CHEMICAL PROCESS INDUSTRIES

UNIVERSITY OF DIYALA

CHEMICAL ENGINEERING DEPARTMENT

LECTURE(2)

Higher olefins:

Olefins can be classified as:

1- LO:2-4 carbon atom:E,P&B.
2-MO:5-8 carbon.
3-HO:9-18 carbon: Raw & basic materials in PC Industries: for production of intermediate final Product.

HO Is classified in to:

1-Olefins withC12-18:Use in production of active Material in detergent.

2-Olefins with C9-15 and particularly C11-14:is used in production of alkyl

benzene :i.e. :alkylation of Bz +Alkyl

Sources:

1-HO cannot be separated from MO.
2-HO found in liquids of cracking process of petroleum products. Their separation process is not economical.

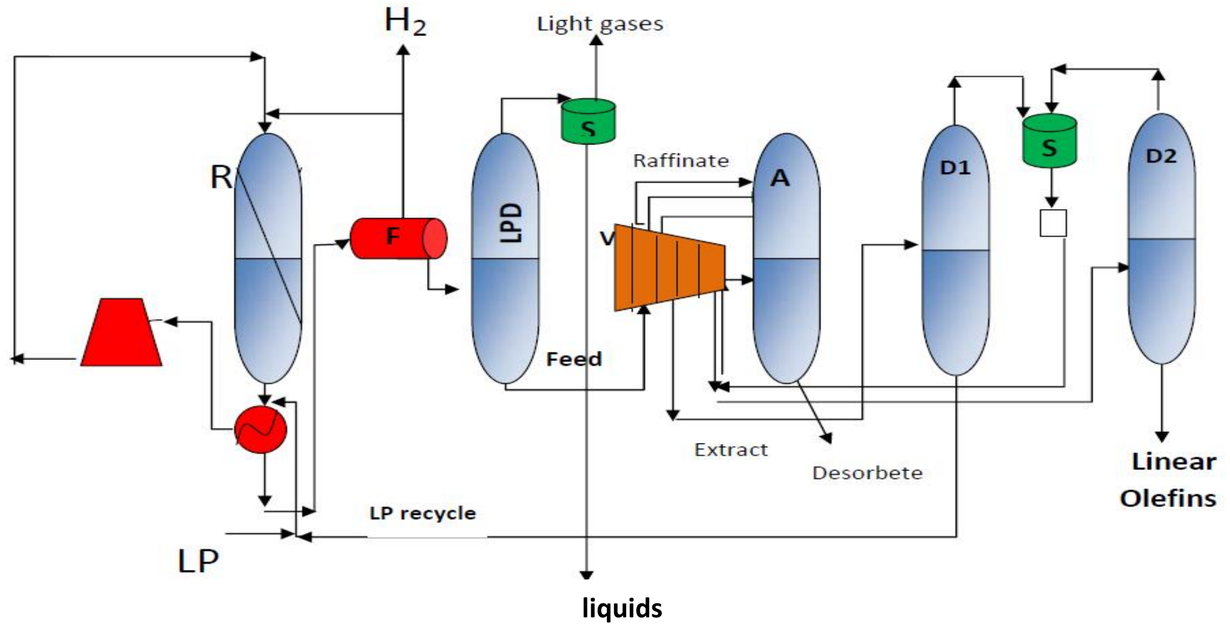
Production of HO:

1-Steam cracking of petroleum waxes.
2-Dehydrogenation of n-paraffin's.
3-Selective polymerization (Oligomerization).
4-Metathesis

Dehydrogenation of n-paraffin:

LP: Linear paraffin $-H_2 \rightarrow$ Linear olefin: LO

$R\text{-}CH_2CH_2\text{-}R'' \leftrightarrow R\text{-}CH{=}CH\text{-}R'' + H_2$



F= Furnace LPD= distillation R= Reactor fix bed S= Storage
F= Flash tank separation vessel V= Valve A= Adsorption
D1= Distillation of Product S= Storage D2= Distillation

F:Furance.

R:Fixed bed reactor in presence of H_2 under low pressure .Dehydrogenation of paraffin occur at selectivity of 90%to olefins in presence of catalyst e.g. oxide of Mo, Cu, Pt on Al_2O_3.Side products are: DO, Ar and light products.

F:Flash tank separating vessel to separate of H_2.

LPD: To separate of light HCS product: by

Extraction of LO in special adsorption unit

S:Storage.

V:Distributer valve: control conversion flow for each current inside and outside the tower.

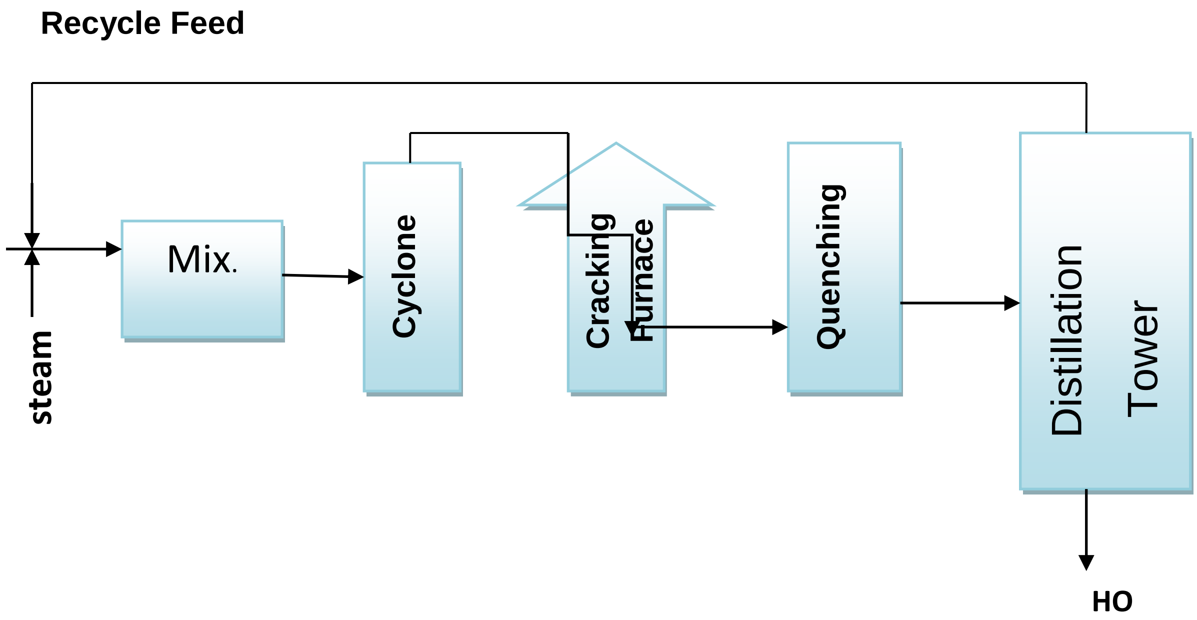
A:Adsorption of product .**D1:**Distillation of product. **S**:Stoage **D2:**Distillaton.

Conditions of Dehydrogenation=420-520^{o}C, P=Low: To increase yield of LO and decrease side products or :Diluents gas like H_2 on N_2 and sometimes steam are used to decrease partial pressure and reduce side reactions and coke formation. Selectivity of LO ≈90%.

Steam cracking of petroleum wax:

Paraffinic wax: raw material in steam cracking under mild conditions for production LO and good yield of HO(linear type).

Steam cracking conditions:



T=550-650^{o}C RT=10 Sec. Conv.=25-35%

Raw materials: mixture of linear paraffin's with carbon no. 21-32.

Operating steps: similar to that of classical steam cracking HCS on production of ethylene and other low olefins. Mix. of paraffin's wax (new and recycle)+steam tubular furnace→ cyclon to isolate unvaporized of wax .Products of cracking are quenched (HE)and steam is produced, distillation is carried out

And separation of unconverted paraffin wax.

Yield olefins=90% C1-C4+H_2 40% C5-C9 15% C10-C13 15%

C14-C20 30% HO Liquid 60% ὰ-olefin.

Linear Alkyl Benzene Complex LAB:

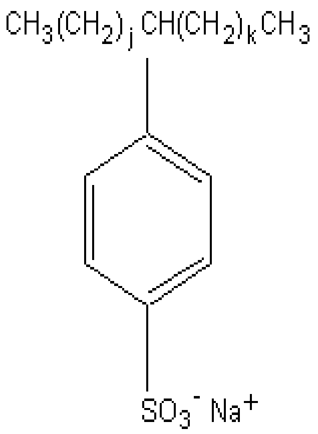
LAB: Chemical compounds contains two active parts.

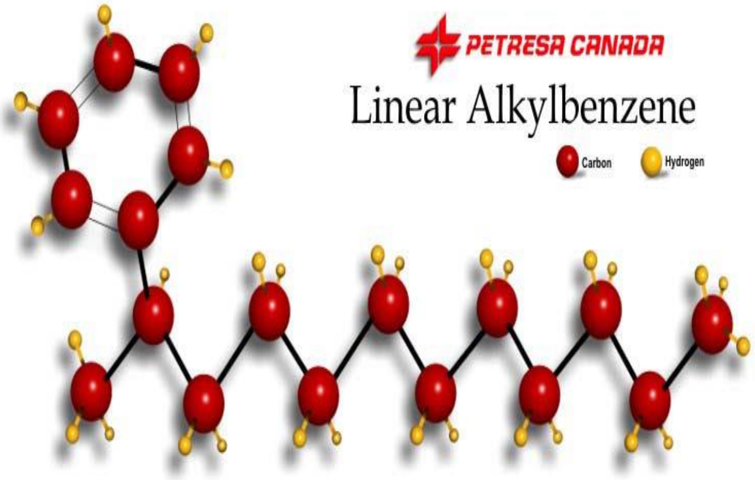
Part(1)concerning with cleaning process.

Part(2)concerning with dissolving dirt's in water.

Cleaning process as follows: **1st part** surrounds dirt by inactive layer. The **2nd part** pull the dirt and dissolve them in water and prevent its deposition on the surface.

Example of LAB: Sodium salt of sulfonic acid.



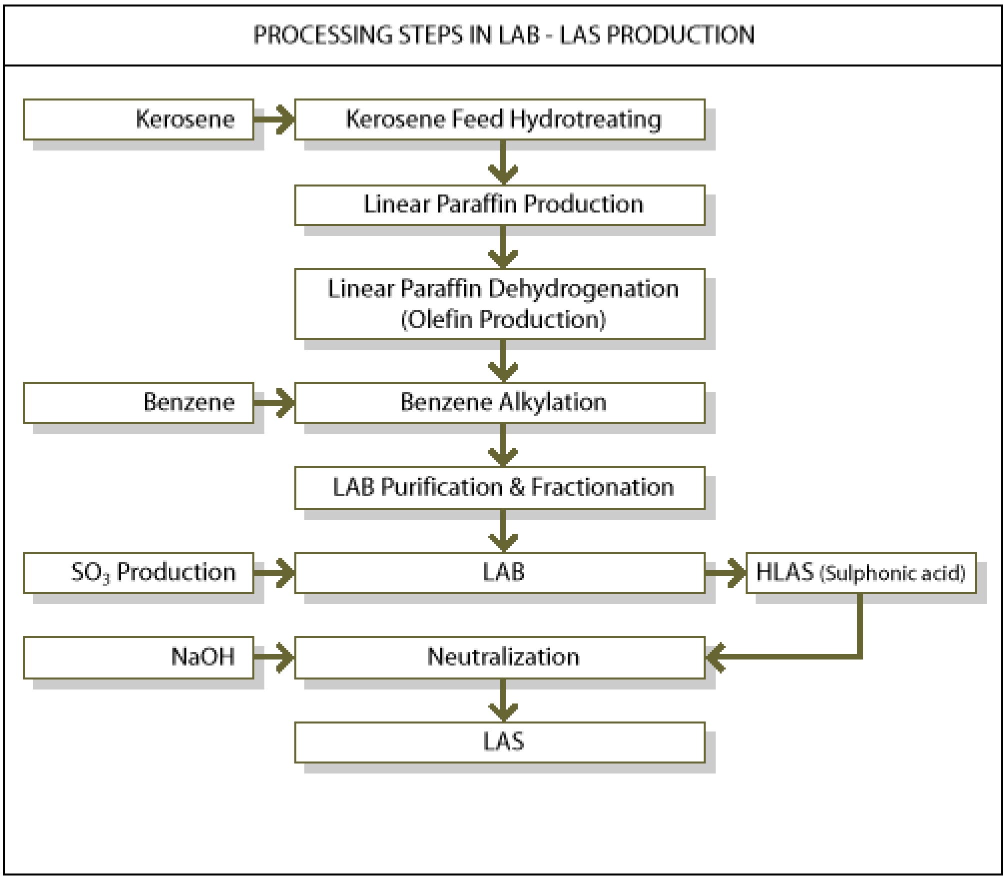


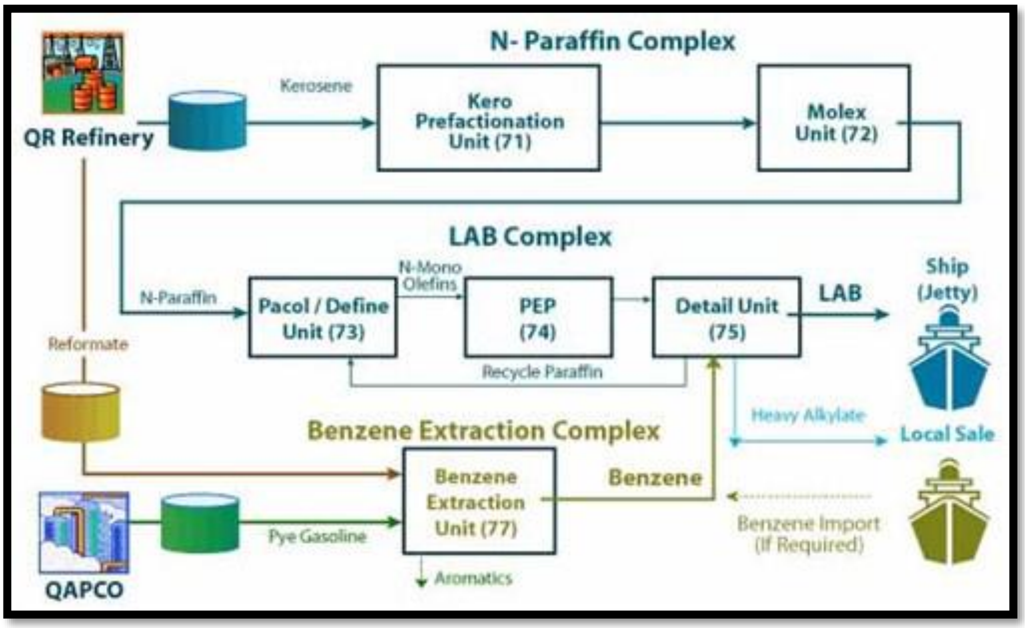
Chemical equation of preparation:

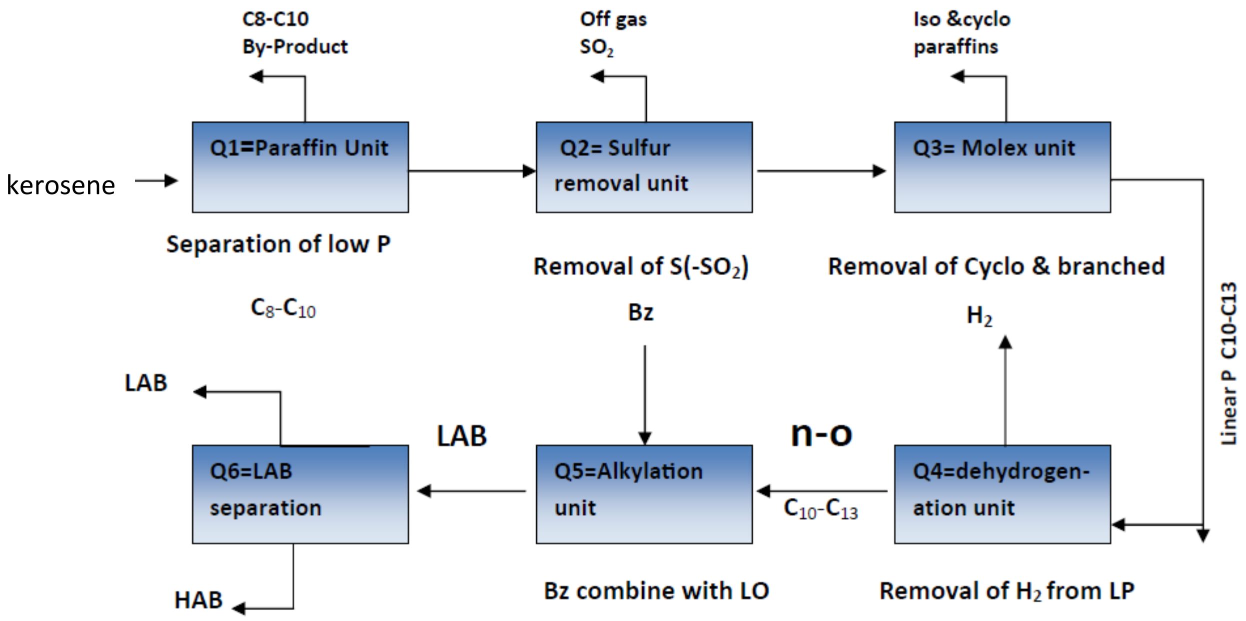
Reaction of LO with Bz(Alkylation)→Alkylbenzene

n-paraffin - H_2→n-olefin: C-C-C-C-C- -H_2→ C-C-C=C-C

n-olefin+ benzene(from BTX complex)→(Alkylation)→Alkylbenzene→ (sulfonation) →Alkylbenzene sulfonate→Neutralization(NaOH)→ABS


PROCESSING STEPS IN LAB - LAS PRODUCTION
Kerosene
Kerosene Feed Hydrotreating
Linear Paraffin Production
Linear Paraffin Dehydrogenation (Olefin Production)
Benzene
Benzene Alkylation
LAB Purification & Fractionation
SO_3 Production
LAB
HLAS (Sulphonic acid)
NaOH
Neutralization
LAS


N- Paraffin Complex
QR Refinery
Kerosene
Kero Prefactionation Unit (71)
Molex Unit (72)
LAB Complex
N-Paraffin
N-Mono Olefins
Pacol / Define Unit (73)
PEP (74)
Detail Unit (75)
LAB
Ship (Jetty)
Recycle Paraffin
Reformate
Heavy Alkylate
Local Sale
Benzene Extraction Complex
Benzene Extraction Unit (77)
Benzene
Benzene Import (If Required)
Pye Gasoline
Aromatics
QAPCO



Main units in LAB complex:

1-Paraffin unit 2-Alkylation unit 3-Aromatics unit

Paraffin unit:

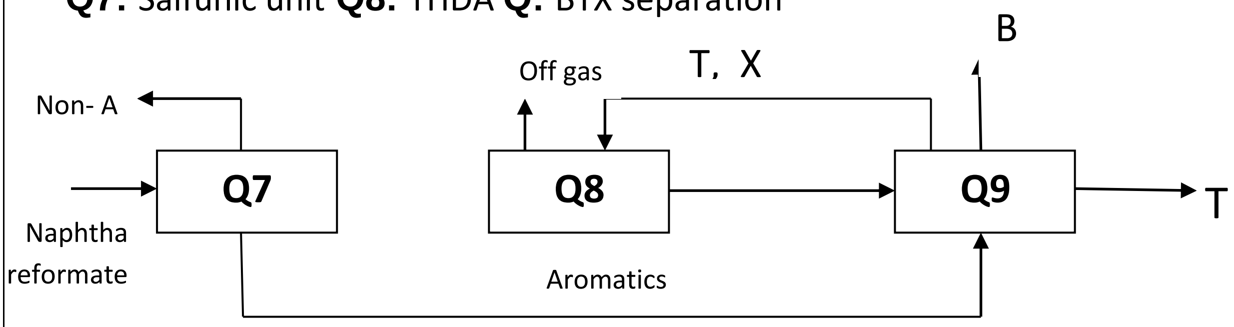
Q1: Paraffin unit **Q2:**Sulfur removal **Q3:**Molex unit.

Alkylation unit:

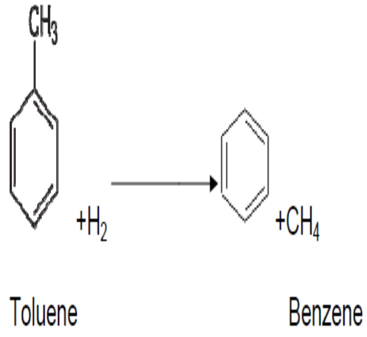
Q4: Dehydrogenation unit **Q5:**Alkylation **Q6**:LAB separation.

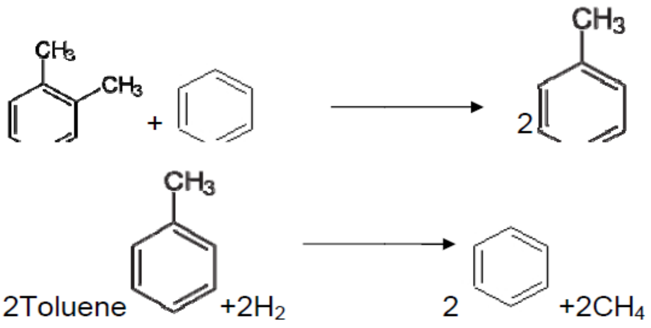
Aromatic unit:

Q7: Salfunic unit **Q8:** THDA **Q:** BTX separation



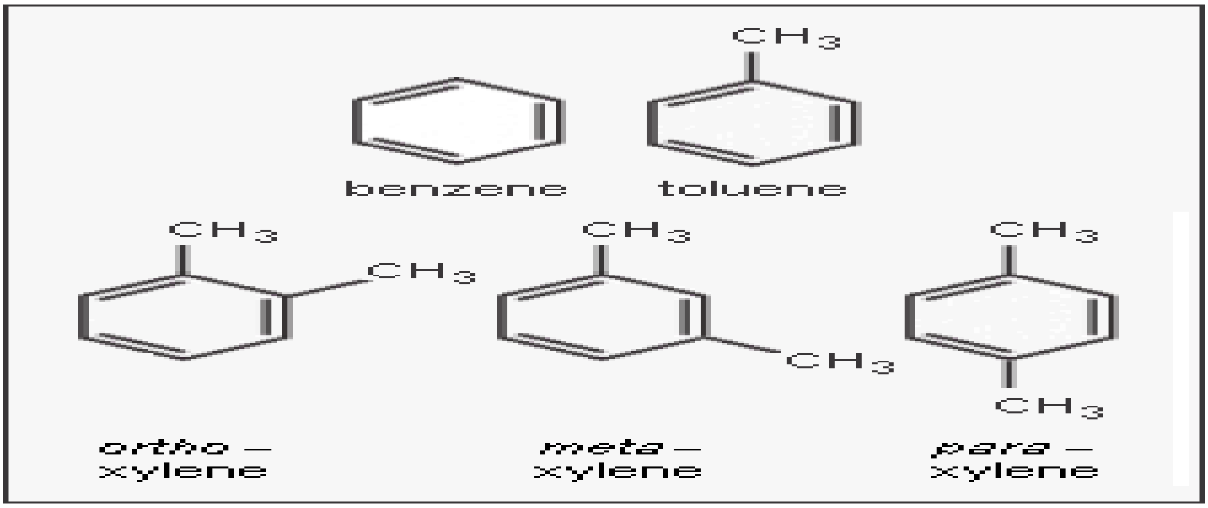
- Salfunic unit: Separation of aromatics from non-aromatics by extraction with salfunic solvent.
- THDA:Thermal hydrogenation dealkylation
- Aim: Change T,X to B thus more benzene is formed.
- <u>Chemical Equation for THDA:</u>





Aromatics:

Compounds with C6-C8 like benzene, toluene ,and xylene(O.M.&P)Known as BTX.



Raw material for basic for PCs.
Uses: Plastic, rubber, fiber, resin adhesive, ,coating, detergents and plasticizer

World production of BTX:

The BTX aromatics are very important petrochemical materials. Global consumption of benzene, estimated at more than 40,000,000 tons in 2010, showed an unprecedented growth of more than 3,000,000 tons from the level seen in 2009. Likewise, the para-xylene consumption showed unprecedented growth in 2010, growing by 2,800,000 tons, a full ten percent growth from 2009.

Production of BTX Hydrocarbons:

1-catalytic reforming of naphtha in petroleum refinery.

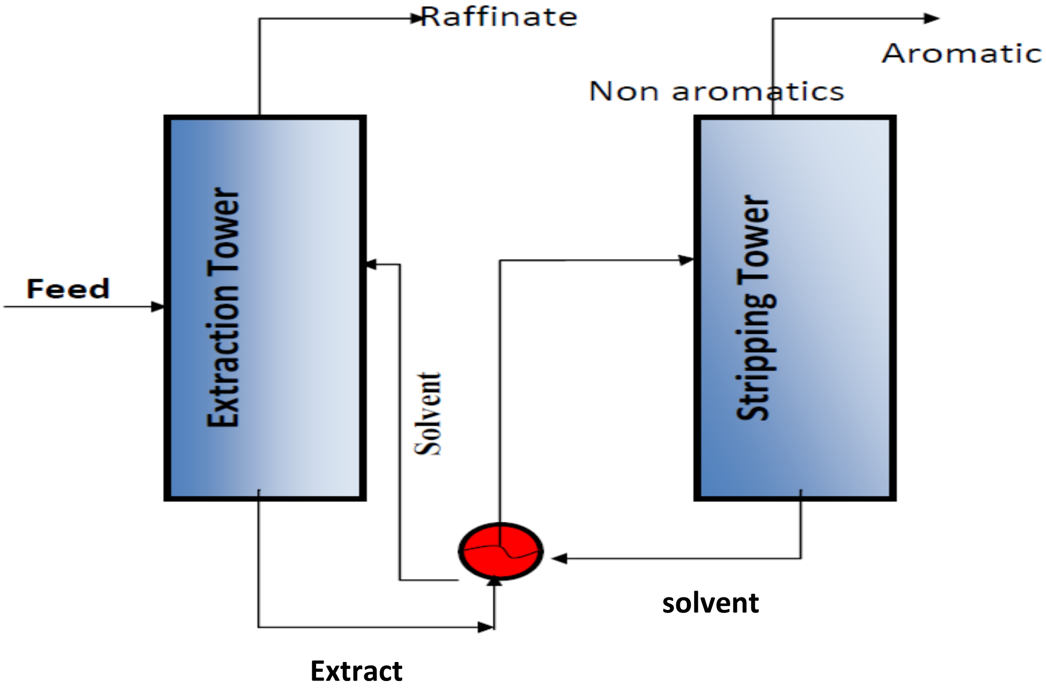
Catalytic reforming usually utilizes a feedstock naphtha that contains nonaromatic hydrocarbons with 6 to 11 or 12 carbon atoms and typically produces a reformate product containing C_6 to C_8 aromatics (benzene, toluene, xylenes) as well as paraffins and heavier aromatics containing 9 to 11 or 12 carbon atoms.

2- steam cracking of hydrocarbons which typically produces a cracked naphtha product commonly referred to as pyrolysis gasoline, pyrolysis gas or pygas. The pyrolysis gasoline typically consists of C_6 to C_8 aromatics, heavier aromatics containing 9 to 11 or 12 carbon atoms, and non-aromatic cyclic hydrocarbons (naphthenes) containing 6 or more carbon atoms.

Aromatics separation

1-Solvent extraction

The BTX aromatics can be extracted from catalytic reformate or from pyrolysis gasoline by many different methods. Most of those methods, but not all, involve the use of a solvent either for liquid-liquid extraction.



Liquid–liquid extraction, also known as **solvent extraction** and **partitioning**, is a method used to extract of a substance from one liquid phase into another liquid phase. Liquid–liquid extraction is a basic technique in chemical laboratories, where
it is performed using a separatory funnel.

Solvent extraction can also refer to the separation of a substance from a mixture by preferentially dissolving that substance in a suitable solvent. In that case, a soluble compound is separated from an insoluble compound.

Solvent: from the top of extractor.

Feed: middle of the extractor, countercurrent to solvent. Solvent dissolve Aromatic
Form a heavy phase :(Extract): bottom, while non-aromatic :(Raffinate) :top.

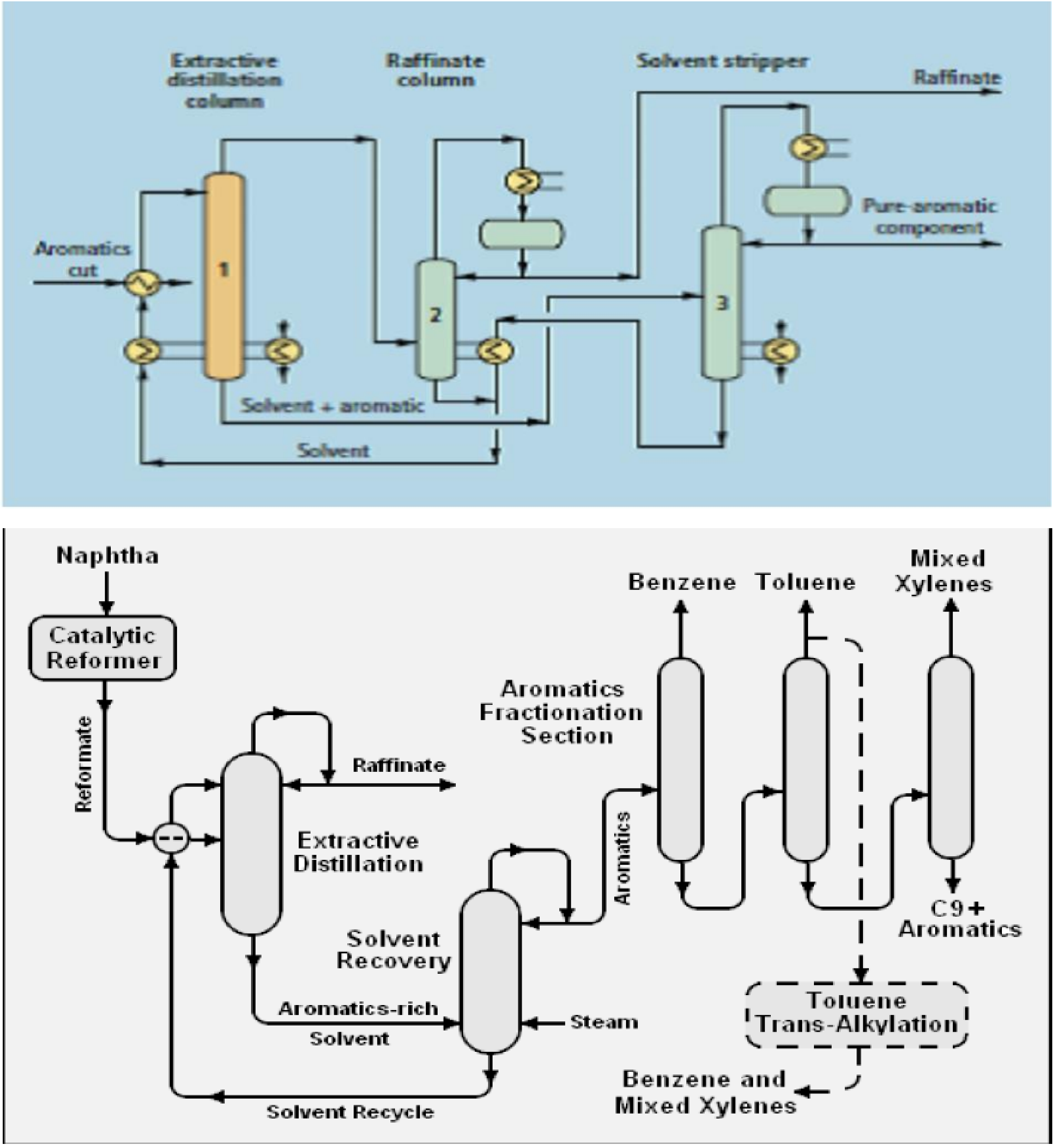
Properties of solvent:

1-Density higher than feed.
2-Higher boiling point than aromatics.
3-Higher dissolving properties.
4-Higher thermal stability.
5-Does not cause corrosion.

Example :DEG,NMP,DMSO.

2- Extractive distillation:

Many different solvents are suitable, including sulfolane ($C_4H_8O_2S$), furfural ($C_5H_4O_2$), tetraethylene glycol ($C_8H_{18}O_5$), dimethylsulfoxide (C_2H_6OS), and N-methyl-2-pyrrolidone (C_5H_9NO). Below is a schematic flow diagram of one method, involving extractive distillation, for extraction of the BTX aromatics from a catalytic reformate:

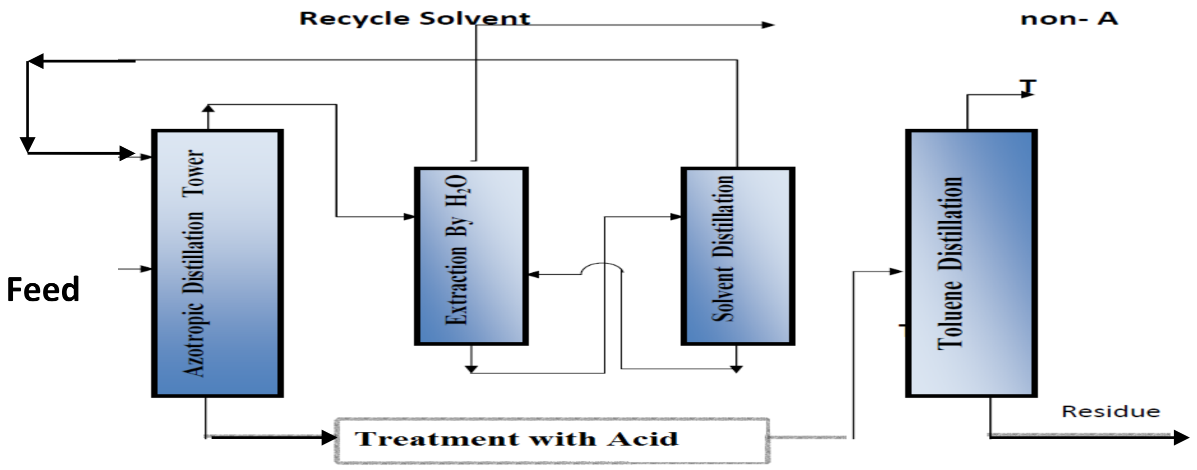


Schematic flow diagram for the extraction of BTX aromatics from a catalytic reformate.

Distillation occur in the presence of solvent with:

1-high B.pt 2-Selective for aromatics comps. Solvent reduce the partial pressure of aromatics more than non-aromatics .Thus the distillation will be easier because the difference in B.pt. Fraction boils 65-92°C is separated and supply to Extractive distillation tower with 102 tower at90 tray. non-aromatics are isolated from the top as Raffinate. BTX +solvent to the stripper then to isolate the solvent which is recycle. Aromatics to the aromatics fractionation section. From which BTX where separated.

3-Azeotropic distillation:



It a distillation which occur in presence of solvent formed with non-aromatics an azotropic system at temp. lower than b.pt of aromatics in a mixture.

Separation process:

1-Feed :is supplied to the middle of azotropic distillation tower(ADT).

2-T flows from the bottom of ADT, treated with acid or bleach with clay then distillate to required purity.

3-From the top of ADT ,mixture of non-aromaics+ solvent (MEK) +H_2O to extractive and distillation towers where the solvent is extracted ,wash and concentrated and recycled.

Comparison between Extractive and Azeotropic distillation:

Extractive	Azotropic
System:Solvent+Aromatics:bottom of distillation tower(DT)	Solvent+non-aromatics:top (DT)
Feed:low aromatics content:less than 40%	Aromatics :higher than 40%
Slvent:phenol+H_2O,N-methyl pyrolidine,Formal morpholine	Acetone+H_2O for Bz Methanol+H_2O for T MEK+H_2O fot T
Fraction: need fraction with narrow range of b.pt	Fraction: need fraction with narrow range of b.pt

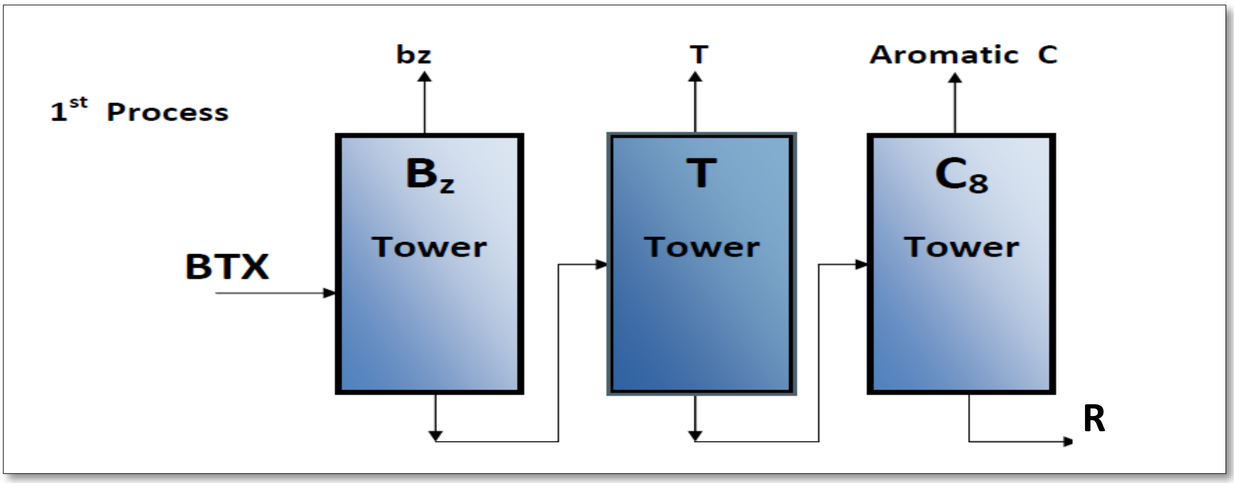
BTX Separation:

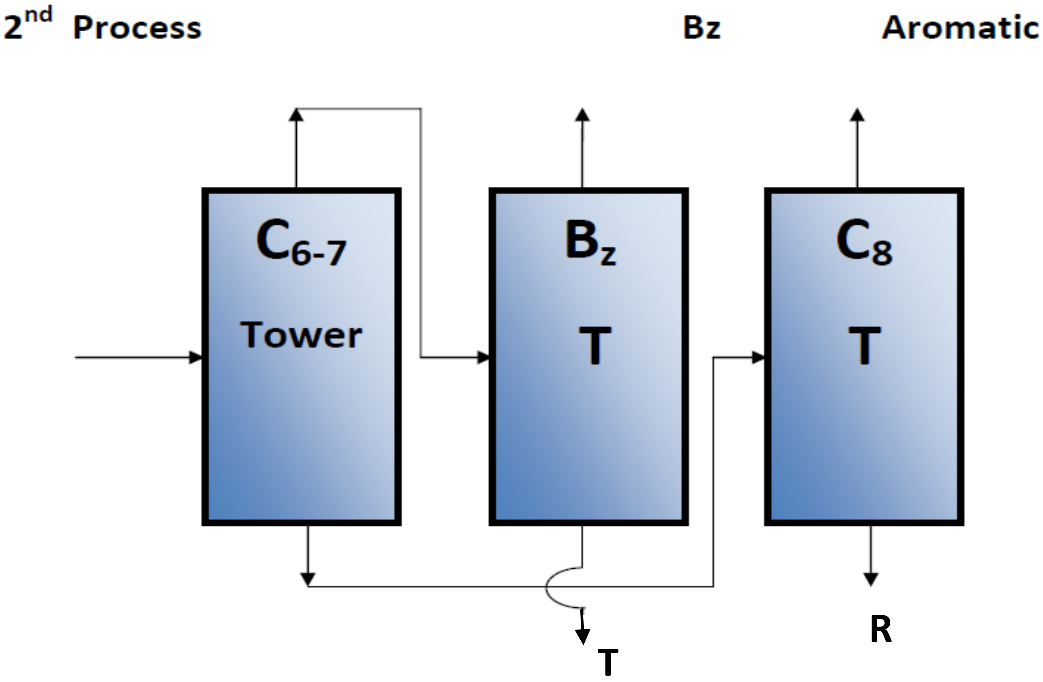
B B.pt=80°C Mwt:78 T B.pt=110.6 °C Mwt=92

X B.pt=136-144°C Mwt=107 C8: X &EB

To separate BTX : Supper fraction is applied as follows:

Super Fractionation:





Isomerization of C8:

C8:Aromatics Mwt=106

Isomers of C8:o-xylene,m-xylene,p-xylene and Ethylbenzene.

Source:1-Catlytic reforming of Naphtha.

2-Cracking of liquid feed(thermo pyrogasoline).

Isomerization: Process carried out in presence of selective catalyst and special conditions were used to produce certain compound over the other.

1-Gas phase catalyst:
a)-compose of metal such as Mo, W over Al_2O_3 or
b)- pt over Al_2O_3.

2-Liquid phase cata.
Compose of dry $AlCl_3$ or HF on BF_3

Synthetic gas (syn gas): (H_2+CO)

Importance:

1- Raw material and basic for production of a lot of materials such as methanol .

2- Uses in process where H_2 is required.

Syn gas production:

1940:from coal $C + H_2O \rightarrow CO+H_2$
Coke+ steam

Now: from petroleum fraction or natural gas HCs feed:

1-NG

2-Pet.fraction

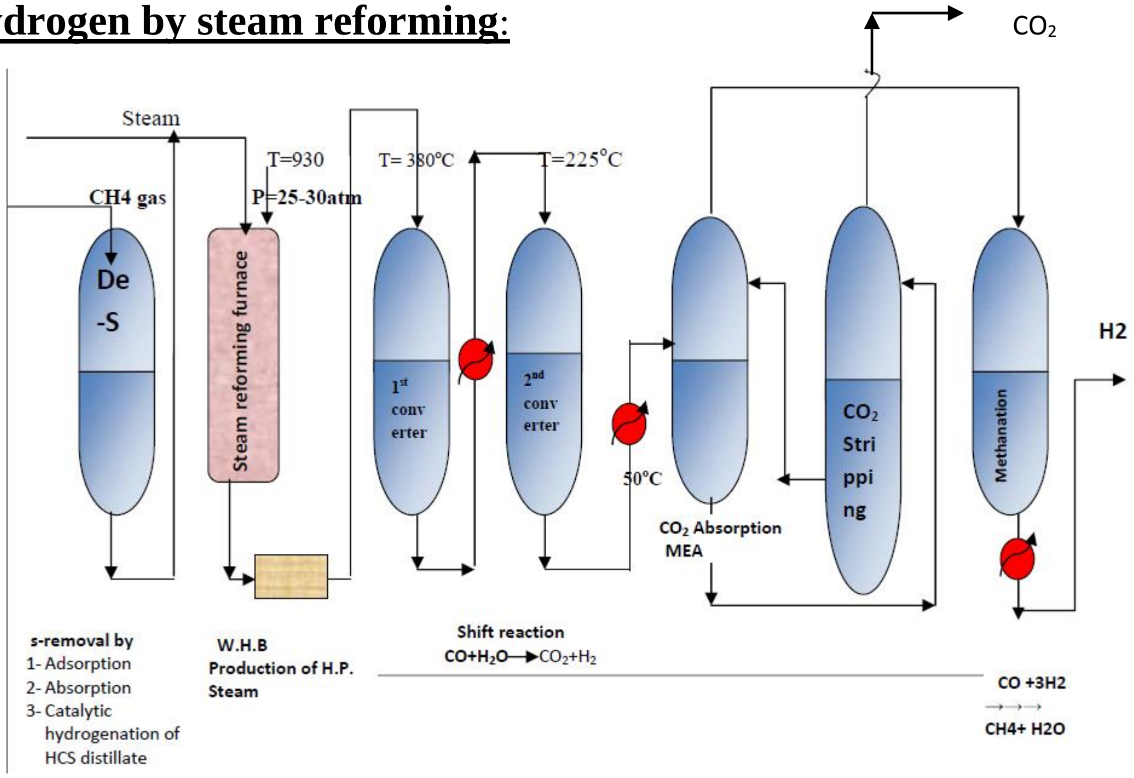
Syn.gas:$CO+H_2$ If H_2 is required only $CO \rightarrow CO_2$

Source of H_2:

1-Cata.reforming 80-85%
2-Cata. Cracking 60-80%
3-Dehydrogentation 90%
4-Electrolysis of water high purity 1m3 required 4940 Kw of electricity.

Hydrogen production from HCs feed

Hydrogen by steam reforming:



Reactions:

1-$CH_4+H_2O \rightarrow CO+3H_2$

2-$CO+H_2O \rightarrow CO_2+H_2$ Shift reaction.

3-$CO+3H_2 \rightarrow CH_4+H_2O$ Methanation.

Operating conditions:

$T=800\text{-}900^{\circ}C$ P=25-30 atm. Cata.=Ni(SRF)

H_2O/C high ratio.

Partial oxidation:

Partial oxidation (**POX**) is a type of chemical reaction. It occurs when a substoichiometric fuel-air mixture is partially combusted in a reformer, creating a hydrogen-rich syngas which can then be put to further use, for example in a fuel cell.

PO:Advantages:

1-Flexibility of use of HCs fuel, pet. fraction, crude oil with high sulfer content and residue.

2-It is used when NG or light fractions is not available or when its prices are high.

3- Dose need catalyst.

4-Need of oxygen unit to produce oxygen.

Reactions:

$CH_4+O_2 \rightarrow CO_2+H_2O$

$CH_4+CO_2 \rightarrow 2CO+2H_2$

$CH_4+H_2O \rightarrow CO+3H_2$

Basic steps:

1-Gasification:

a- process occur in reactor lined with fire bricks without cata.
b-reaction occur between primary heated feed with oxygen, steam and it is supplied through burners.
c-T=1300-1500°C P=Higher than 10 atm.(40-90 atm.)
2-Cooling: Two types according to companies:
a-Quench system: Texco process .
b- W.H.B.: Shell process.
3- Removal of soot. **4-**Conversion of CO to CO_2 **5-**Removal of CO_2,H_2S.
6-Removal of inert gases like Ar, CO.
7-Compression of resultant gases(H_2) or mixture(CO,H_2)

Comparison between Steam reforming(SR)and Partial oxidation(PO)

Feed	More important when CH_4 or NG as feed	Used for heavy pet. Fraction and residue
Cata.	Need Cata.	Does not need Cata
Economic	More economic due to low investment cost, also no need to oxygen unit	Less economic due to high investment cost, and the demand of oxygen unit.