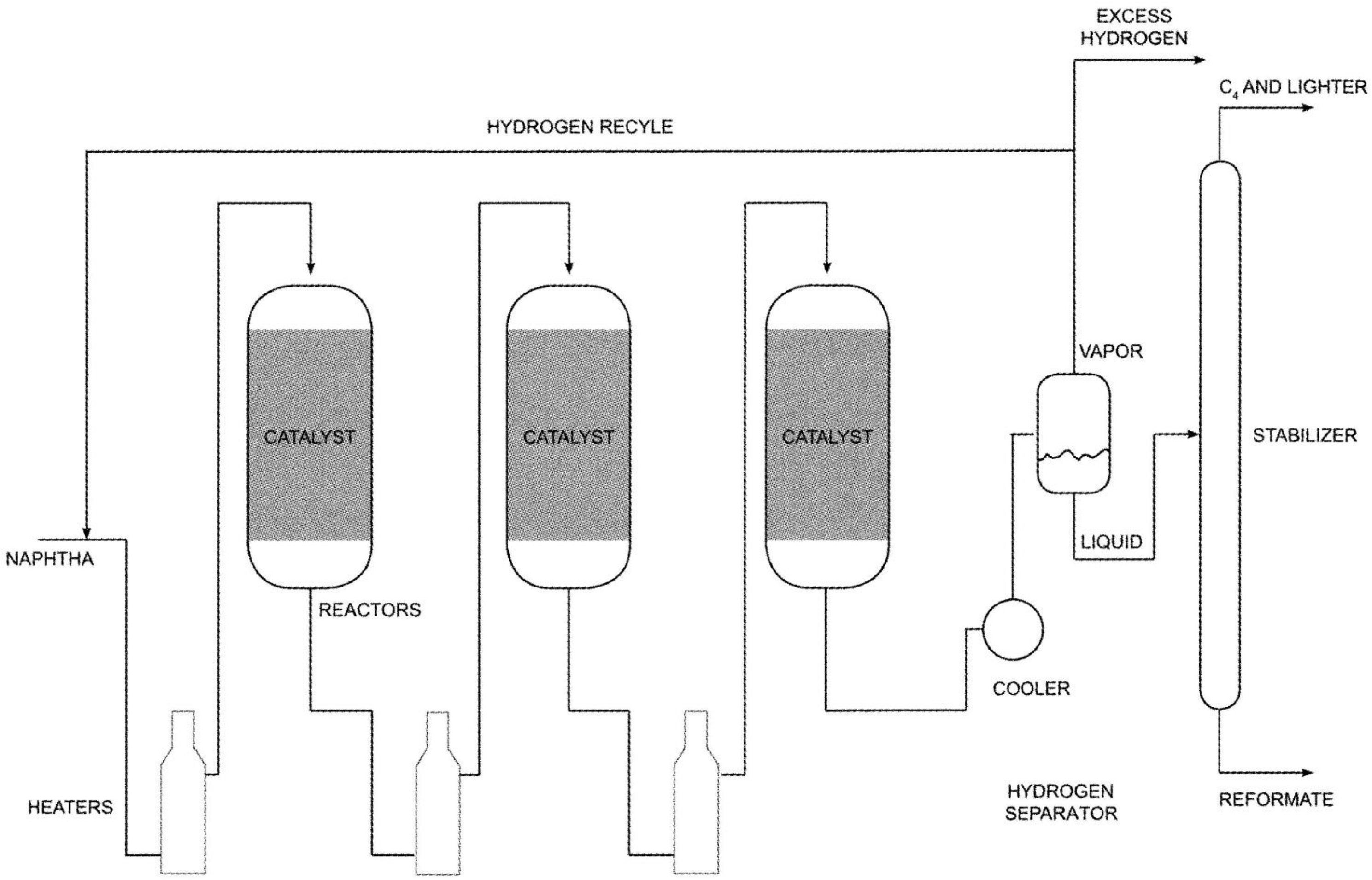
Reforming – **Driving forces**

- **First half of the XX. century**
  - Rapid growth of gasoline demand due to the expansion of motorisation (limousines in the USA, 5-6 lane highway)
  - Gasoline quality improvement in parallel with the compression ratio increase in the Otto engines
- **1949 – UOP** – introduction of platforming process
  - Octane gain with 30-40 unit
  - Patenting of novel bifunctional catalyst
- **Since the 1970'ies** – lead additive confinement
  - Discontinuation of lead-tetraethyl usage as octane improver (Hungary: termination of usage in 1999)
- **1971 – UOP** – introduction of CCR process
  - Continuous Catalyst Regeneration (low pressure, „continuous" regeneration) octane number: 100-105
- **Hydrogen** – supply for desulphurisation needs

Reforming – **Reactions**

- Isomerisation (paraffin → isoparaffin)
- Dehydrogenation (naphthene → aromatic)
- Dehydrocyclization (paraffin → aromatics)
- Hydrodealkylation (alkyl-aromatics → aromatics)
- Hydrocracking (bigger → smaller molecules)
- Coke formation (polyaromatics → coke)
- Alkylation (aromatics → alkyl-aromatics)

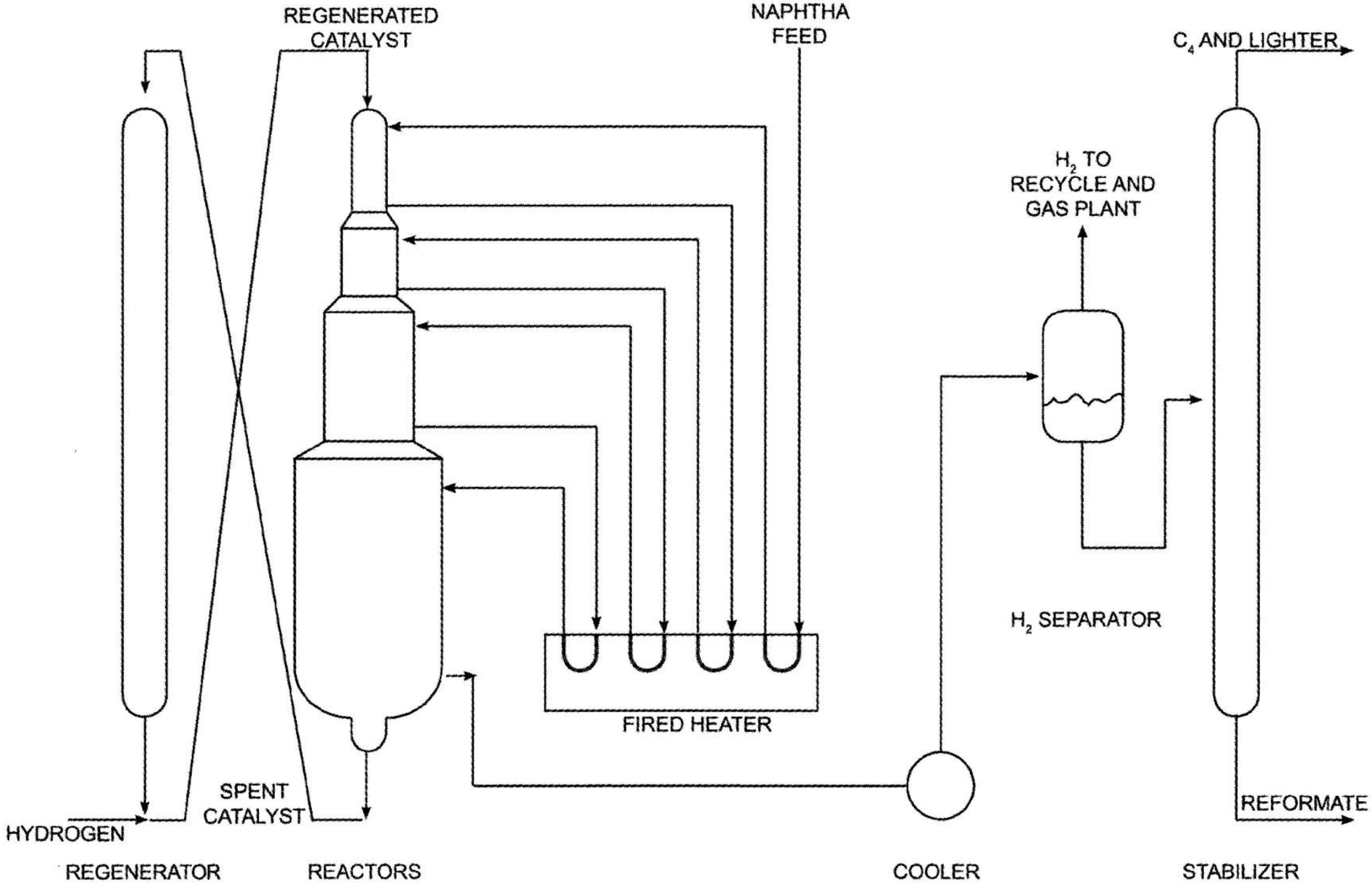
Reforming – **Fixed bed process**



Reforming – **Fixed bed process**

- Gross endothermic reactions
- Increasing volume reactors in series, in order to maintain the heat balance (1:1 → 1:3 → 1:5)
- Temperature: ~500°C
- Pressure: ~15-30 bar
- Cycle time: ~3-12 months
- Catalyst: Pt/Al2O3
- Predominantly formerly built units

Reforming – **CCR process**



Reforming – **CCR process**

- Gross endothermic reactions
- Increasing volume reactors in series, in order to maintain the heat balance (1:1 → 1:3 → 1:5)
- The catalyst is in continuous, slow movement
- Temperature: ~500°C
- Pressure: ~6-8 bar
- Cycle time: ~3-4 year
- Catalyst lifetime: ~10-12 year
- Catalyst: typically $Pt\text{-}Re/Al_2O_3$
- Newer built units
- High octane number reformate

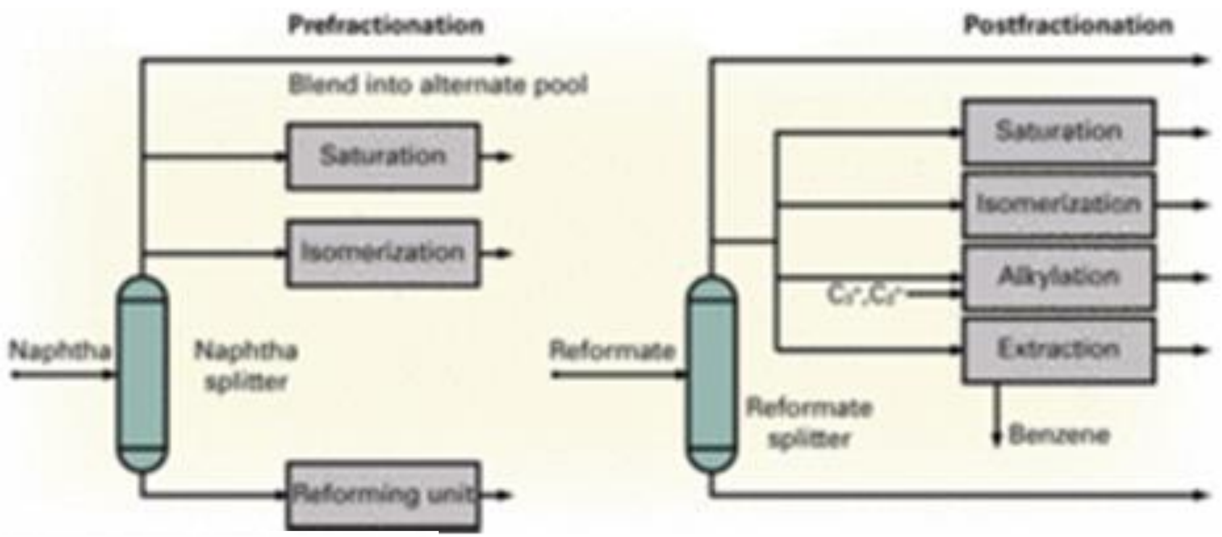
Reforming – **Gasoline quality**

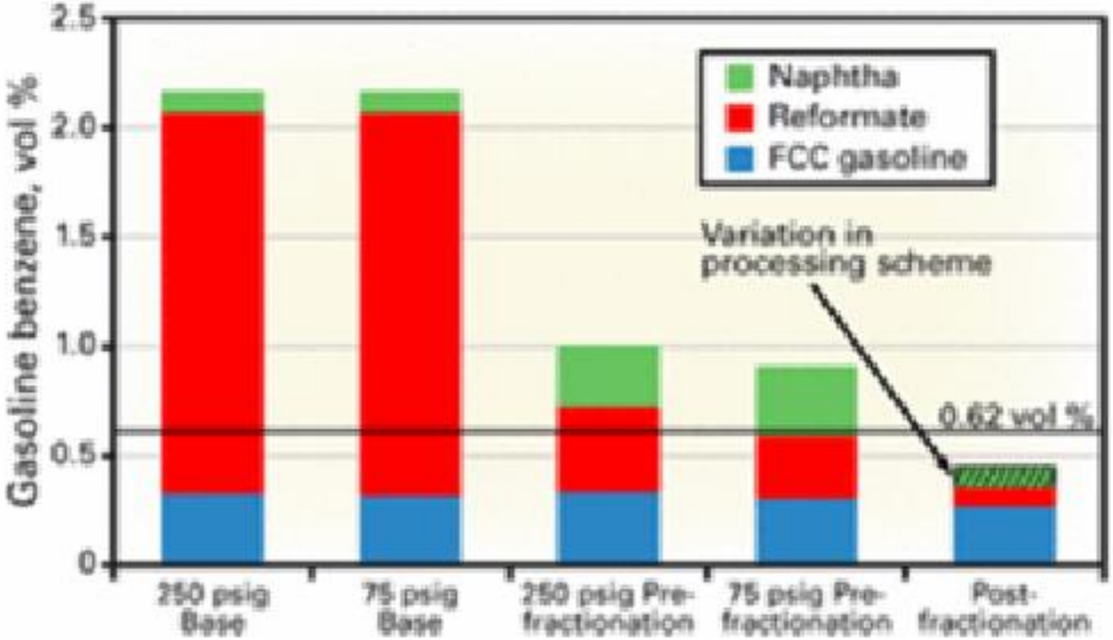
- Standardised aromatic and benzene content of motor gasolines were decreased in the near past

Parameter	MSZ 1998	EU 2000	EU2005
Reid vapor pressure, max kPa	45-90	60	60
Sulphur content, max ppm	500	150	50 (10)
Benzene content, max %	2,0	1,0	1,0
Aromatic content, max %	-	42	35
Olefin content, max %	-	18	14

Reforming – **Benzene content reduction**

- **Pre-fractioning**
  reduction of precursor molecules
- **Post-fractioning**
  direct benzene content reduction

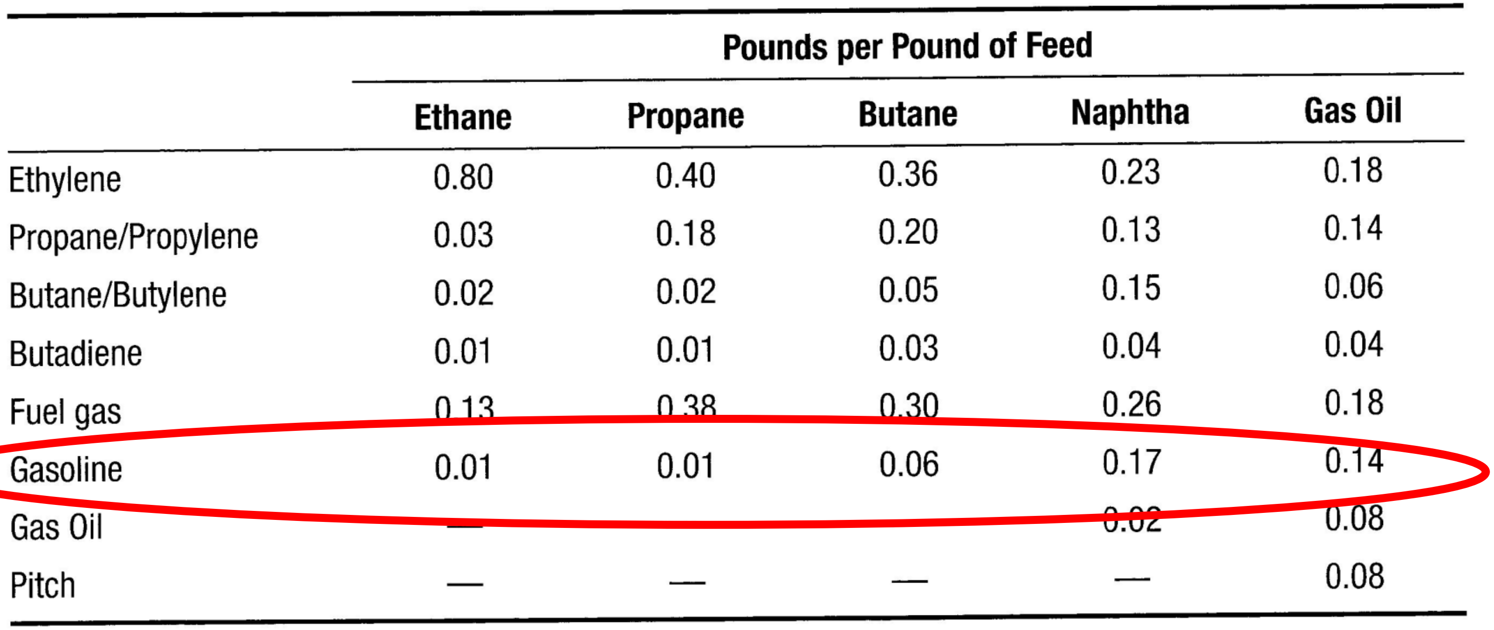




- **Technology dependence**
  independent of process pressure
- **FCC sources**
  contribution is constant
- **USA benzene limit**
  0,62 vol%
- **Post-fractioning**
  necessary

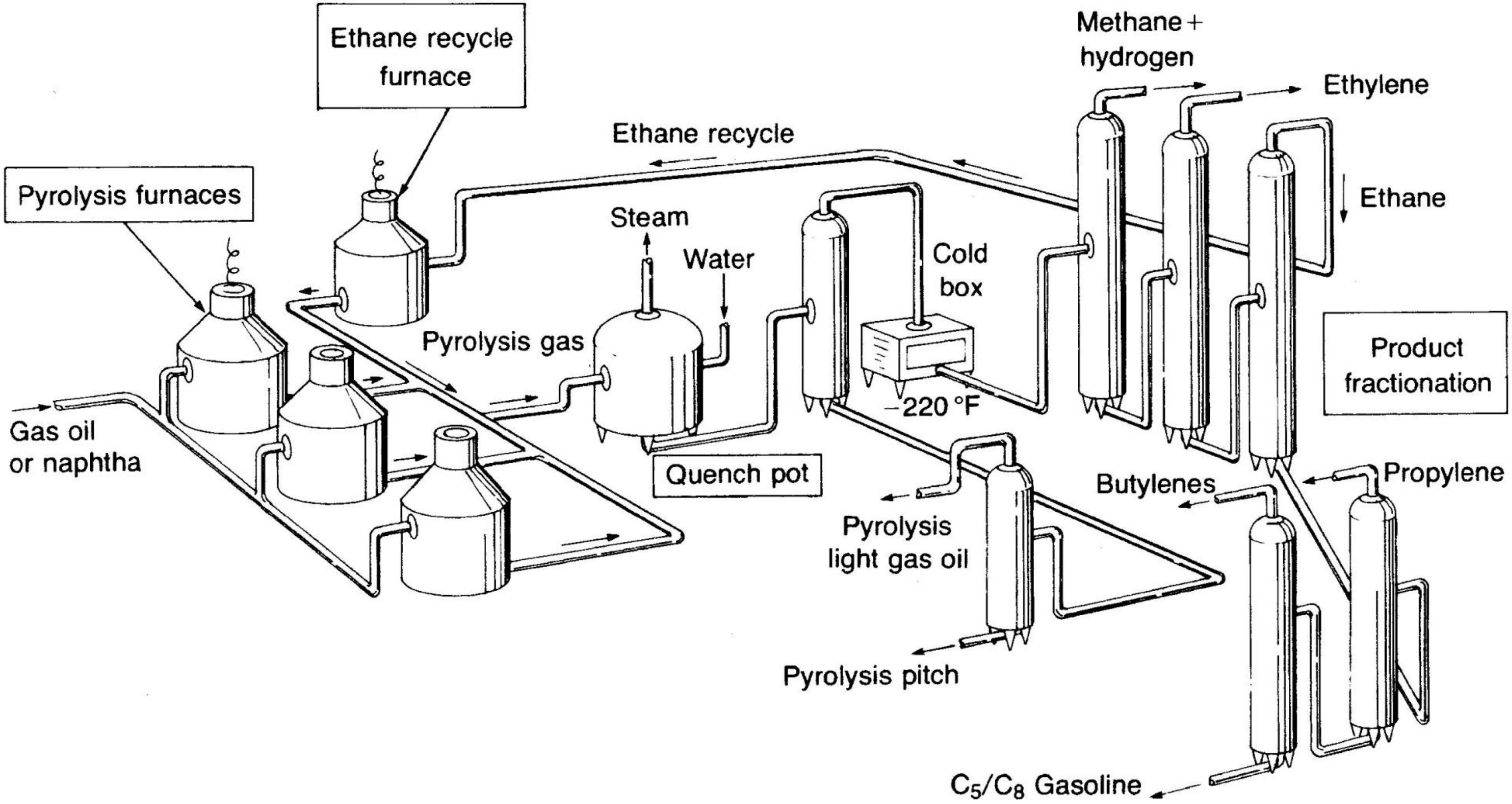
Sources – **Steam cracking**

- Old technology – since the 1930'ies
- **The economic plant capacity** is in the range of a couple hundred thousand t/year
- **Different yields** according to the feedstock
- In Hungary, the feedstock is **petrochemical naphtha** (virgin naphtha)
- Strong competition with the newly built, high capacity, gas based Arabic plants

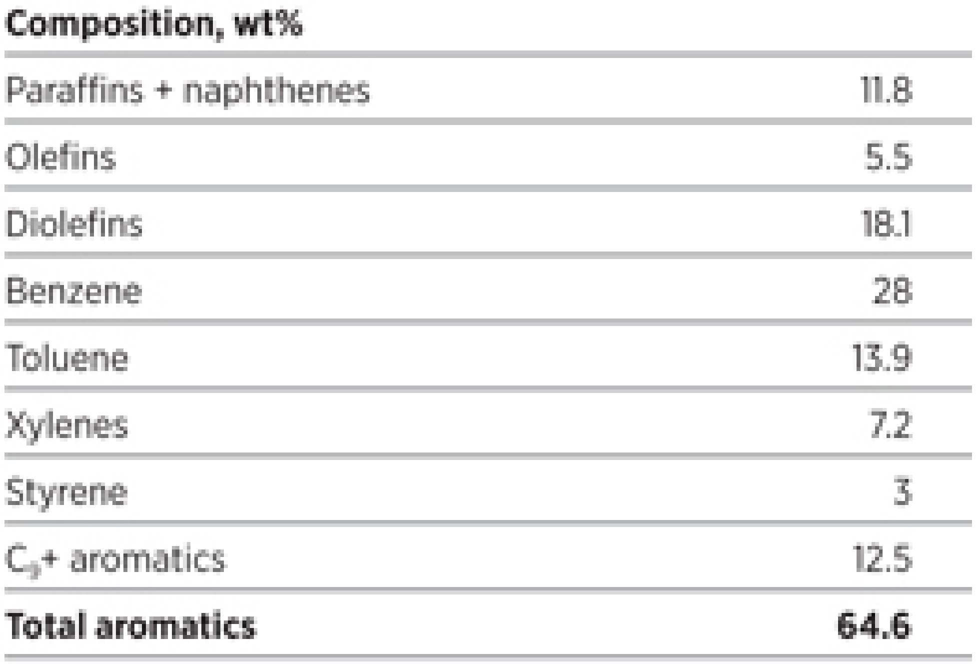


	Pounds per Pound of Feed				
	Ethane	Propane	Butane	Naphtha	Gas Oil
Ethylene	0.80	0.40	0.36	0.23	0.18
Propane/Propylene	0.03	0.18	0.20	0.13	0.14
Butane/Butylene	0.02	0.02	0.05	0.15	0.06
Butadiene	0.01	0.01	0.03	0.04	0.04
Fuel gas	0.13	0.38	0.30	0.26	0.18
Gasoline	0.01	0.01	0.06	0.17	0.14
Gas Oil	—			0.02	0.08
Pitch	—	—	—	—	0.08

Steam cracking – **Technology**

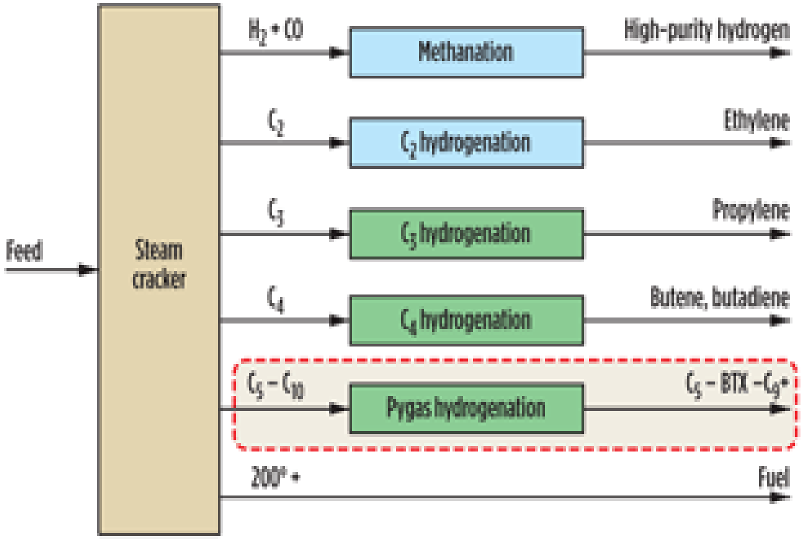


Steam cracking – Pygas composition



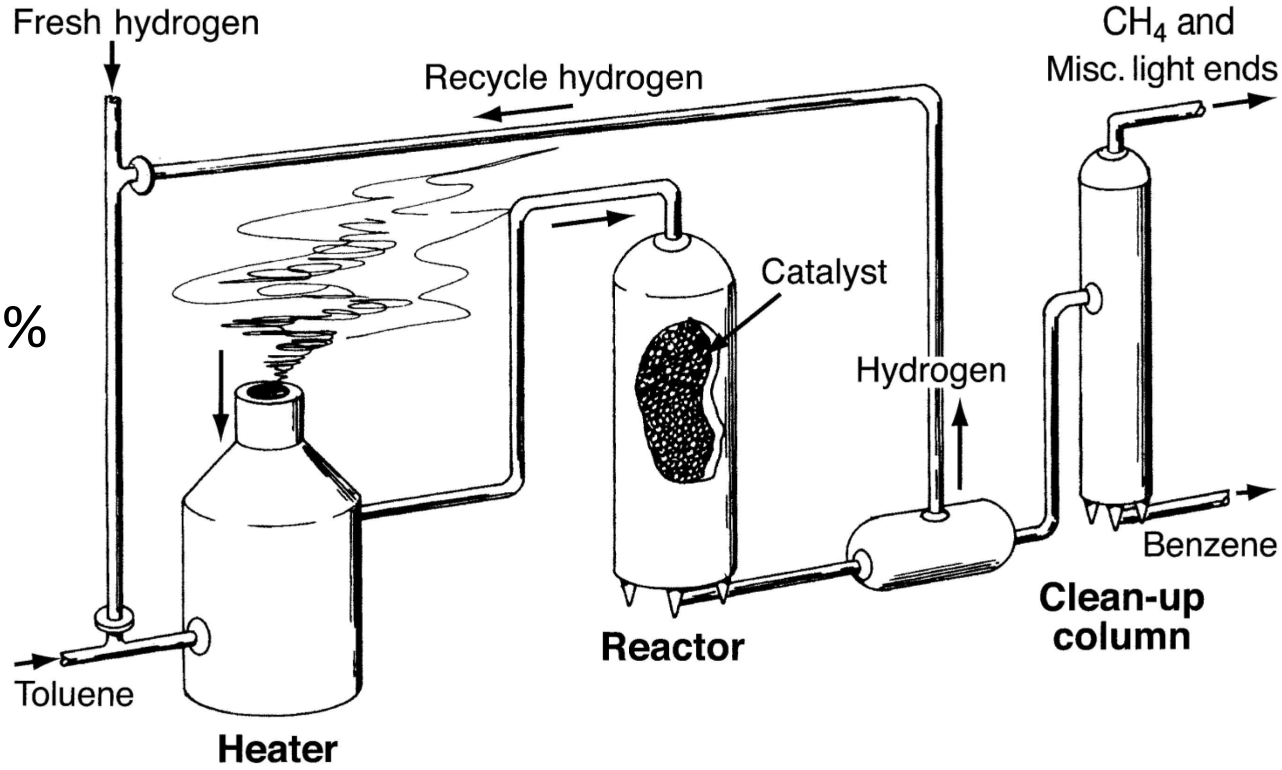
Composition, wt%	
Paraffins + naphthenes	11.8
Olefins	5.5
Diolefins	18.1
Benzene	28
Toluene	13.9
Xylenes	7.2
Styrene	3
C_9+ aromatics	12.5
Total aromatics	**64.6**

- **Pygas may be used**
  - as gasoline blending component
  - as aromatic extraction feedstock



Sources – Toluene hydrodealkylation

- In the case, when toluene demand is lower than the supply, benzene may be produced by hydrodealkylation
- **Catalyst**:
  - Noble metal catalysis: Pt on alumina support
- **Parameters**:
  - 500-650°C
  - 20-60 bar
- **Yields**:
  - Benzene: ~90%
  - Others: ~10%

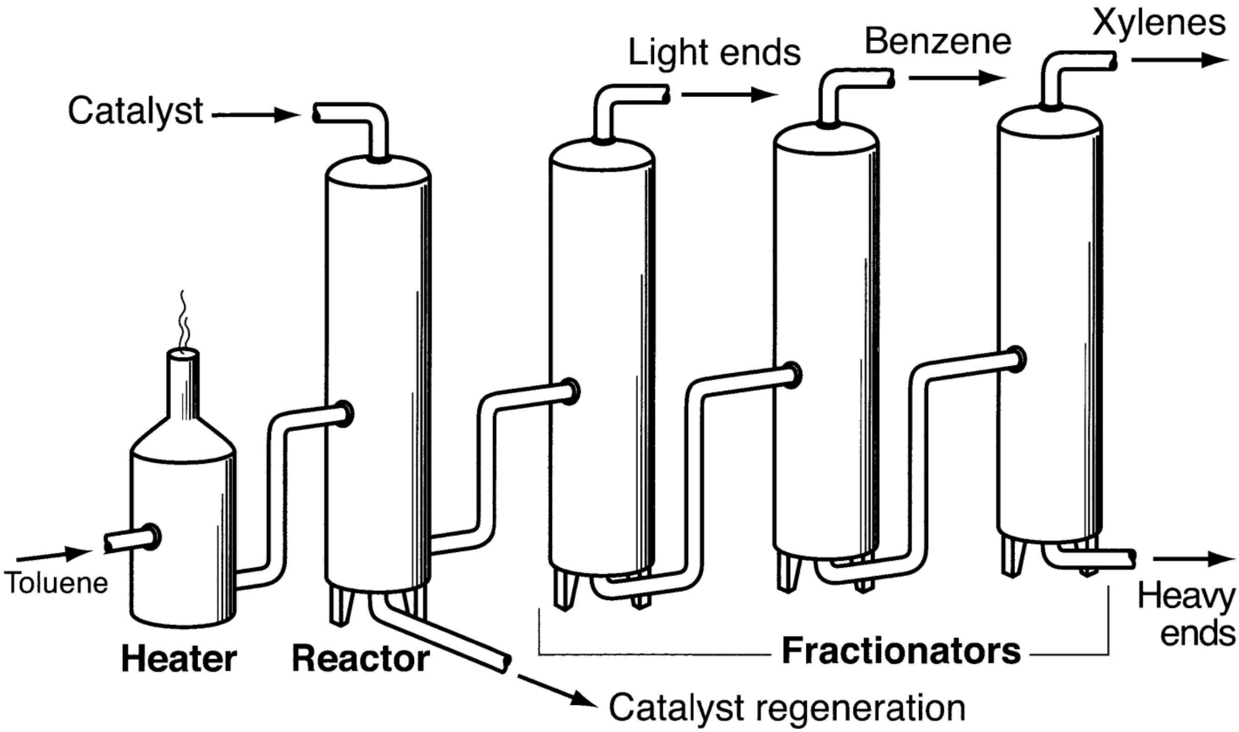


Sources – Toluene disproportioning

- In the case, when toluene demand is lower than the supply, benzene and xylenes may be produced by disproportioning
- **Catalyst**:
  - Noble metal catalysis: Pt and Pd on alumina support + Ce and Nd
  - Non-noble metal catalysis: Cr on alumina/silica support
- **Parameters**:
  - 350-500°C
  - 10-35 bar
- **Yields**:
  - Benzene: ~40%
  - Xylenes: ~55%

$$2C_6H_5CH_3 \rightarrow C_6H_6 + C_6H_4(CH_3)_2$$

Toluene Benzene Xylene



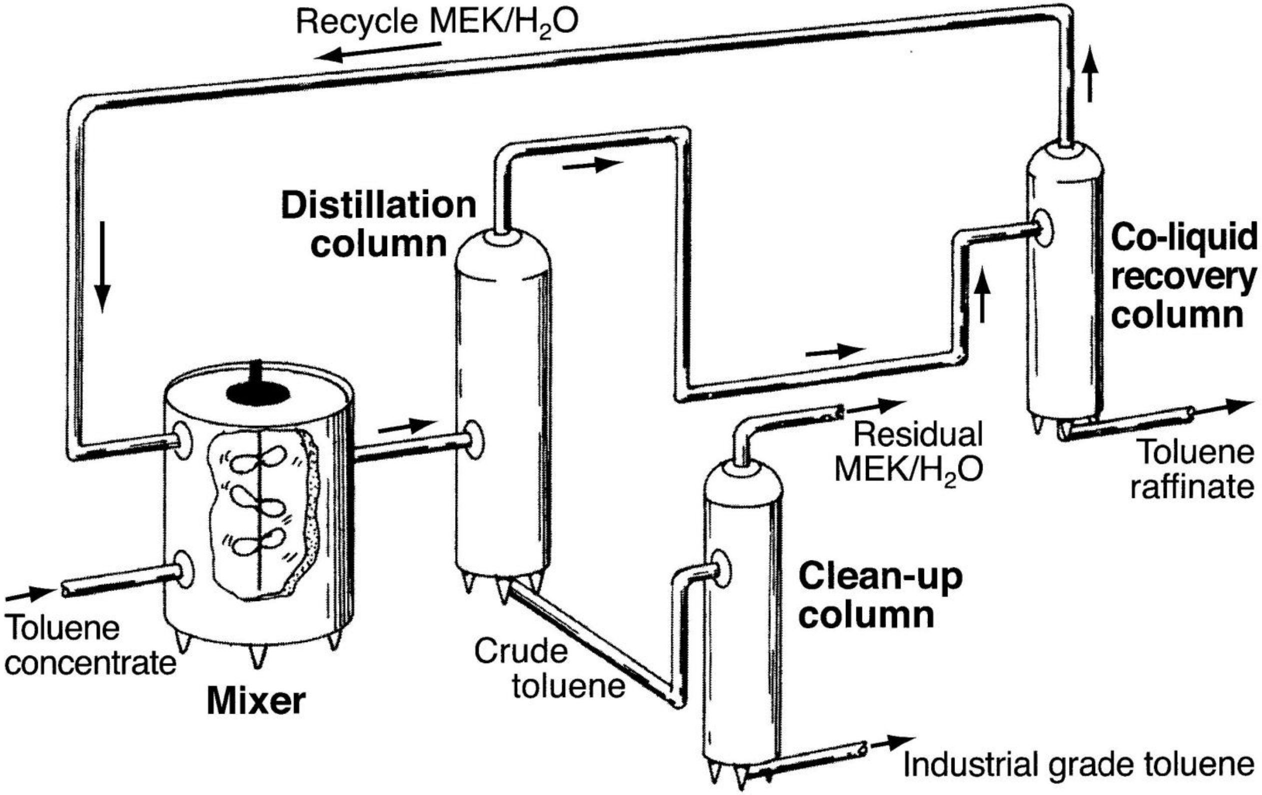
Toluene

Toluene – Sources, demand

- **Sources**, like at benzene, but
  - Reforming ~ 2/3
  - Steam cracking ~ 1/3
  - Coke-oven light oil ~0
- **Demands** are lower
  - than of benzene in absolute volume
  - than of supply in relative volume
- **Demand increased during WWII**
  - explosives – TNT
  - aviation gasoline (RON 103-106)
- **Since the 1960'ies**
  - aviation gasolines were overpaced by kerosene/JET
  - main area is the motor gasoline octane (+ petrochemistry)

Toluene – **Azeotrope distillation**

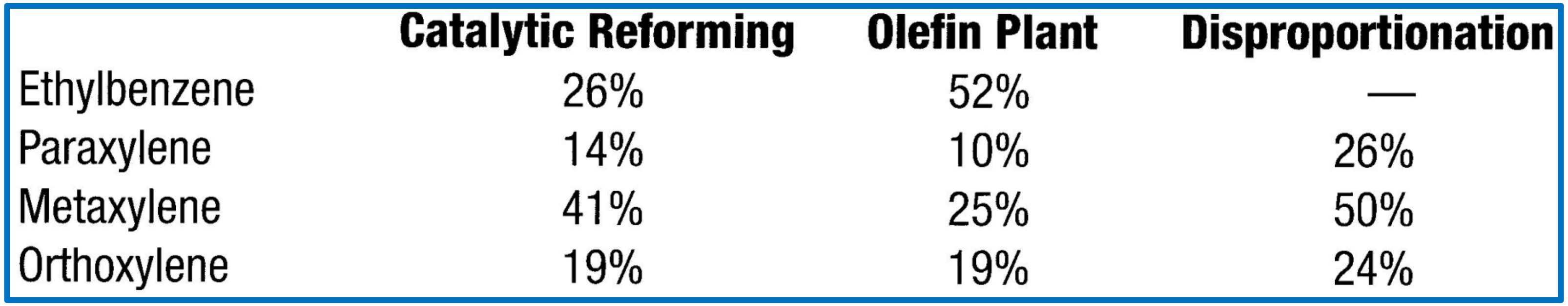
- Methyl-ethyl-ketone (MEK) – water (10%) solvent produces azeotrope mixture with the accompanying components (paraffin, naphthene)



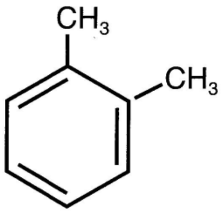
Xylenes

Xylenes – **Sources, demand**

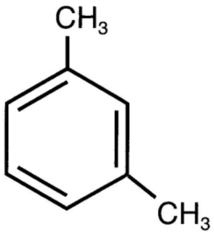
- **Sources**, like at benzene, but in different ratio
  - Reforming
  - Steam cracking
  - Toluene disproportioning



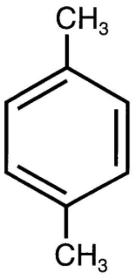
	Catalytic Reforming	Olefin Plant	Disproportionation
Ethylbenzene	26%	52%	—
Paraxylene	14%	10%	26%
Metaxylene	41%	25%	50%
Orthoxylene	19%	19%	24%



Ortho-xylene



Meta-xylene



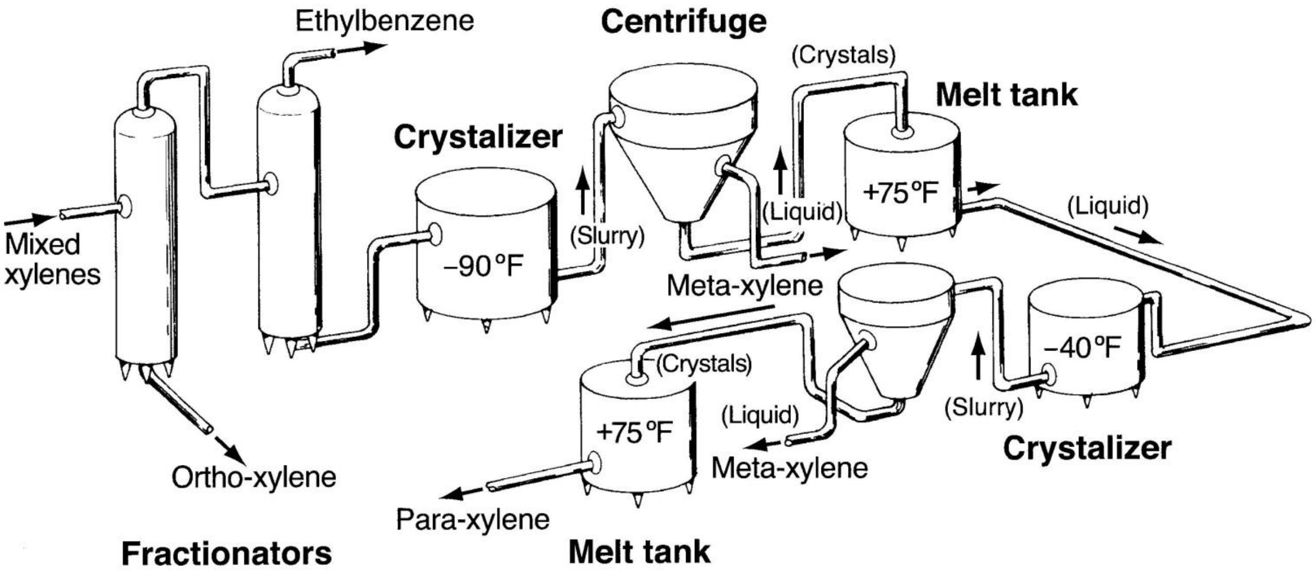
Para-xylene

Xylenes – **Separation possibilities**

- **o-Xylene and ethyl-benzene** separation is easily executed by distillation, due to their fairly differing boiling points (oX144°C, EB136°C)
- **Meta and para isomers** physical behaviour
  - **Boiling points** are closer than <1°C, so separation by distillation would be very expensive (mX139°C vs. pX138°C)
  - **Freezing points**, however, are largely differing (60°C), so the separation by crystallisation is quite easy (mX-48°C vs. pX13°C)
  - **Geometrical conformations** are different, so the separation by molecular sieves is also possible (p-xylene is thin) or selective adsorbing on the molecular sieve (m-xylene)

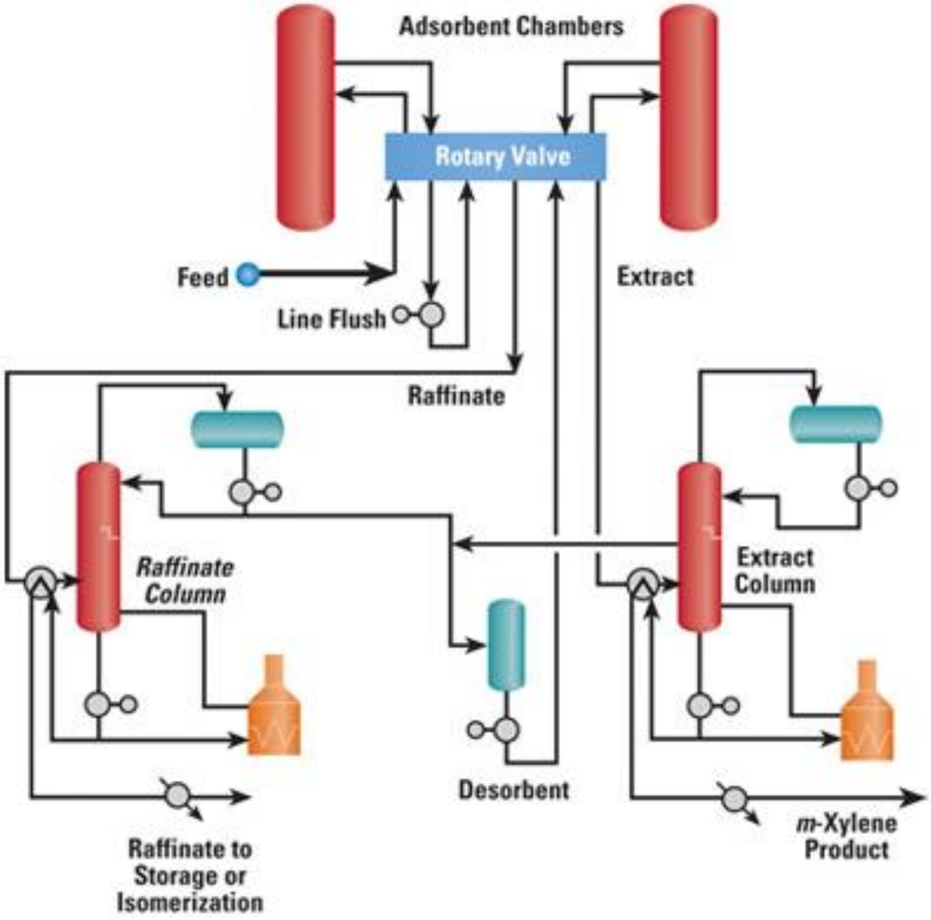
Xylenes – Cryogenic crystallisation

- The process is done normally in two crystallisation steps
  - In the **first step** big p-xylene crystals are formed due to the ultra deep temperature (80-90% purity)
  - In the **second step** (after melting) the cooling temperature is just between the freezing point of the two compounds, so 99% purity p-xylene may be produced



Xylenes – **Adsorption by molecular sieves**

- **UOP MX Sorbex** process
  - **m-xylene** is adsorbed
  - The process is executed on two parallel adsorbers
  - One is in adsorption mode, the other in desorption mode
  - Toluene is used as **desorbent** typically



Separation methods

Aromatic extraction

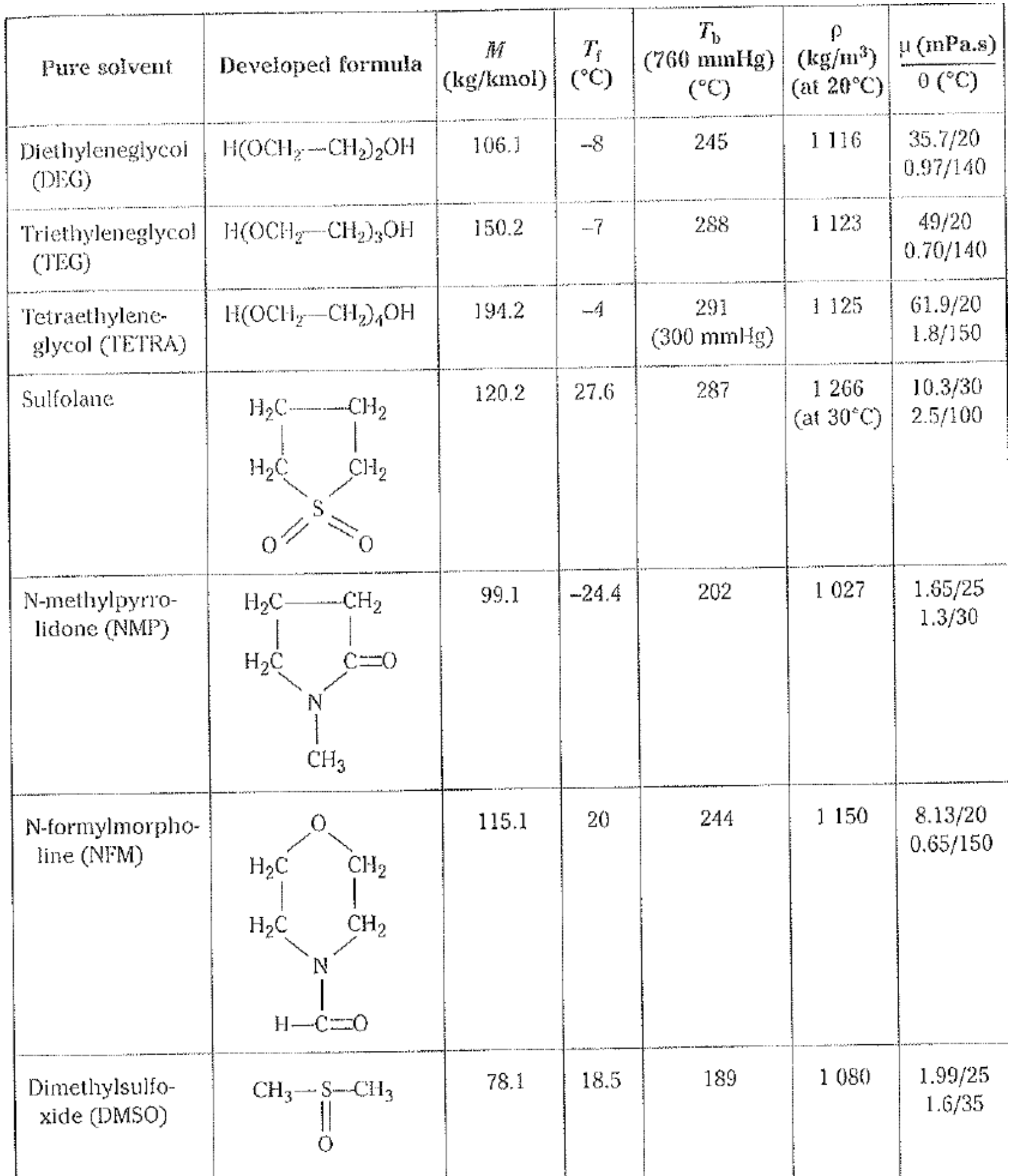
Aromatic extraction

- Aromatic compounds are typically separated by **extraction** from the non-aromatic components
  - Classical extraction
  - Extractive distillation
- By **prefractioning** the boiling range of the source fractions are narrowed (depending on feedstock and goal)
  - Less material needed to be extracted
  - Extraction would be more economic
  - Benzene/toluene/xylene rich fraction
  - Combined fraction
- The different feedstocks may be processed **one-by-one** or **together**

Aromatic extraction – Solvents

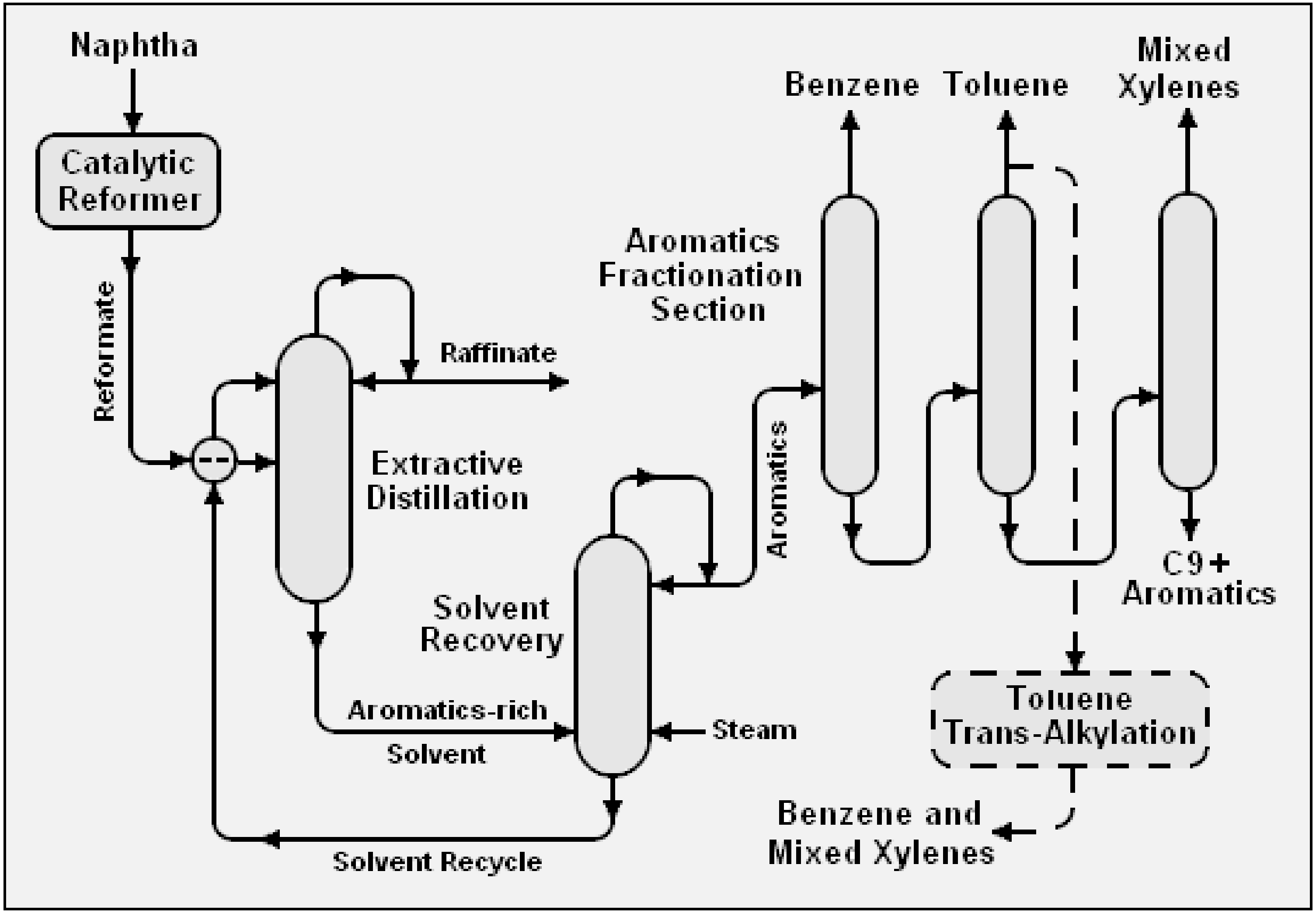
- **Requirements of the solvent**
  - Thermal stability
  - Chemical stability
  - Low toxicity
  - Low corrosivity
  - availability
  - Moderate cost
  - Sufficiently low crystallisation temperature
  - Boiling point to be significantly higher than of o-xylene bp
  - Specific gravity to be higher than 1,1
  - Viscosity to be lower than 2,5 mPa at operating temperature

Aromatic extraction – Solvents

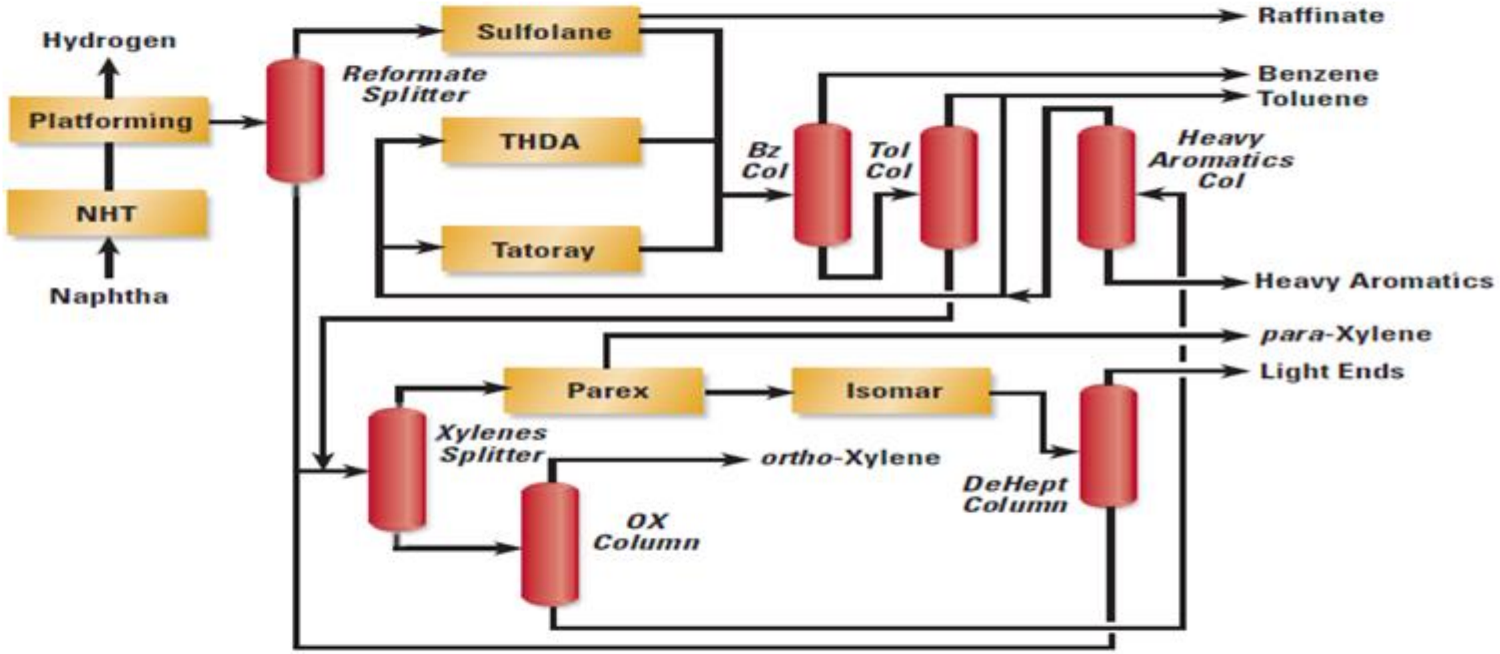


Pure solvent	Developed formula	M (kg/kmol)	T_f (°C)	T_b (760 mmHg) (°C)	ρ (kg/m³) (at 20°C)	μ (mPa.s) / θ (°C)
Diethyleneglycol (DEG)	$H(OCH_2—CH_2)_2OH$	106.1	–8	245	1 116	35.7/20 0.97/140
Triethyleneglycol (TEG)	$H(OCH_2—CH_2)_3OH$	150.2	–7	288	1 123	49/20 0.70/140
Tetraethyleneglycol (TETRA)	$H(OCH_2—CH_2)_4OH$	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)	$CH_3—\underset{\underset{O}{\Vert}}{S}—CH_3$	78.1	18.5	189	1 080	1.99/25 1.6/35

Extractive distillation

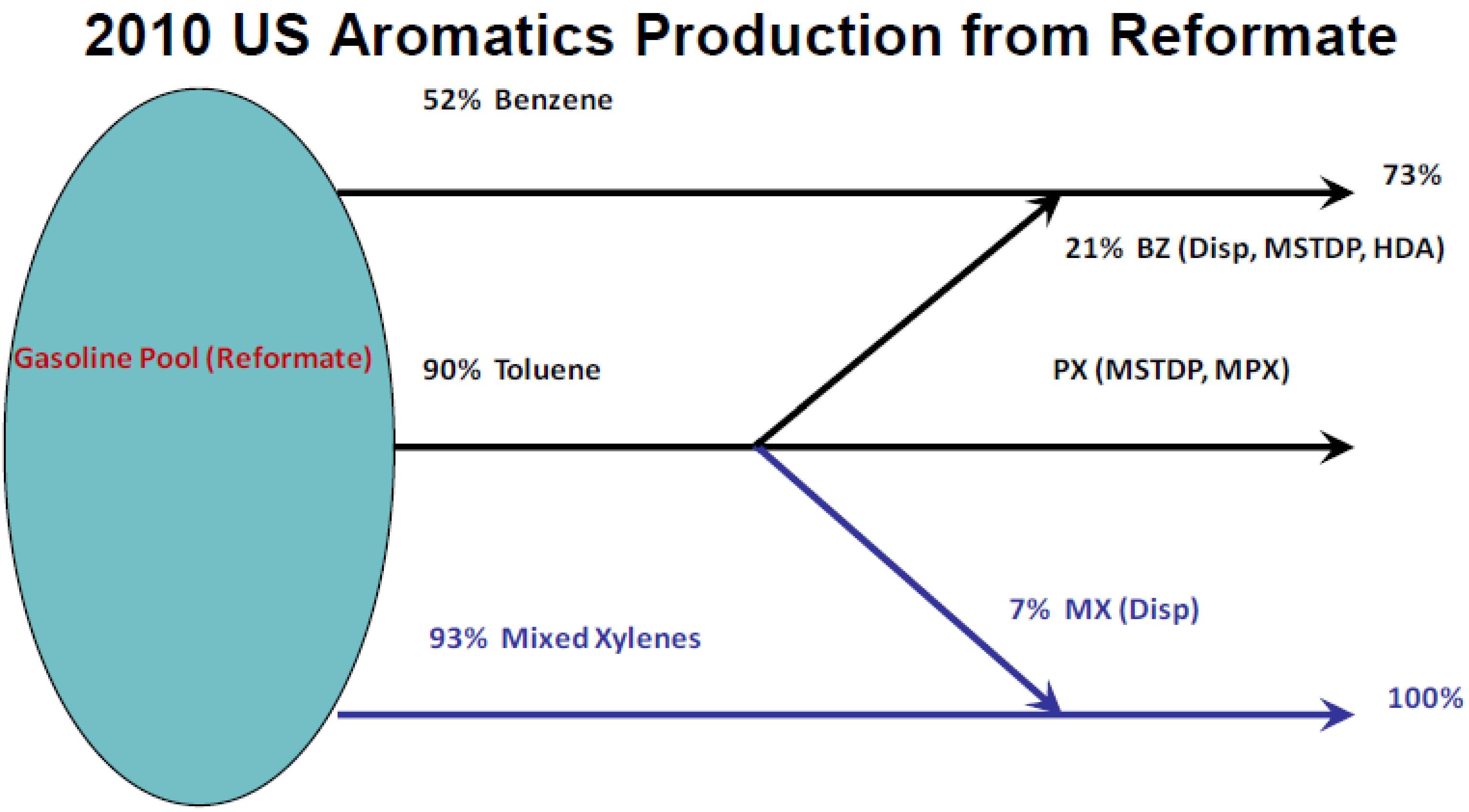


Integrated aromatic scheme – UOP



- **ED Sulfolane™ –** yields benzene and toluene by extractive distillation
- **THDA ™ –** toluene and heavier aromatics hydrodealkylation to benzene
- **Tatoray™ –** toluene and C9/C10 aromatics transalkylation to benzene and xylenes
- **Parex™ –** high purity p-xylene removal from C8 aromatic mixture
- **MX Sorbex™** – m-xylene separation from xylene mixture
- **Isomar™ –** xylene isomerisation according to equilibrium composition

US aromatics production from reformate



2010 US Aromatics Production from Reformate

Gasoline Pool (Reformate)

52% Benzene

73%

21% BZ (Disp, MSTDP, HDA)

90% Toluene

PX (MSTDP, MPX)

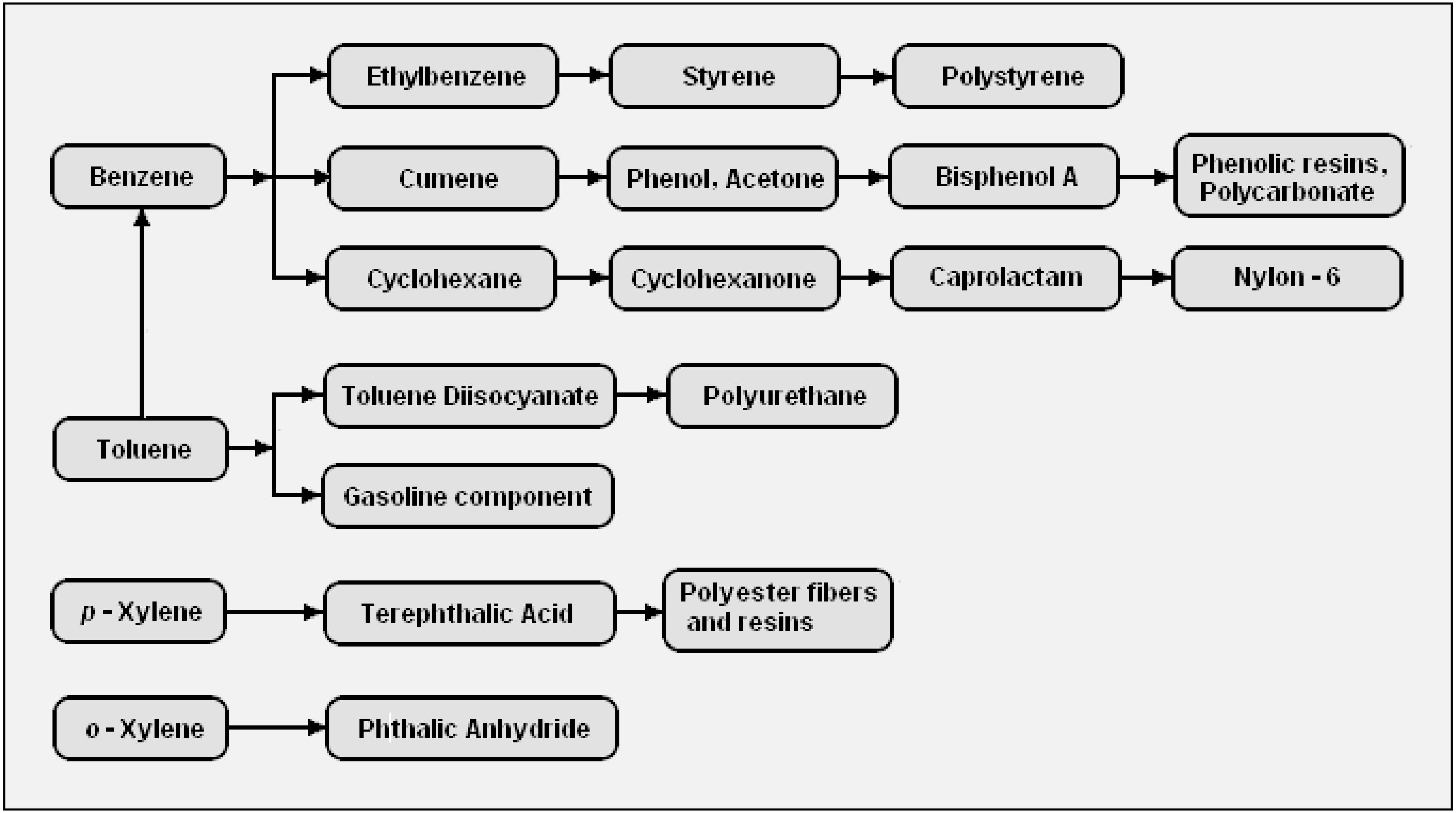
7% MX (Disp)

93% Mixed Xylenes

100%

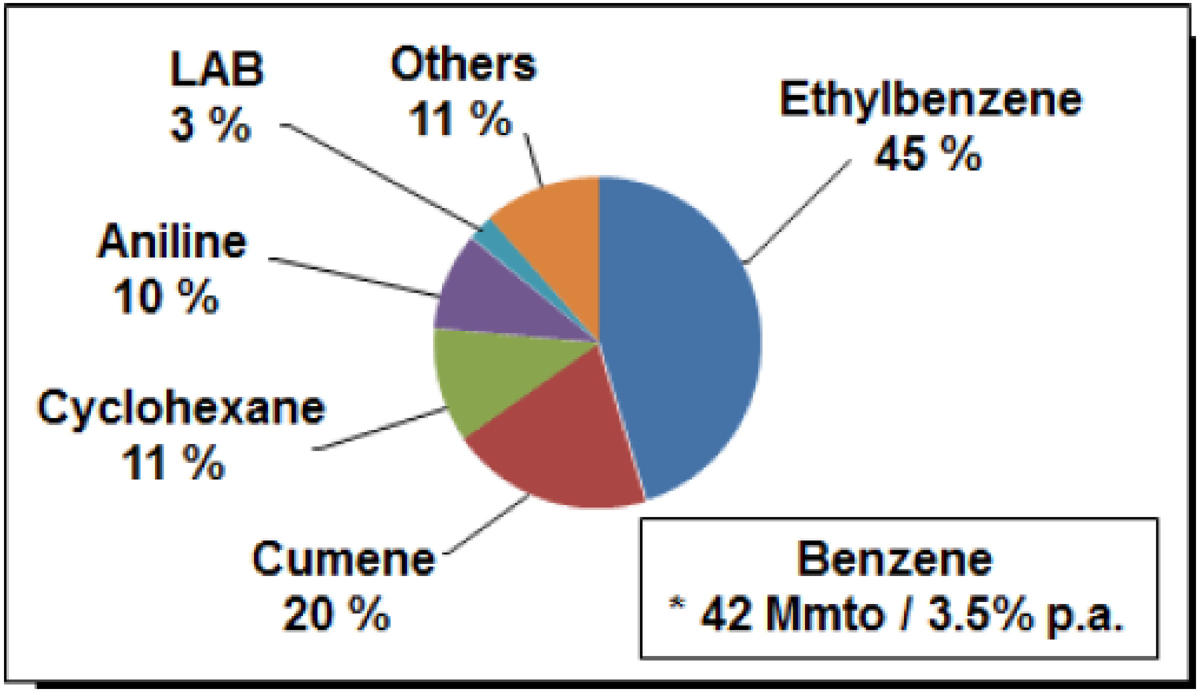
Utilisation of aromatics

Utilisation – **Main products**



Utilisation – **Benzene**

- Ethyl-benzene → styrene →
  - Polystyrene (PS)
  - Acrylonitrile-butadiene-styrene (ABS)
  - Styrene-butadiene rubber (SBR)

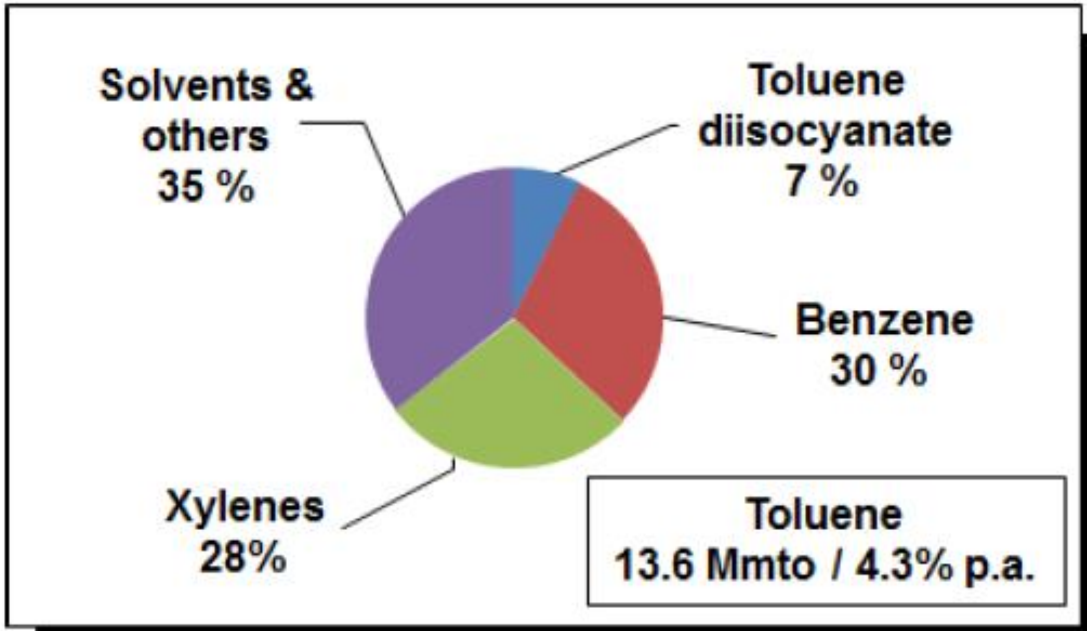


Utilisation – **Benzene**

- Cumene → Phenol (+ Acetone) →
  - Phenolic resins (plywood adhesives, electric industry/insulation resins)
  - bisphenol-A →
    - Produced since 1891 (2 phenol and 1 acetone molecules)
    - 70% - polycarbonate (CD, DVD, bullet proof „glass”)
    - 25% - epoxy resins (coatings)
- Cyclohexane →
  - nylon 6
  - nylon 66
- Aniline →
  - 90% MDI → polyurethane
  - 10% paint industry, pigments, weed-killers

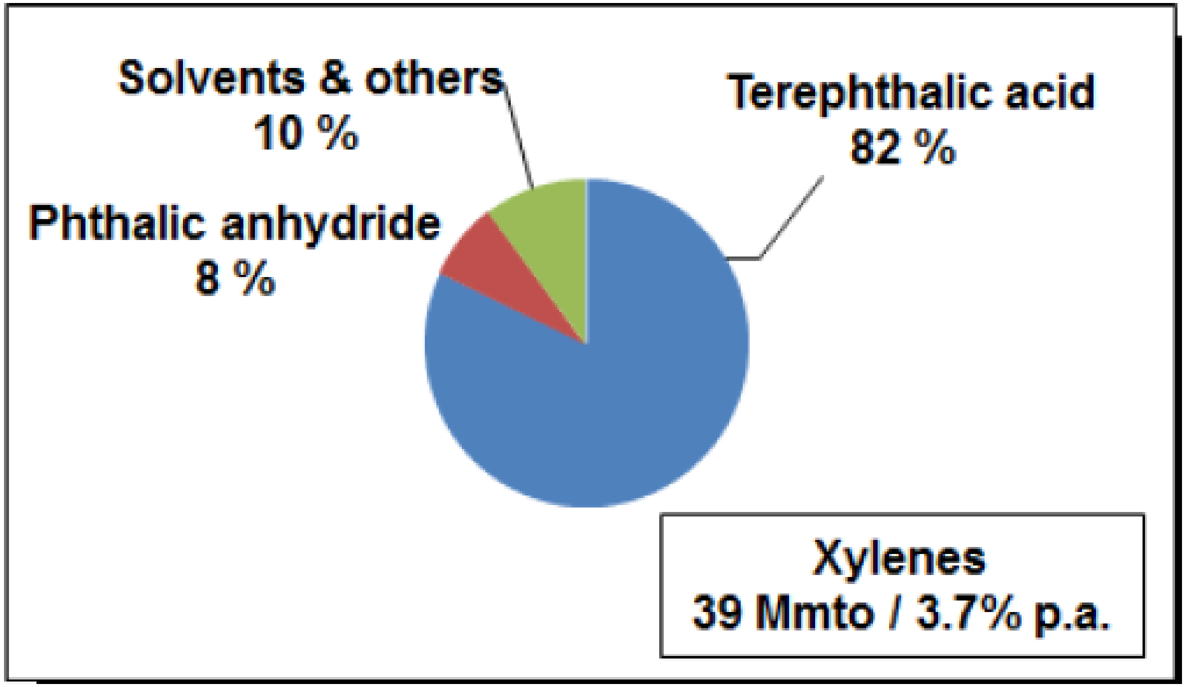
Utilisation – **Toluene**

- Disproportioning →
  - Benzene
  - Xylenes
- Hydrodealkylation → benzene
- TDI → polyurethane



Utilisation – **Xylenes**

- p-xylene → terephthalic acid → PET
- o-xylene → phthalic acid anhydride (polyester, alkyd resins, PVC plasticisers)
- m-xylene → isophthalic acid (low volume)

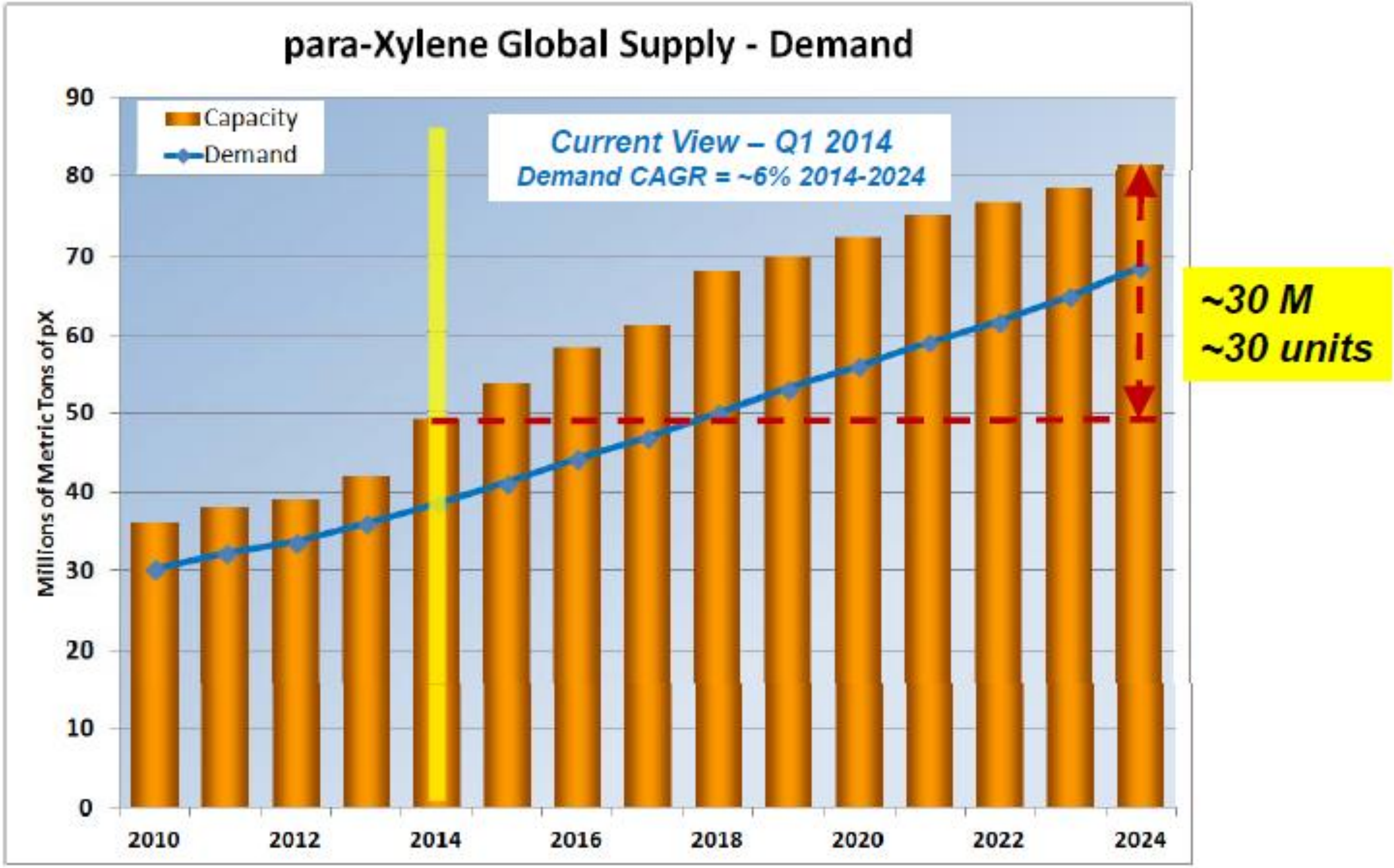


Trends

Market prices 2014

Product	2014. jan-jul.	2014. nov.
BRENT DTD CRUDE OIL PLATTS	$ 760	$ 557
DIESEL 10PPM FOB ROTT PLATTS	$ 920	$ 737
PREM UNL 10PPM (95RON) FOB ROTT PLATTS	$ 994	$ 768
NAPHTHA FOB MED PLATTS	$ 903	$ 600
BENZENE NWE CONTRACTS PLATTS	$ 1 280	$ 1 169
BENZENE SPOT BARGES FOB ROTT PLATTS	$ 1 419	$ 1 033
ORTHOXYLENE NWE MONTH CONTR PLATTS	$ 1 184	$ 1 137
XYLENE SPOT BARGES FOB ROTT PLATTS	$ 1 079	$ 866

p-Xylene – Supply-demand balance



Restrictions on supply

- **Decreasing demand for reforming**
  - **Decreasing fuel demand,** lower engine consumptions
    - Europe is moving towards dieselisation, lower consumptions, electric/hybrid drives
  - **More stringent quality requirements** (aromatics/benzene), alternative/renewable components ratio
    - Bio-ethanol, bio-ETBE
  - Very **law US natural gas price** (third-half of European) → hydrogen demand is cheaper to satisfied by alternatives (SMR)
    - Due to environmental regulations, many refinery implemented its hydrogen producing capacities (10 ppm motor fuels, residue upgrading hydrogen demand)
  - **Reformers are utilised at minimum capacity**, older ones to be mothballed

Conversion to petrochemical feedstock production???

Literature

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