

Catalysts & Catalytic Processes in Petrochemical Industry



Dr.K.R.Krishnamurthy

National Centre for Catalysis Research (NCCR)

Indian Institute of Technology

Chennai-600036

INDIA

Contents

- Petrochemicals from:
 - Ethylene
 - Propylene
 - Butadiene
 - Pyrolysis gasoline
- Linear alkyl benzene
- Processes for production of Xylenes
- Processes for production of other aromatics
- Hydrodesulphurization

Thermal cracking



Ethylene stream

Polyethylene (LDPE, LLDPE, HDPE)

- ☺ Zeigler - Natta MgCl_2 - TiCl_4 Supported catalyst
- ☺ Metallocene based catalyst
- ☺ New generation single site catalyst

Ethylene dichloride - Vinylchloride - Polyvinylchloride(PVC)

- ☺ Chlorination of ethylene in a bubble column reactor to EDC
- ☺ EDC on pyrolysis give vinyl chloride monomer (VCM) & HCl
- ☺ Catalytic Oxochlorination of ethylene & HCl to give EDC
- ☺ VCM on polymerization gives PVC.

Ethylene stream...

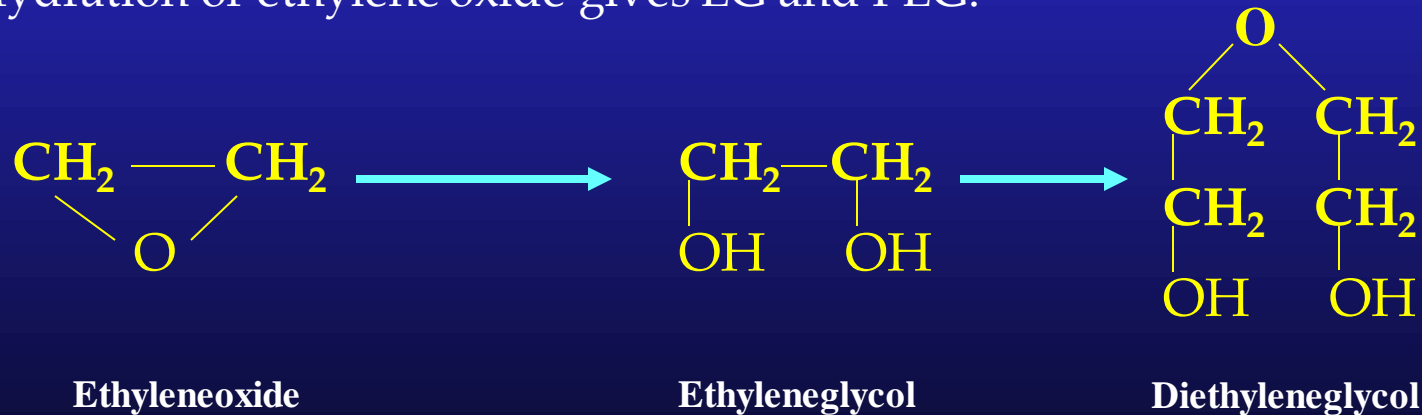
Ethylene oxide (EO) / Ethylene glycol (EG) / Polyethylene glycol (PEG)

Oxidation of ethylene with Oxygen in multi tubular reactor

Catalyst : Silver on alpha alumina carrier



Hydration of ethylene oxide gives EG and PEG.



Propylene stream

Polypropylene Slurry reactor

☺ Catalyst : FT1SS - MgCl_2 (Titanium catalyst)

Acrylonitrile

Ammoxidation of propylene in fluidized bed reactor

Catalyst : Molybdates of Bi, Fe, Co, Ni etc.

400 - 450°C, 2 Atm. Pressure



Butene-butadiene stream

Butane → **Butene** → **Butadiene**

Catalyst: Chromia - alumina; 600°c
90% Fe₂O₃ - 4% Cr₂O₃ - 6% K₂CO₃
Calcium nickel phosphate
Ca₈Ni(PO₄)₆ + 2% Cr₂O₃

Polybutadiene rubber (PBR)

- ☺ Polymerization reaction
- ☺ Cobalt octoate 6.8 mg/100g monomer
- ☺ Diethylaluminum chloride (deac) 0.0013mol / 100g monomer
- ☺ 25°c, 55% benzene, 23% butene-1, 22% 1,3-butadiene
- ☺ > 97% cisamer

Pyrolysis gasoline - Hydrogenation

Raffinate from Naphtha cracker

Components: Diolefins, alkenylaromatics, olefins, paraffins, naphthenes and sulfur compounds

Hydrogenation

- ◆ Remove diolefins and alkenylaromatics
- ◆ Obtain gasoline blend stock
- ◆ Removal of sulfur
- ◆ Benzene extraction

Pyrolysis gasoline – Hydrogenation...

Two stage processing

Stage-1: Ni/Al₂O₃ Catalyst, 80-200°C

Liquid phase hydrogenation at 30 bar pressure

To remove diolefins and alkenylaromatics

The product is split into four cuts

1. C₅ cut 23% for gasoline / fuel
2. C₆ cut 31% for benzene extraction after 2nd stage hydrogenation.

Stage-2: Hydrogenation of olefins and HDS

Ni-MoS₂ / Al₂O₃ (310 - 320°C)

Co-MoS₂ / Al₂O₃ (345 - 370°C)

3. C₇ cut 42% gasoline blending stock
4. Heavy cut 4% carbon black feed

Linear Alkyl Benzene (LAB)

Feed: Superior kerosene C₉-C₁₉ stream & Benzene

- Hydrodesulphurization to remove sulphur (HDS Process)
- Adsorptive separation of C₁₀-C₁₃ non-normal paraffins (MOLEX Process)
- Dehydrogenation C₁₀-C₁₃ non-normal paraffins to mono-olefin



☞ Catalyst : Pt-Sn-In-Li/Al₂O₃

☞ Low bulk density spheroidal alumina

☞ UOP Pacol Process [IPCL/RIL Catalyst DHC Series]

⇒ Alkylation of benzene with mono-olefins to LAB

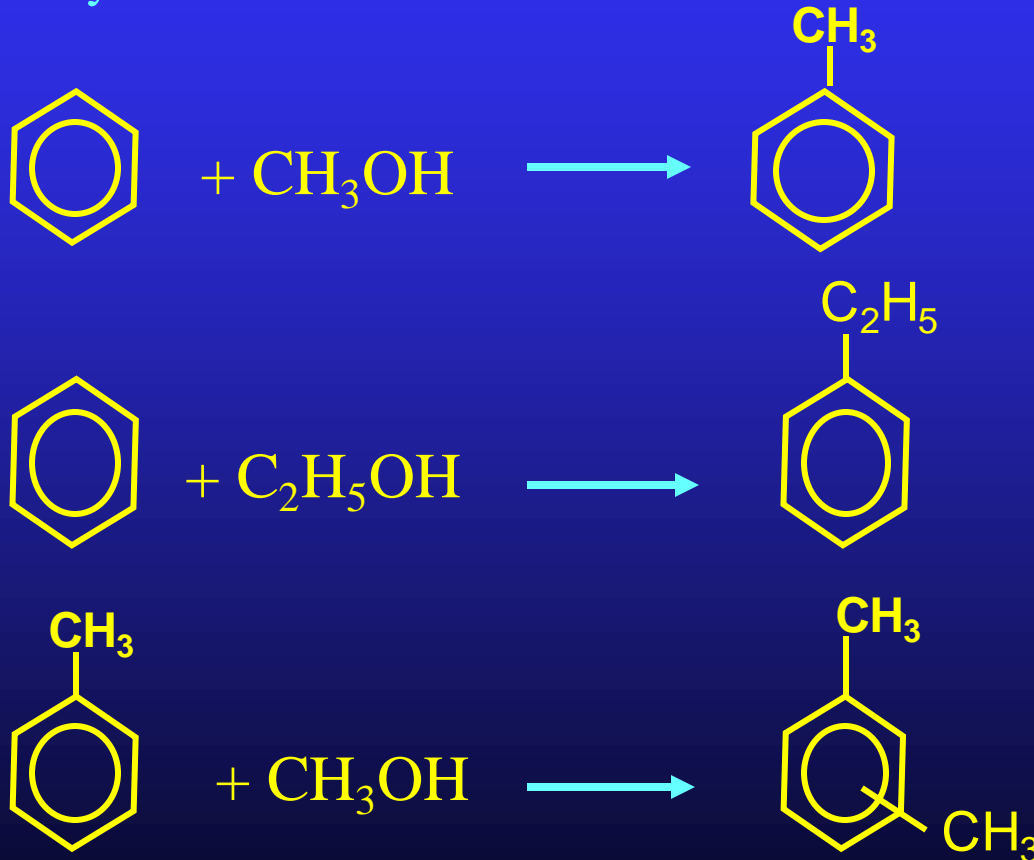
Catalyst: HF Liquid phase, near ambient temperature reaction

(Eco-friendly solid acid based process available currently- DETAL®- Process of UOP)

LAB is the raw material for detergent industry

Aromatics in Petrochemicals

- * **Primary aromatics:** Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)
- * Catalytic naphtha reforming
- * Catalytic alkylation of benzene



Catalytic Naphtha Reforming

Naphtha: B.R. (110-140°C)

Catalyst: Pt/Alumina (IPCL)
Pt-Re/Alumina (IPCL-IIP)

Products: Benzene, Toluene, Ethylbenzene,
Xylenes (ortho, meta & para), C₉₊ Aromatics

Reactions in reforming process

Dehydrogenation of paraffins and naphthenes.

Olefinic products oligomerize (polymerize) and remain adsorbed.

Continued dehydrogenation results in the formation of coke

(Coke is highly carbonaceous deposit having very high C/H ratio)

Effect of coking

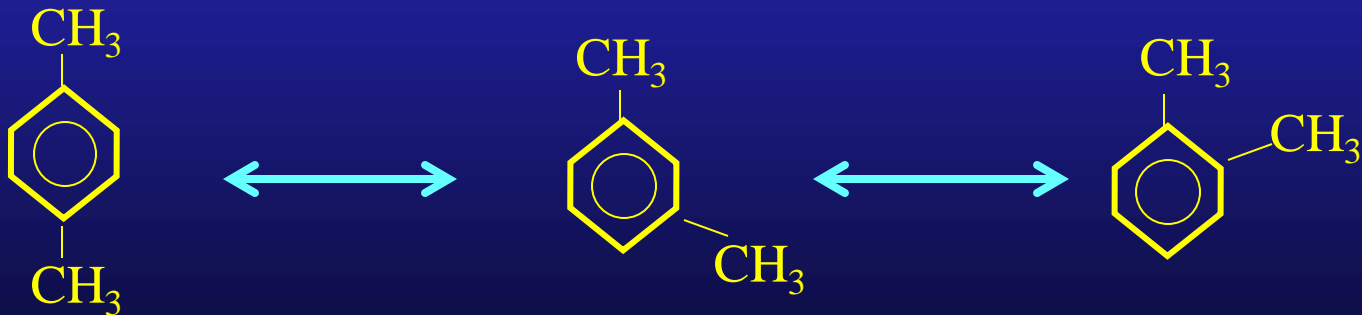
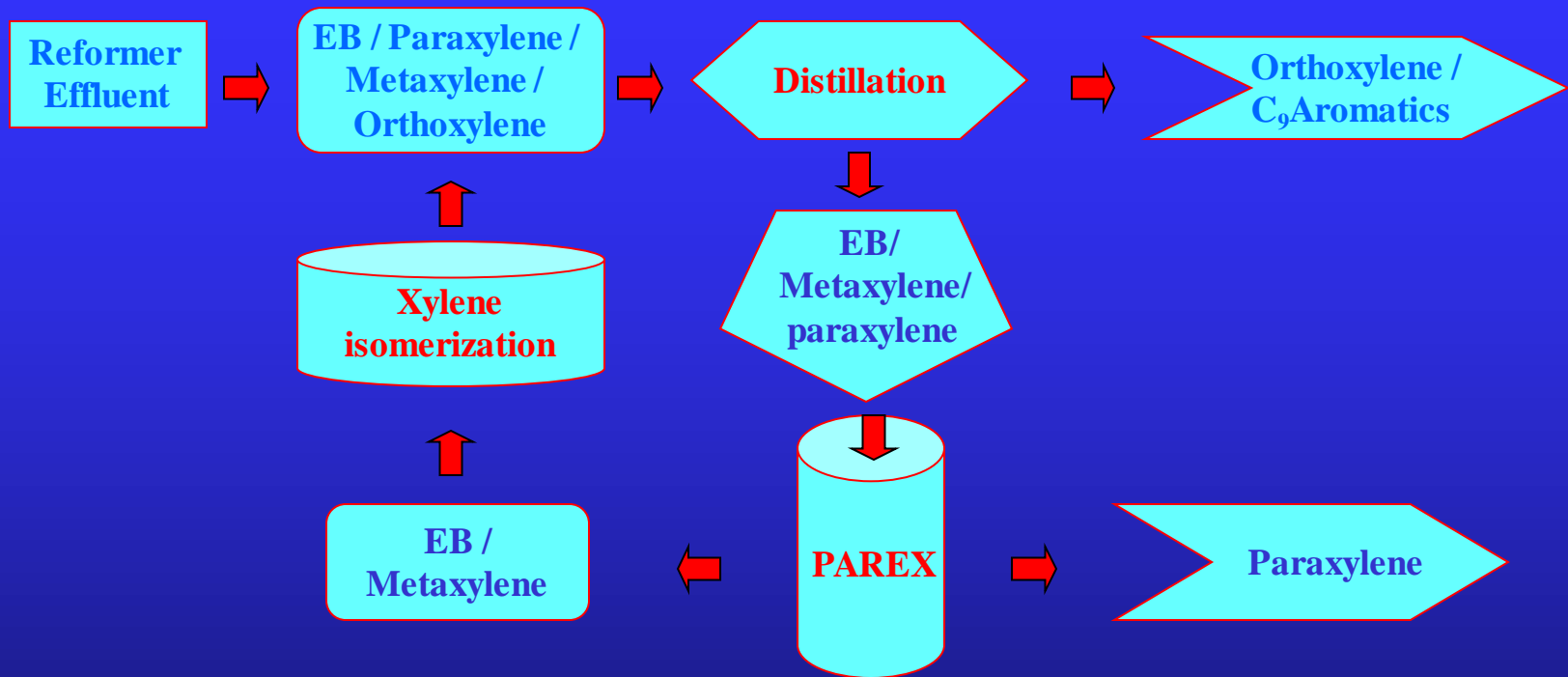
Masking of active sites - drop in activity.

Termination of operation - too low activity economically not viable.

Benzene, toluene, orthoxylene and paraxylene and C₉ Aromatics are recovered

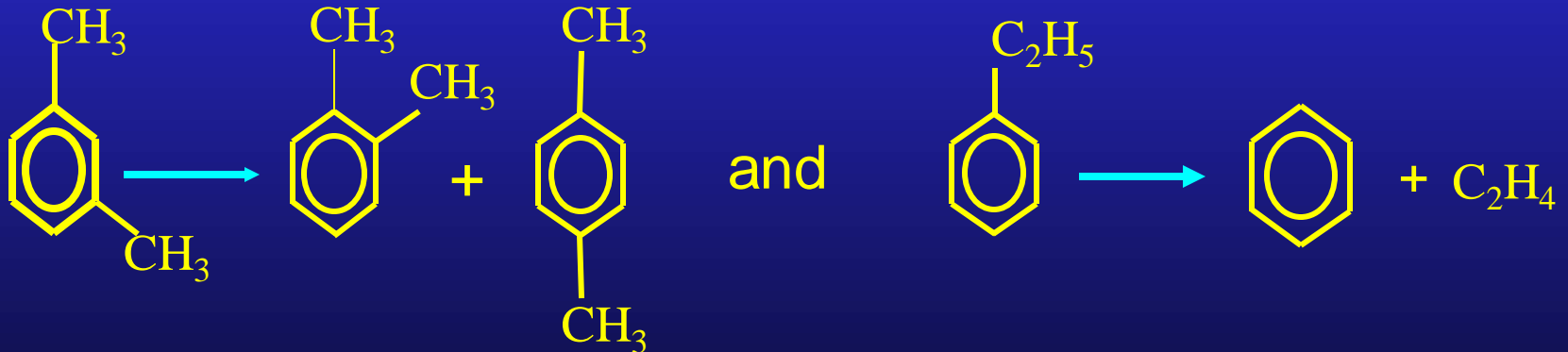
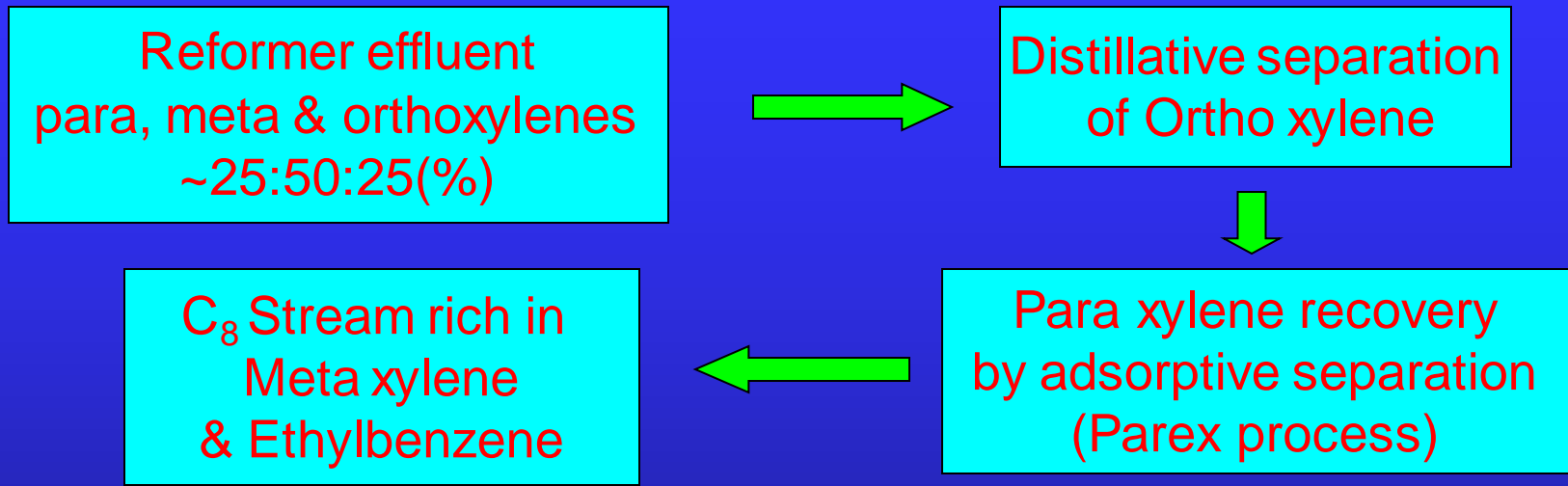
For Petroleum sector, the catalyst produce High Octane Gasoline for blending purpose

Xylene Isomerisation



Encilite-501 catalyst – IPCL-NCL - Zeolite based catalyst
Extremely long life – Rugged performance

Xylene Isomerisation



Catalyst:

Al_2O_3 / ZSM-5 Containing Pt (Encilite-501, IPCL-NCL)

Xylene Isomerization Process

Feed & Product composition

Component (wt%)	Feed	Product
Saturates	11.6	10.3
Benzene	--	6.0
Toluene	3.2	3.0
Ethylbenzene	22.3	15.1
Para Xylene	1.2	15.1
Meta Xylene	54.1	32.7
Ortho Xylene	7.29	14.7
C ₉ & C ₁₀ Aromatics	--	3.0

Xylene Isomerization Technology

Platinum based
catalyst

- Engelhard
- UOP

Zeolite based
catalyst

- Mobil
- IPCL-NCL

Around 80% plants in the world use Zeolite based catalyst

- ↓ Lower plant size
- ↓ Lower energy cost
- ↓ Less catalyst
- ↓ Less Platinum

Catalytic routes for aromatics production

Reforming :Catalytic reforming of naphtha to Benzene, Toluene, Ethylbenzene & Xylenes

Isomerization :Isomerization of meta xylene to para and ortho xylenes

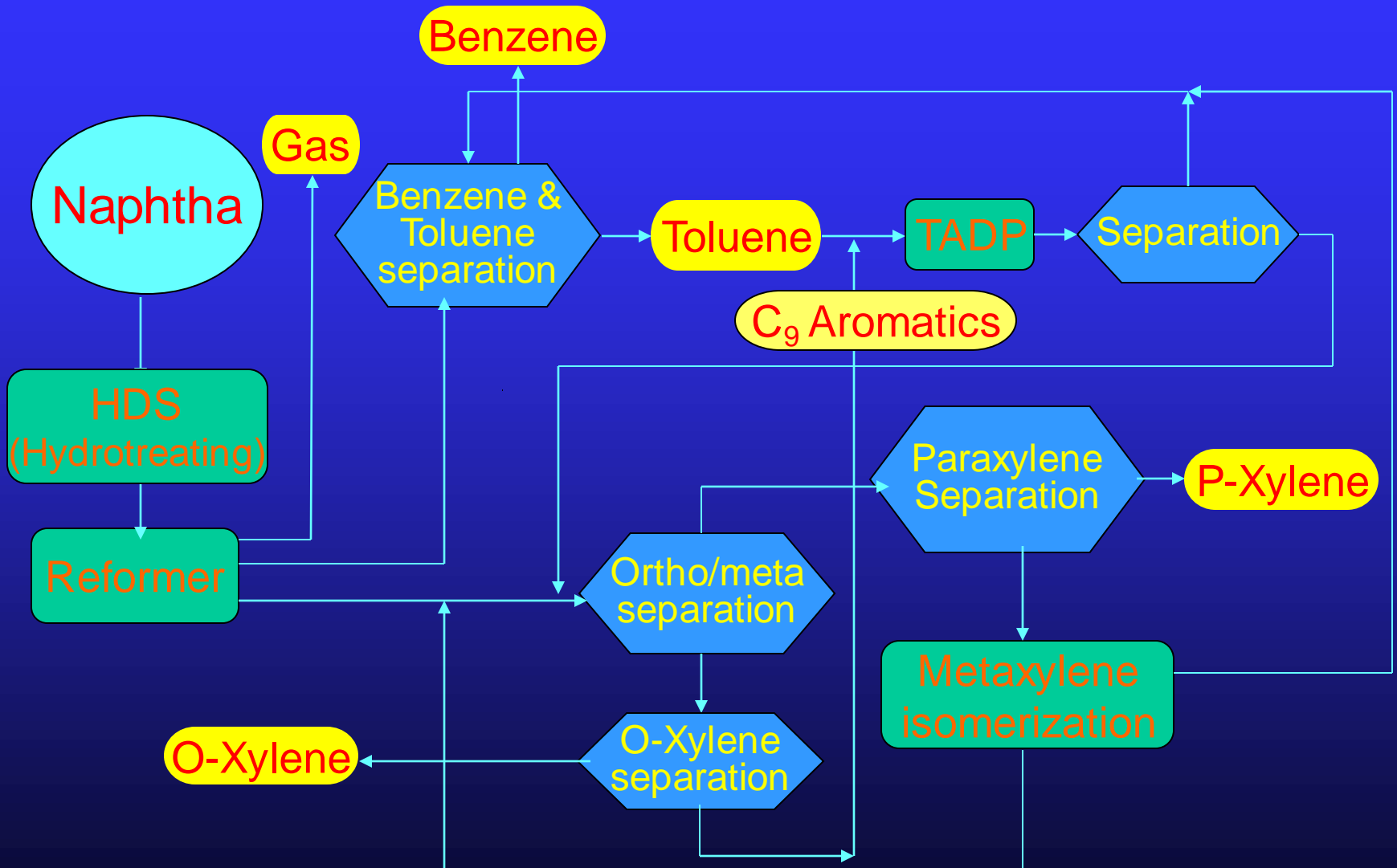
TADP :Transalkylation and Disproportionation of C₇ and C₉ aromatic molecules

TDP :Toluene disproportionation to xylenes and benzene

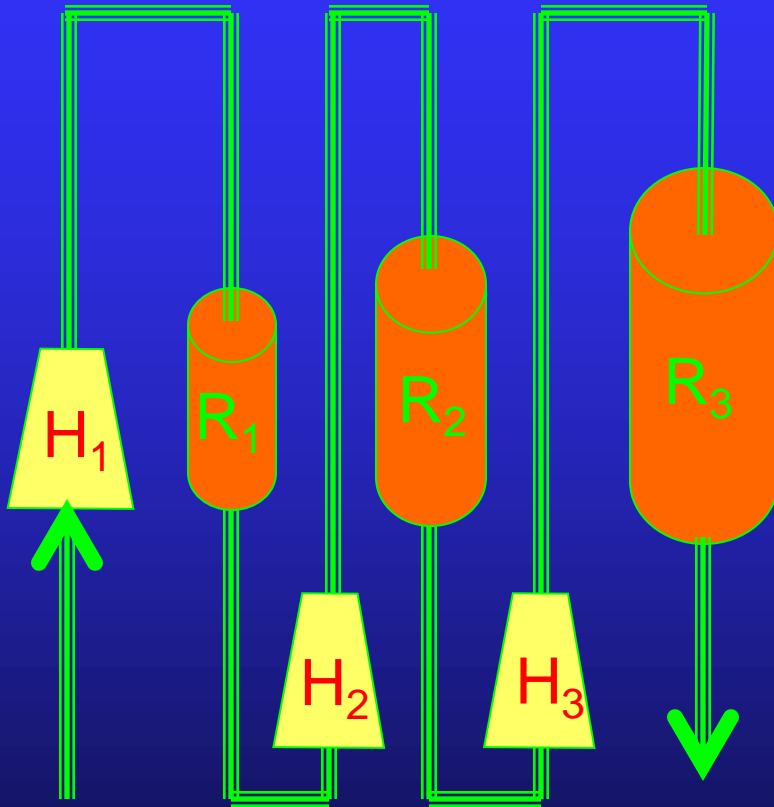
STDP :Selective conversion of Toluene to para xylene by disproportionation

Aromatization :Conversion of light hydrocarbons to benzene, toluene and xylenes

Aromatics complex

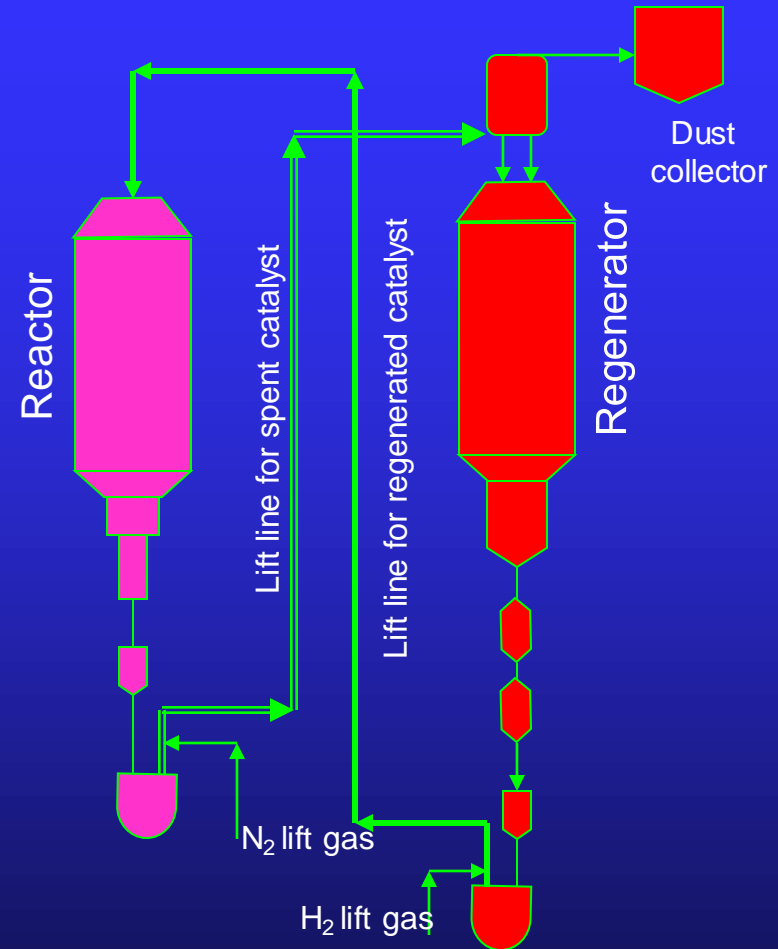


Reformer Reactor systems-SR & CCR modes



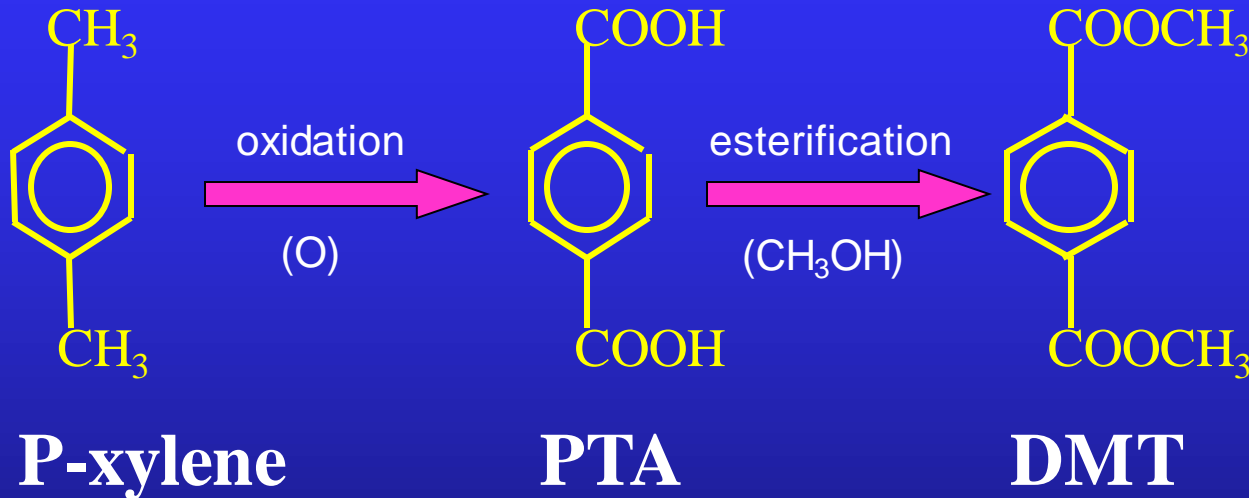
Semi Regenerative (SR)

Recent trend: Use of (CCR) mode



Continuous Catalyst
Regeneration (CCR)

Purified Terephthalic Acid (PTA) & Dimethylterephthalate (DMT)

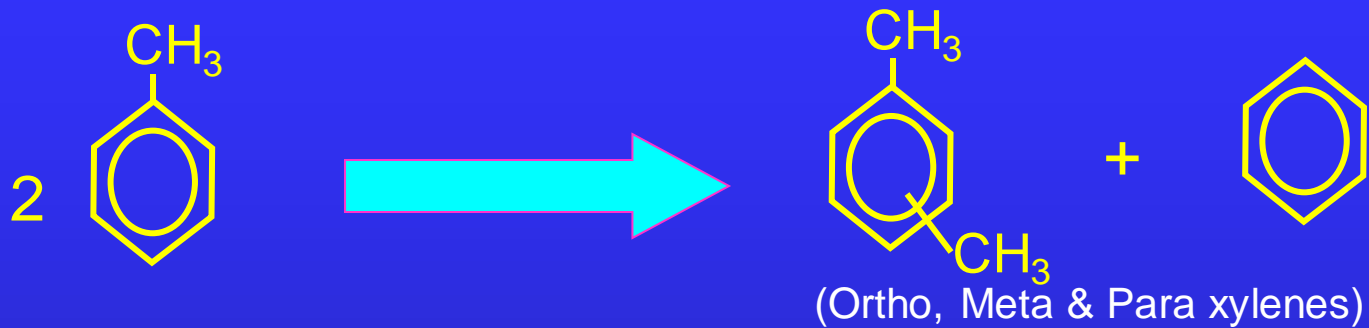


Liquid phase reaction

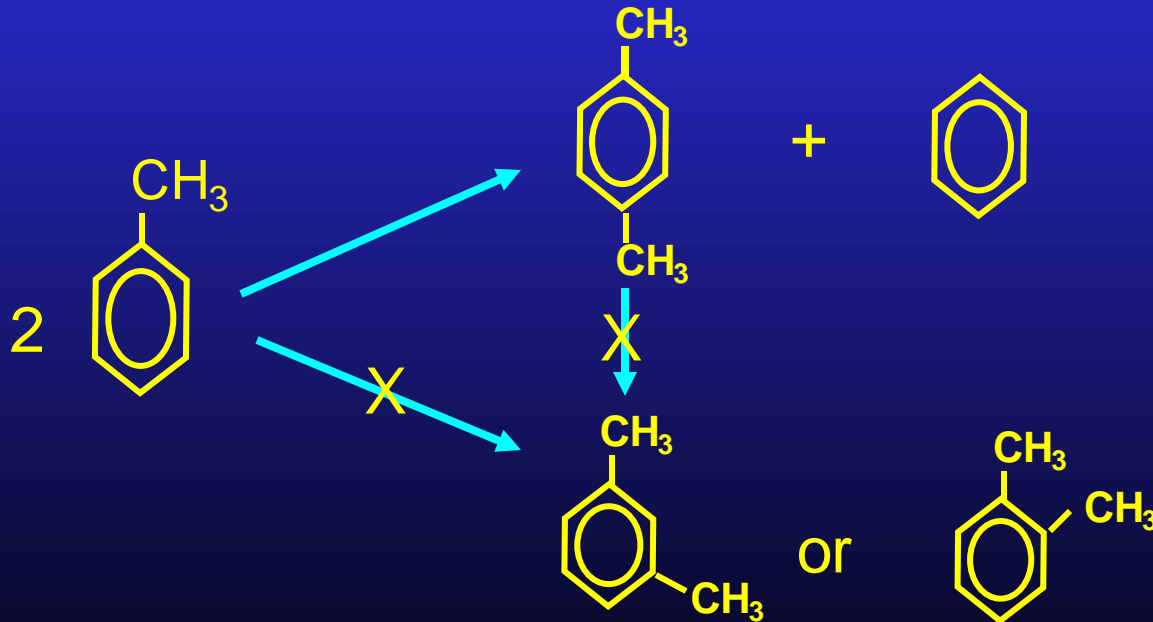
Catalyst : Co & Mn salts of C₆-C₁₂ fatty acids and bromides of heavy metals in acetic acid solvent.

PTA/DMT is subjected to condensation polymerization with EG to obtain Polyethylene terephthalate (PET)

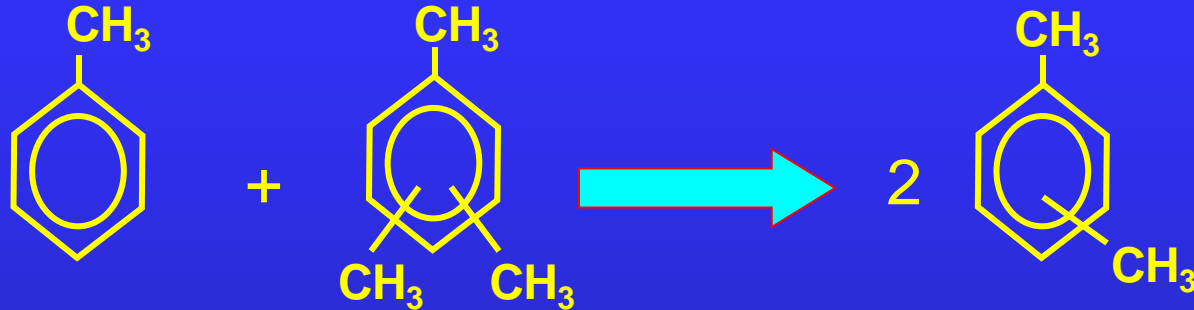
Toluene Disproportionation Process



Selective Toluene Disproportionation Process



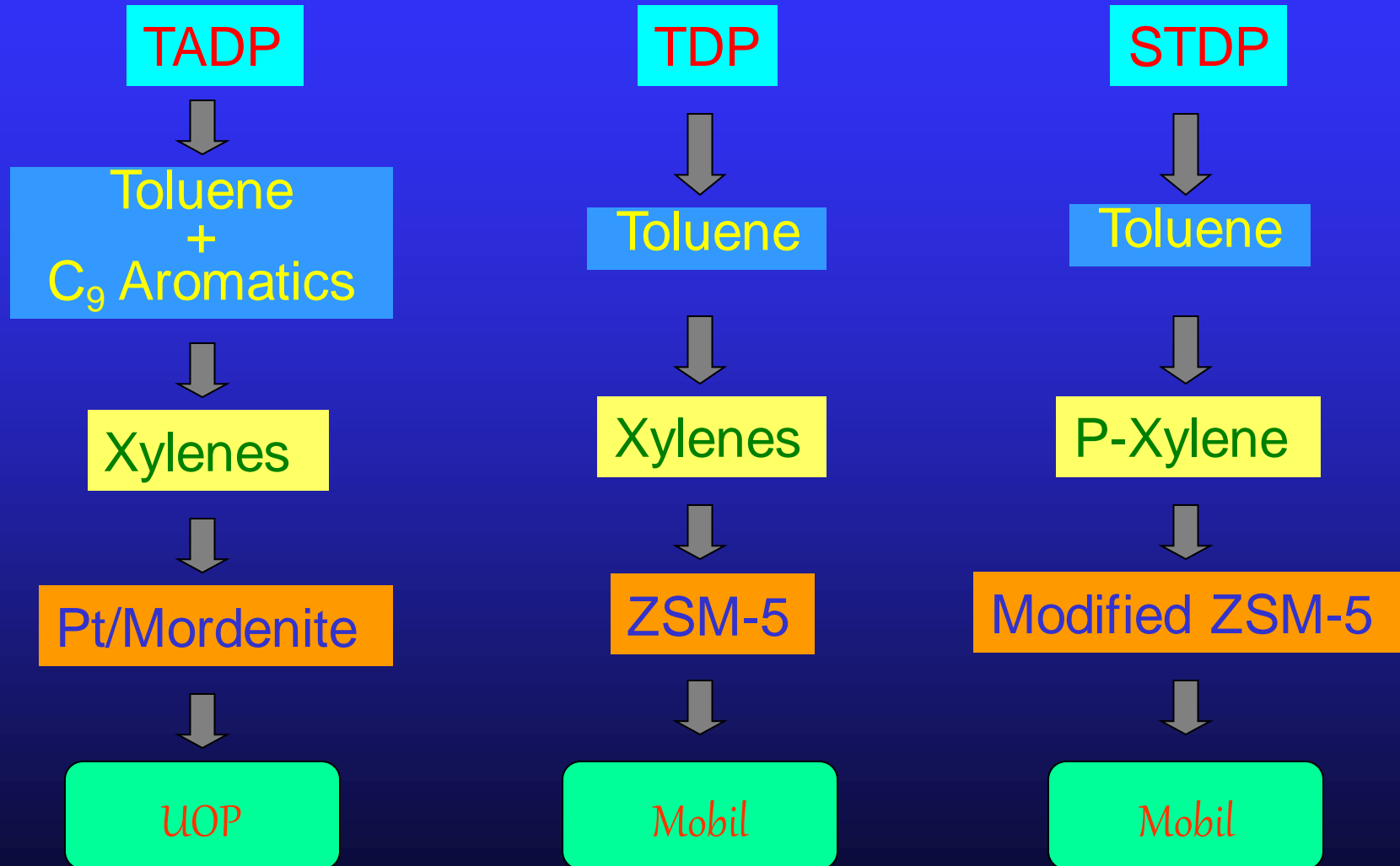
TADP Process



UOP's TATORAY Process

Parameter	Range
Temperature (°C)	380- 490
Pressure (kgcm ⁻²)	20- 30
Toluene: C ₉ Aromatics (wt%)	100:0 – 60:40
Toluene conversion (%)	40 – 45
Catalyst Life	>3 years

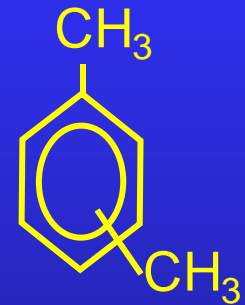
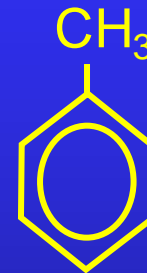
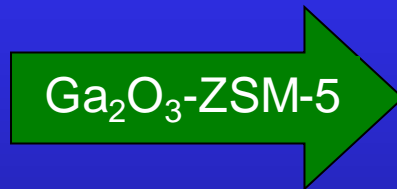
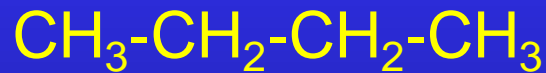
TADP Process-variations



Paraffin Aromatization

Conversion of lower hydrocarbons to aromatics

⇒ Value Addition



- ✎ Aromatics for petrochemicals
- ✎ Aromatics for gasoline octane boosting
- ✎ Developed in 1980s

Paraffin Aromatization Process Technology

Process	Licensors
Cyclar	UOP-BP
Aroforming	IFP-Sheddon Technology Management
M-2 Forming	Mobil
Z-Forming	Research Association of Japan

UOP-BP CYCLAR[®] Aromatization Process

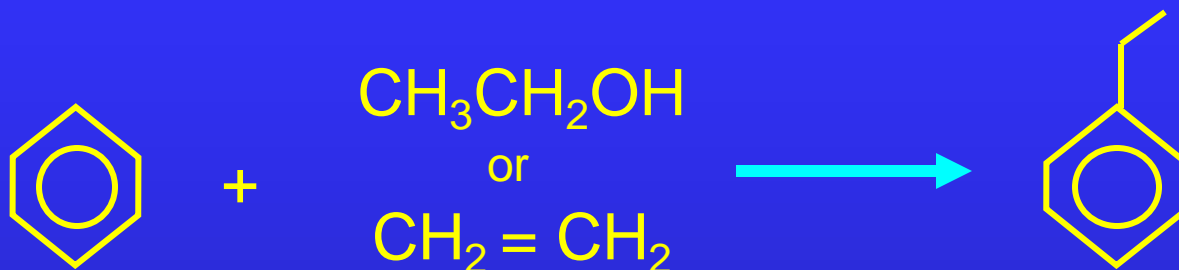
Ga₂O₃/ZSM-5 catalyst : BP

CCR Technology : UOP

Commercial Plant : SABIC, KSA

Conversion of Propane to Aromatics

Ethylbenzene Synthesis



Conventional Catalysts

Sulphuric acid, Alumina etc

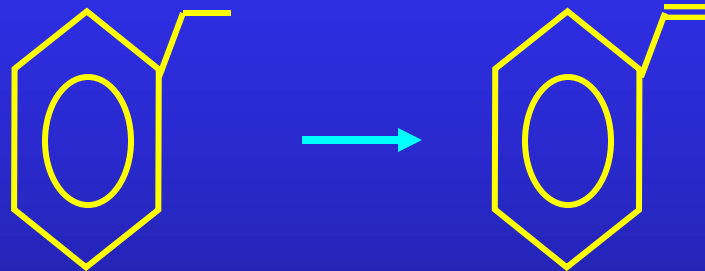
Zeolite based catalysts & processes

✌ Mobil - Badger Process

✌ NCL's - ALBENE Process

Styrene Synthesis

Catalytic dehydrogenation of Ethylbenzene



Catalyst: $\text{Fe}_2\text{O}_3\text{-K}_2\text{O}$

Temperature: 550-680°C

Pressure: low/vacuum preferred

Endothermic process

Byproducts: Toluene, benzene, (phenylacetylene)

DOW, BASF, United Catalyst etc.

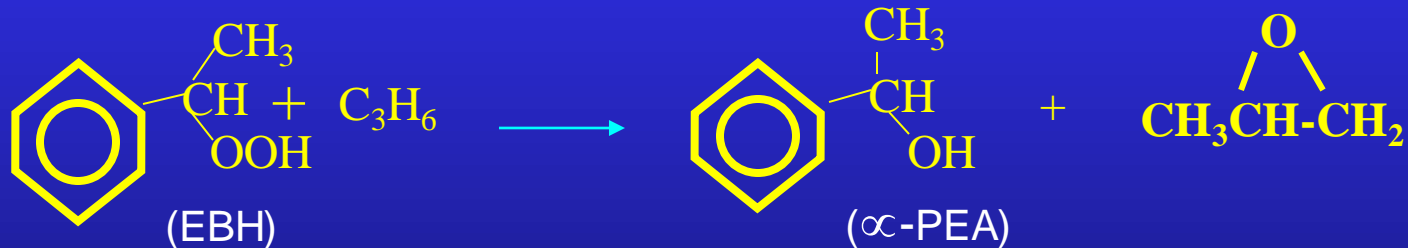
Styrene Production

PO-SM Coproduction process

1. Ethylbenzene oxidation to ethylbenzene hydroperoxide



2. Epoxidation of propylene by EB hydroperoxide



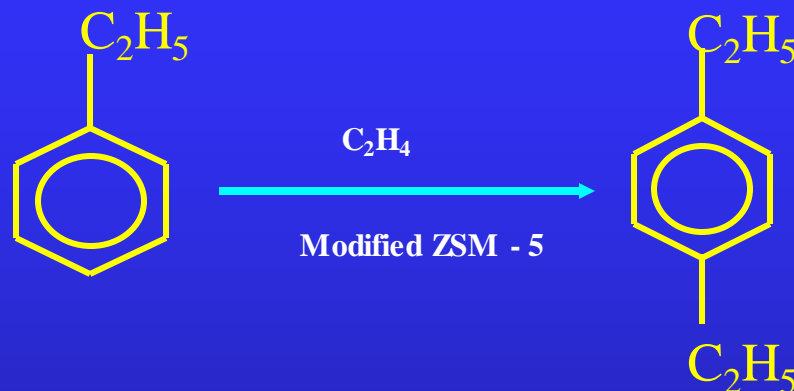
3. Dehydration of α -phenyl ethyl alcohol to styrene



Uses:

PS-(packaging, toys, furniture), ABS-(sewer pipes, auto parts), SBR-(tyres, auto parts, electrical components)

Alkylation of Ethylbenzene to PDEB



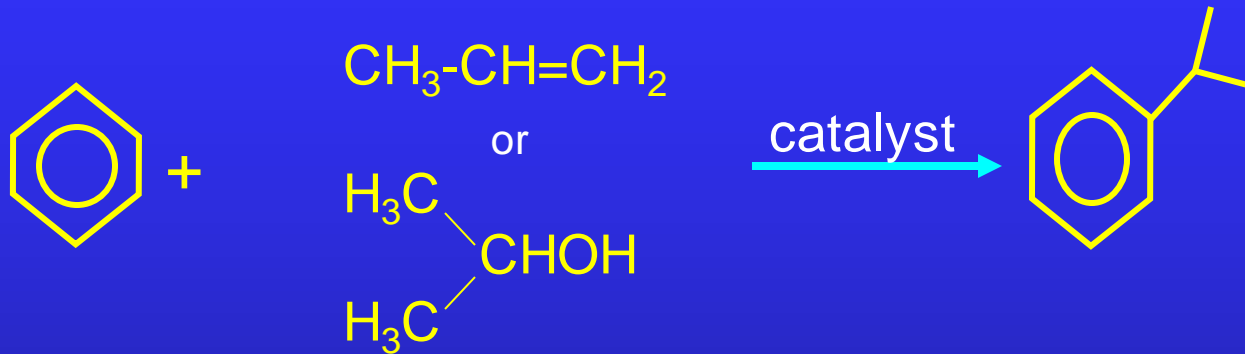
PDEB: Desorbent for Parex process for Xylene separation

- ⇒ Pore-size regulated ZSM-5 zeolite based catalyst
- ⇒ A proprietary catalyst developed by RIL
- ⇒ 5000 TPA plant in operation at Hazira, RIL
- ⇒ Ex-reactor PDEB selectivity- > 99.5%;
- ⇒ Product purity > 99.2%

Para Selectivation via Nano pore Engineering

Process/ Target product	Selectivity towards para Isomer (%)	
	Prior to Silanation	After Silanation
Ethylation of Ethyl benzene/ Para Di Ethyl Benzene (PDEB)	54.41	99.78
Disproportionation of Ethyl benzene/ PDEB	33.4	99.4
Ethylation of Toluene p-Ethyl Toluene	31.8	98.9
Methylation of Toluene/p-Xylene	24.6	90.0
Disproportionation of Toluene/ p-Xylene	24.10	90.29
Iso-propylation of Toluene/p- Cymene	28.9	100
Ethylation of Phenol p-Ethyl phenol	37.1	88.2
Aromatization of n-Pentane/p-Xylene	24.82	98.78

Cumene Synthesis



- ☒ Phosphoric Acid on Kiesulghur
- ☑ Zeolite Catalyst (Zeolite- β)
 - ☺ Regeneration of catalyst
 - ☺ Multiple cycle operation
 - ☺ Low by-product formation

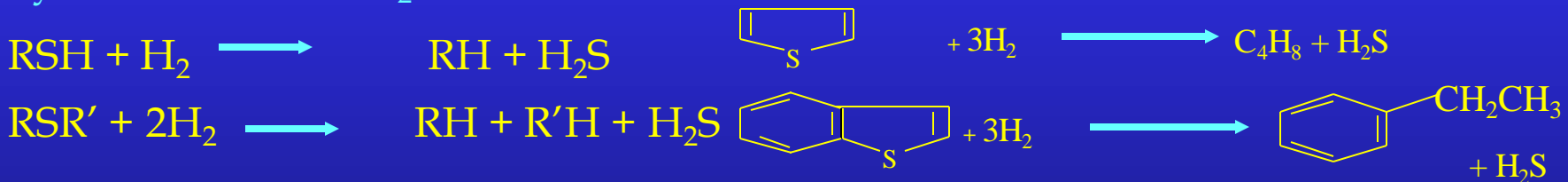
Hydroprocessing

SULFUR COMPOUNDS & NITROGEN COMPOUNDS

- * act as catalyst poisons.
- * removal by reaction with H₂ in presence of catalyst.

HYDRODESULFURIZATION (HDS)

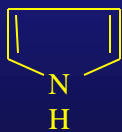
Sulphur compounds such as thiols, sulphides & thiophene are converted to hydrocarbons and H₂S



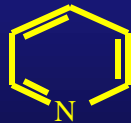
Co-Mo Oxides on γ -alumina ; 450°C ; 50 - 100 ATM

HYDRODENITROGENATION (HDN)

Heterocyclic ring saturation \rightarrow ring fracture at C-N bond removal of nitrogen as NH₃



PYRROLE



PYRIDINE



QUINOLINE



INDOLE

Catalysts : Ni - Mo oxides on γ - Alumina