

Introduction

Industrial Countries

The world petrochemical industry has changed drastically in the last twenty to thirty years. The United States, Western Europe and Japan previously dominated production of primary petrochemicals, not only to supply their own domestic demand but also to export to other world markets. These areas accounted for over 80% of world primary petrochemical production prior to 1980. However, world-scale construction of petrochemical facilities in other parts of the world has been on the rise. Countries with vast reserves of crude oil and natural gas (e.g., Saudi Arabia and Canada) have constructed plants to add value to their resources. Since these countries generally have smaller domestic demand, a significant share of petrochemical production is earmarked for the export market.

The need for synthetic rubber and synthetic chemicals for explosives during [World War II](#) prompted the development of the highly specialized petrochemical industry in America. After 1952 the state's share in the American petrochemical industry increased dramatically, and during the 1960s played an increasingly diversified role in all phases of the petrochemical industry: furnishing and processing oil and gas, producing petrochemicals, and manufacturing commercial commodities. By 1965 200 petrochemical plants in Texas processed such basic petrochemicals as ethylene, propylene, butadiene, benzene, isoprene, and xylenes, which are the building blocks for innumerable chemical products spanning the range of the plastic, rubber, and synthetic fiber industries.

The petrochemical industries in the United States, Western Europe and Japan have experienced lower growth rates. In 2010, these three regions accounted for only 37% of world primary petrochemicals production.

Petrochemicals

Petrochemicals in general are compounds and polymers derived directly or indirectly from petroleum and used in the chemical market. Among the major petrochemical products are plastics, synthetic fibers, synthetic rubber, detergents, and nitrogen fertilizers. Many other important chemical industries such as paints, adhesives, aerosols, insecticides, and pharmaceuticals may involve one or more petrochemical products within their manufacturing steps.

The primary raw materials

In general, primary raw materials are naturally occurring substances that have not been subjected to chemical changes after being recovered. Natural gas and crude oils are the basic raw materials for the manufacture of petrochemicals for the production of petrochemicals are natural gas and crude oil. However, other carbonaceous substances such as coal, oil shale, and tar sand can be processed (expensively) to produce these chemicals.

Coal, oil shale, and tar sand are complex carbonaceous raw material and possible future energy and chemical sources. However, they must undergo lengthy and extensive processing before they yield fuels and chemicals similar to those produced from crude oils (substitute natural gas (SNG) and synthetic crudes from coal, tar sand and oil shale).

Secondary raw materials, or intermediates, are obtained from natural

gas and crude oils through different processing schemes. The intermediates may be light hydrocarbon compounds such as methane and ethane, or heavier hydrocarbon mixtures such as naphtha or gas oil. Both naphtha and gas oil are crude oil fractions with different boiling ranges.

Two petrochemical classes are olefins including ethylene and propylene, and aromatics including benzene, toluene and xylene isomers. Oil refineries produce olefins and aromatics by fluid catalytic cracking of petroleum fractions. Chemical plants produce olefins by steam cracking of natural gas liquids like ethane and propane. Aromatics are produced by catalytic reforming of naphtha. Olefins and aromatics are the building blocks for a wide range of materials such as solvents, detergents, and adhesives. Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants, and gels.

Primary petrochemicals are divided into three groups depending on their chemical structure:

- Olefins includes ethylene, propylene, and butadiene. Ethylene and propylene are important sources of industrial chemicals and plastics products. Butadiene is used in making synthetic rubber.
- Aromatics includes benzene, toluene, and xylenes. Benzene is a raw material for dyes and synthetic detergents, and benzene and toluene for isocyanates MDI and TDI used in making polyurethanes. Manufacturers use xylenes to produce plastics and synthetic fibers.
- Synthesis gas is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol. Ammonia is used to make the fertilizer urea and methanol is used as a solvent and chemical intermediate.

Factors affecting development and growth of petrochemical industries:

- 1-Avaliability of oil and natural gas and development of refining technology and industries.
- 2-Great development in production and purification of basic PCs.

- 3-The characterization properties of PCs produced: Tensile corrosion resistance and easy of production.
- 4-Cost of PCs produced equal or less than natural or classical materials.
- 5-Great demand on commodity product and limited availability of natural product thus are replaced by PCs product.

Characterization petrochemical industries

- 1-Different processing stages from oil and NG to final product.
- 2-Its demand of high developed and complex technology and efficient stuff from various levels.
- 3-High capital cost: cost of civil, processing are high on other hand this industry characterizes by high profit especially final products.
- 4- High production capacity is considered to be economic due to technological development in using equipment and also recovery of by-products.
- 5- By-product associated with basic PCs produced can be utilized in economics of project: production of Ethylene from Naphtha :by-products are:Proplene and BD.
thus are replaced by PCs product.

Generation of petrochemical industry:

1st Generation PCs:From NG and Petroleum fraction.

Processes: Steam cracking for production of Olefins and Aromatics.

2nd Generation PCs:Intermediate :From Basic PCs .

Processes:Alkylation,Hydrogenation.

3rd Generation PCs,End product. Represent all the commodity used for different purposes. These may be used alone or composites.

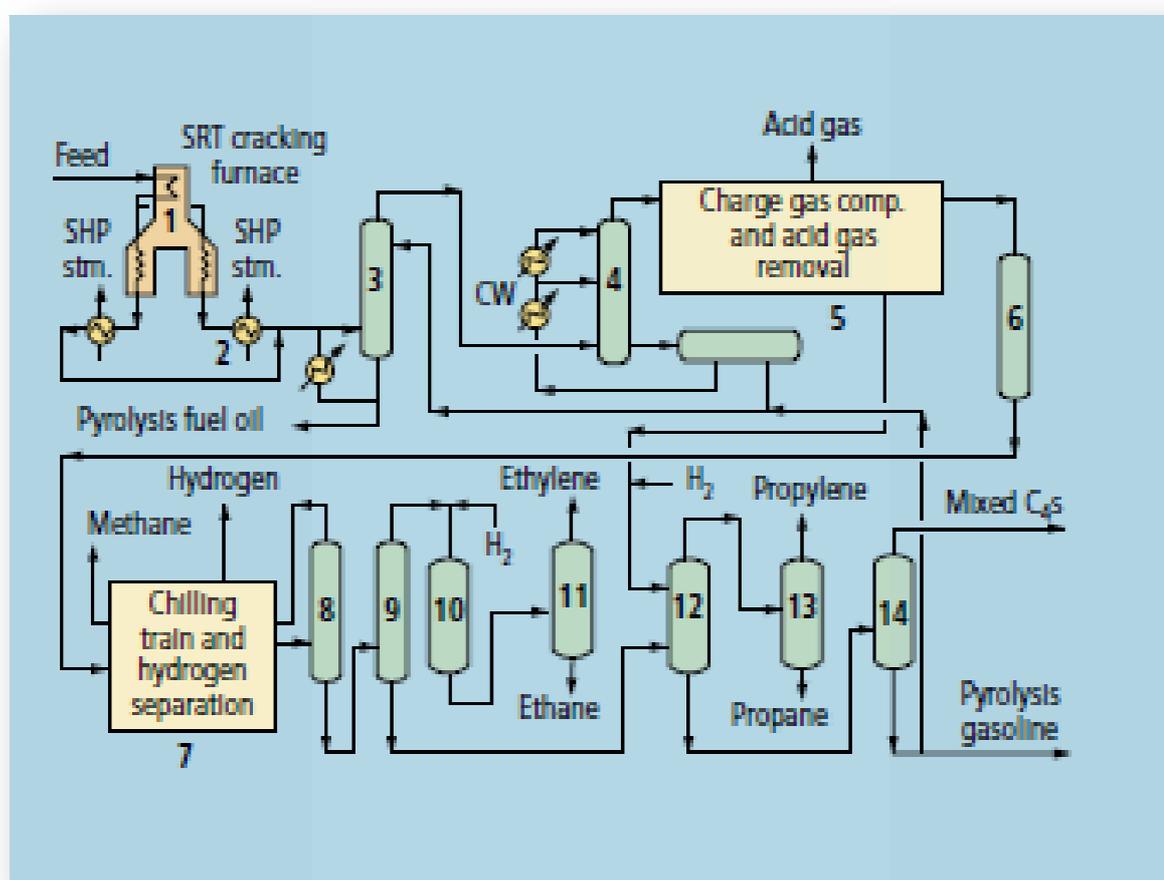
Another feed stocks for PCs industries:

1-Nuclear energy. 2-Radinet energy. 3-Electrowater energy

4-Thermal-underground energy.

Ethylene

Application: To produce polymer-grade ethylene (99.95 vol%). Major byproducts are propylene (chemical or polymer-grade), a butadiene-rich C₄ stream, C₆ to C₈ aromatics-rich pyrolysis gasoline and high-purity hydrogen



Description: Hydrocarbon feedstock is preheated and cracked in the presence of steam in tubular SRT (short residence time) pyrolysis furnaces(1). This approach features extremely high olefin yields, long run length and mechanical integrity. The products exit the furnace at 1,500°F to 1,600°F and are rapidly quenched in the

transfer line exchangers (2) that generate super high-pressure (SHP) steam. The latest generation furnace design is the SRT VI.

Furnace effluent, after quench, flows to the gasoline fractionators(3) where the heavy oil fraction is removed from the gasoline and lighter fraction (liquids cracking only). Further cooling of furnace effluents is accomplished by a direct water quench in the quench tower (4). Raw gas from the quench tower is compressed in a multistage centrifugal compressor (5) to greater than 500 psig. The compressed gas is then dried (6) and chilled. Hydrogen is recovered in the chilling train (7), which feeds the demethanizer (8). The demethanizer operates at about 100 psia, providing increased energy efficiency. The bottoms from the demethanizer go to the deethanizer (9). Acetylene in the deethanizer overhead is hydrogenated (10) or recovered. The ethylene-ethane stream is fractionated (11) and polymer grade ethylene is recovered. Ethane leaving the bottom of the ethylene fractionators is recycled and cracked to extinction. The deethanizer bottoms and condensate stripper bottoms from the charge compression system are depropanized (12). Methylacetylene and propadiene are hydrogenated in the depropanizer using CDHydro catalytic distillation hydrogenation technology. The depropanizer bottoms is separated into mixed C4 and light gasoline streams (14). Polymer-grade propylene is recovered in a propylene fractionator (13). A revised flow scheme eliminates ~25% of the equipment from this conventional flow sheet. It uses CD Hydrohydrogenation for the selective hydrogenation of C2 through C4 acetylenes and dienes in a single tower; reduces the cracked-gas discharge pressure to 250 psig; uses a single refrigeration system to replace the three separate systems; and applies metathesis to produce up to 1/3 of the propylene product catalytically rather than by thermal cracking, thereby lowering energy consumption by ~15%.

Energy consumption: Energy consumptions are 3,300 kcal/kg of ethylene produced for ethane cracking and 5,000 kcal/kg of ethylene for naphtha feed stocks. Energy consumption can be as low as 4,000 kcal/kg of ethylene for naphtha feed stocks

with gas turbine integration. As noted above, the new flow scheme reduces energy consumption by 14%.

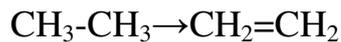
Commercial plants: Approximately 40% of the world's ethylene plants use Lummus' ethylene technology. Many existing units have been significantly expanded (above 150% of nameplate) using Lummus' MCET(maximum capacity expansion technology) approach.

First: Steam cracking process:

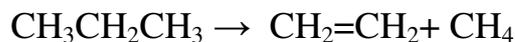
treatment of HCS with steam at high temp and low contact time and pressure.:

Mechanism:

1- Dehydrogenation of ethane:



Ethane Ethylene



Propane Ethylene

2-Dehydrogenation of propane:



Furance design:

Furances:tubular furance:tube arranged either vertical or horizontal, and made of S.S:which is alloy of nickel and chrom and cnotain burners mounted in the bottom or on a side of these burners

NG,reduced crude or fuel oil burns to give heat.

Operating conditions(OC):

Practical design of steam cracking and operating conditions depends on feed.

If the raw material: Ethane-gas oil :then operating conditions are:

Temp: 750-850 °C Residence time(RT)=0.2-0.3 sec.

Steam: feed 0.2-1 Pressure: 1-3 bar.

Effect of Operating conditions(OC):on steam cracking process:

1-RT: low: yield :high and formation of coke: low

In order to lower (RT) a- lower the reactor size(volume) b- reduce pressure c- increase of temp. Ex. to lower (RT) from sec. to a part of sec. the temp. inside the tubes must be increased from 750-900 °C : yield of ethylene will increase from 20-23% to 30-35% .

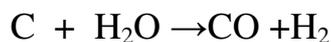
Ratio of steam:HCS:

Advantage of use of steam

1-Reduce the vapour pressure and RT of HCS in the reaction zone which in turn increases %yield.

2-Reduce the partial pressure of aromatic HCS with high molecular weight which limits the formation of coke on the internal tube walls.

3-The reaction which takes place between coke and steam to remove precipitation.



Disadvantages:

1-Reduce the unit capacity. 2-Recovery limited amount of steam.

3- The need of high energy to cool the product.

Second: Cooling:

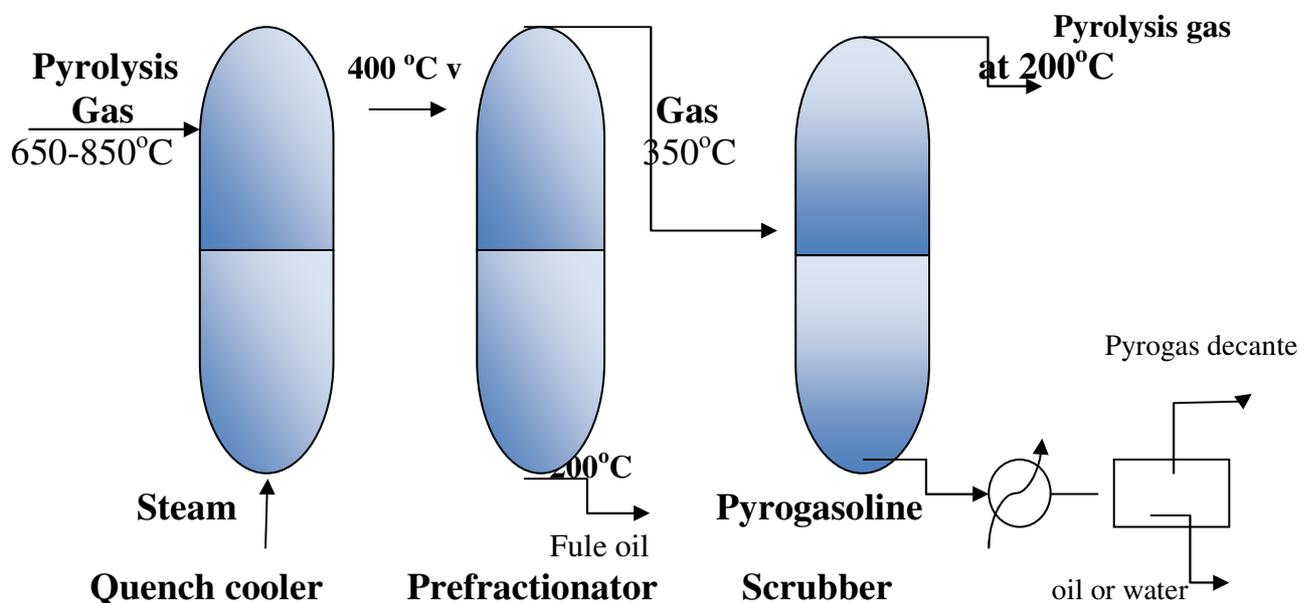
Effluent from steam cracking furnace with temp. 800°C contains a lot of active unsaturated compounds, thus cooling process (quenching) must be carried out for the following:

- 1- The gums and polymeric compounds which form as a result of side reactions must be excluded.
- 2- Recovery of thermal energy as steam

Cooling stages:

Cooling is carried out in 2-3 stages according to feed as follows:

- 1- Quenching (rapid and immediate) and production of high pressure steam.
- 2- Primary fractionation: for product of thermal cracking in case of feed stock and separation of fuel oil.



Quenching:

Is carried out first in TLE (Transfer line exchanger)

To a temp. of (375-500⁰C) by using hot water in the upper part of tubular furnace and production of high pressure steam which is used to operate the compressors in the same complex.

Final cooling:

Cooling is carried out to about 40⁰C as follows:

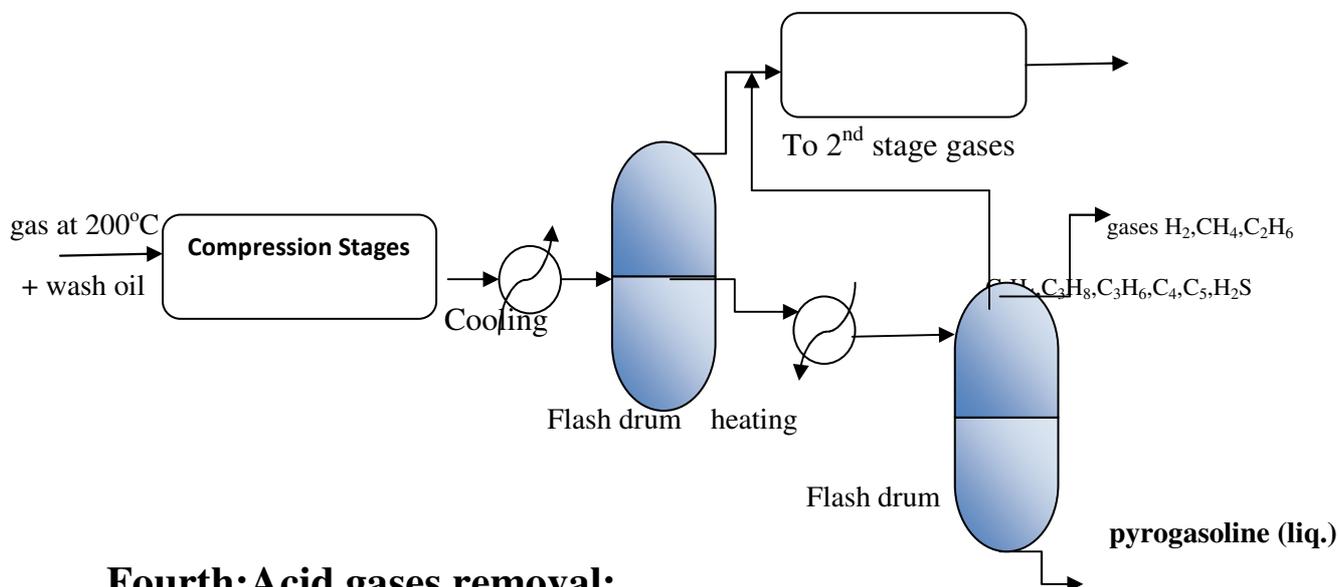
a-Gas feed: direct treatment in water quench unit; where pyro gas leaves from the top of washing tower while pyro gasoline leaves with washing water from the bottom of the washing tower, pyro gasoline is separated, wash water is recycled after cooling in heat exchangers.

b-Liquid feed: cooling is carried out first using direct wash with oil such as gas oil then fractional distillation is carried out for fuel oil separation from heavy gasoline fraction. During direct washing products temp. decrease to 200-220⁰C then products are introduced to primary distillation tower to separate fuel oil and washing gas, temp. of product is reduced to about 100-110⁰C, Final cooling is about 40⁰C.

Third: Compression:

Pyro. gas contains some impurities with different concentrations differs according to feed type and operating conditions. Impurities are acids gases (H₂S, CO₂), acetylene and water.

The compression of gas to 34 atm. occurs in multiple stages (4-5). Condensate HCS are removed from these stages. Acids gases removal is usually carried out during compression using soda or amine wash unit, then gas is dried to prevent hydrate and ice formation when the gas is cooled to low temp. during the distillation under pressure.



Fourth: Acid gases removal:

Purity requirement in low olefins need to reduce the contain of H_2S (1-2)ppm and CO_2 (10-15)ppm.

Reasons for acid gas removal:

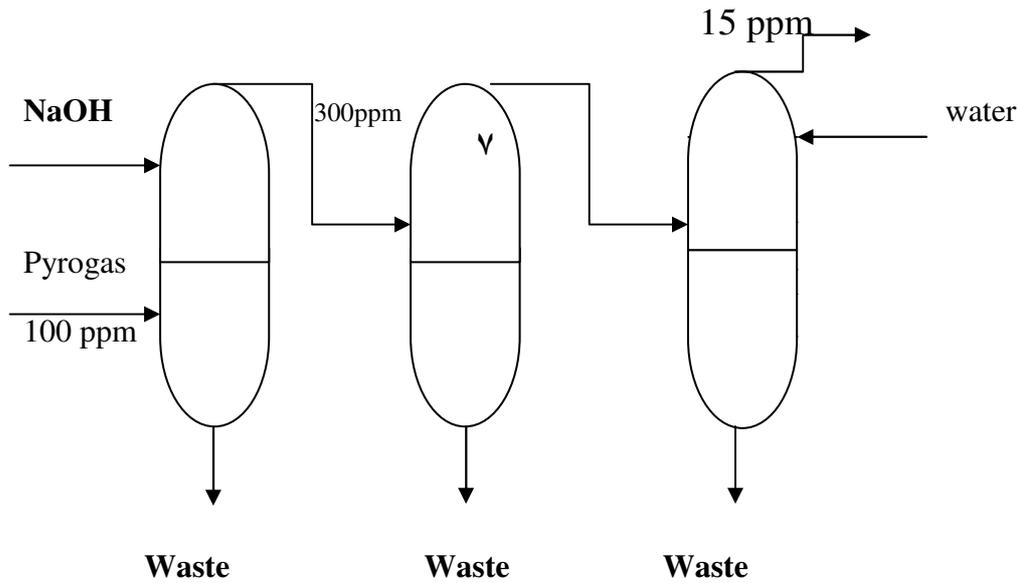
- 1-To avoid corrosion problems, and limit solid CO_2 precepitation at low temp.
- 2- Prevent catalyst (pd) poisoning which is used in acetylene hydrogenation.

Removal process :

Removal is carried out by multi stages washing with caustic soda solution. Usually two stages wathing reduce the amount of CO_2 to(15-20)ppm while the amount is further reduced to less than (5)

ppm when three or more stages are used.

The pyro gas is feed in the lower part of washing tower and run up ward in the reverse direction to soda solution stream(counter current) .The soda solution is supplied with different concentraions in two separated contact stages in side the tower. The paritaly exhauted soda solution after the second washing stage is recycle to the first stage ,then it run outside the tower as rabish.The concentration of the recycle solution to the second stage is neutralised with new dilute solution of soda.



Counter current scrubbing (washing) with dil. NaOH

Washing process :

Treated gas from the second stage is washed with water in a separated region in a tower contain several trays for contact .The water is recycle with different speed to obtained effective washing of gas from residual soda and impurities.

Five:Drying:

Pyro gas is saturated with water steam as a result of its contact with water in different stages of manufacturing .The HCS gases dissolved amount

of water steam differs according to temp. and pressure thus the drying of the gas is nessasry for the following:prevent the solidification of water and hydride formation during distillation at low temp.which result to blockage of pipes and equipment and reduce the efficiency of separating units.

Drying process:

1-It is carried out by:Adsorption:using suitable solid material ;such as active aluminum oxide,silica gel,molecular sieves.

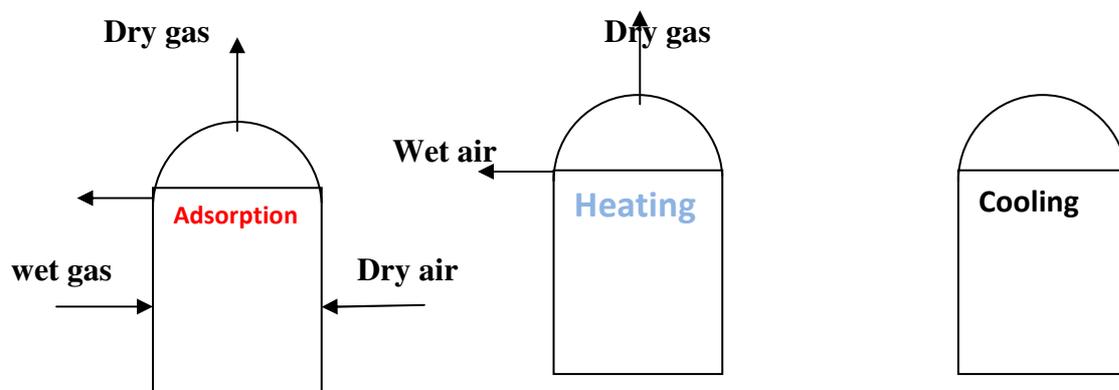
2-Pratically;two towers at least are used in drying units ;one of them in adsorption stage while the other in activation and cooling stage.

The content of water in gas is reduced to(1-2)ppm.

Anti freeze agent(e.g.methanol)is also added thus hydride formation and freezing of water is avoided

When gas is subjected to low temp.in copression and distillatio units.

2- Some times gas is cooled by propylene refregerent after washing by soda inorder to reduce condensation of water and reduce its percentage in gas.



Sixth:Acetylene removal:

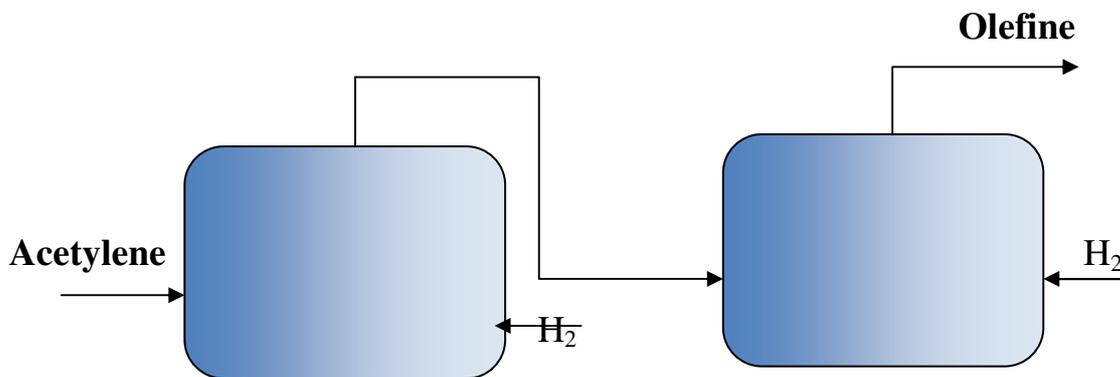
Pyro. Gas contins acetylene which its compound separated with olefins with equivalent carbon no. when distillation processes.Thus acetylene must be removed inorder to get olefins and diolefins with high purity.

Acetylene compound are removed from pyro gas by:1- Selective hydrogenation.

2-Solvent extraction.

Selective hydrogenation :

Used in almost all low olefins production units.



Removal process;

Acetylene removal is carried out either:

1-Front end removal;in copression stage.

2-Tail end removal;in poduct separation stage.

Front end removal:Hydrogenation of pyro gas is carried out before product separation i.e.during compression and in presence of excess of hydrogen especially the gas contains amount of hydrogen.

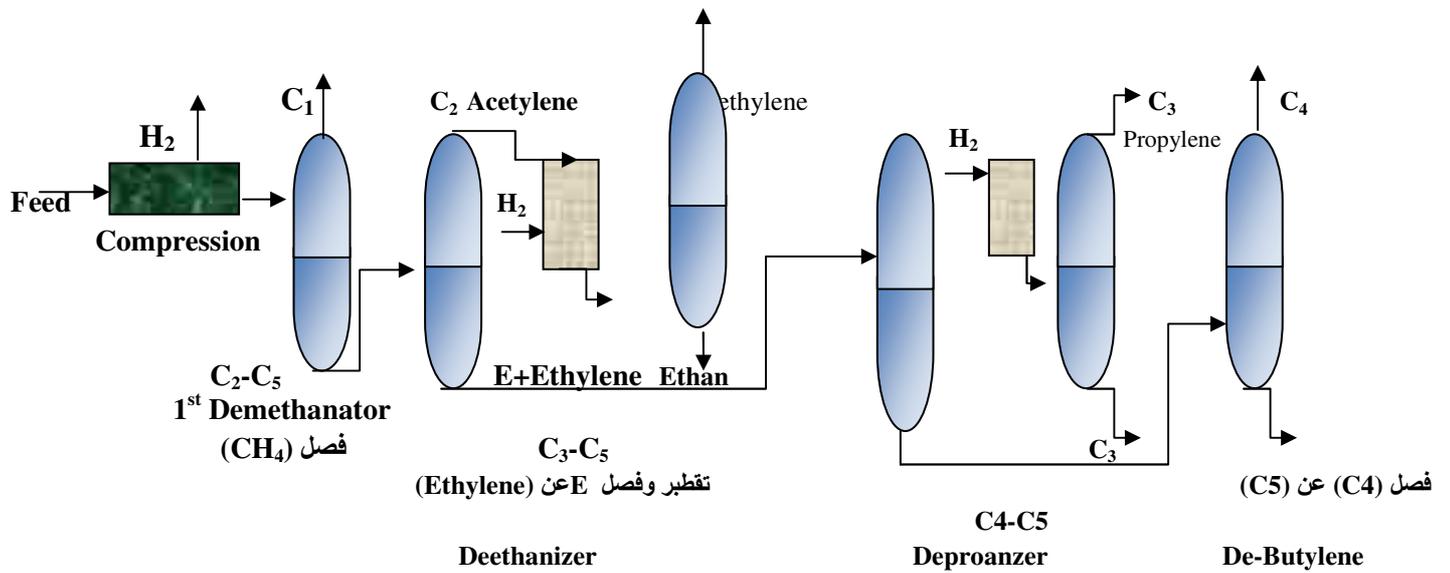
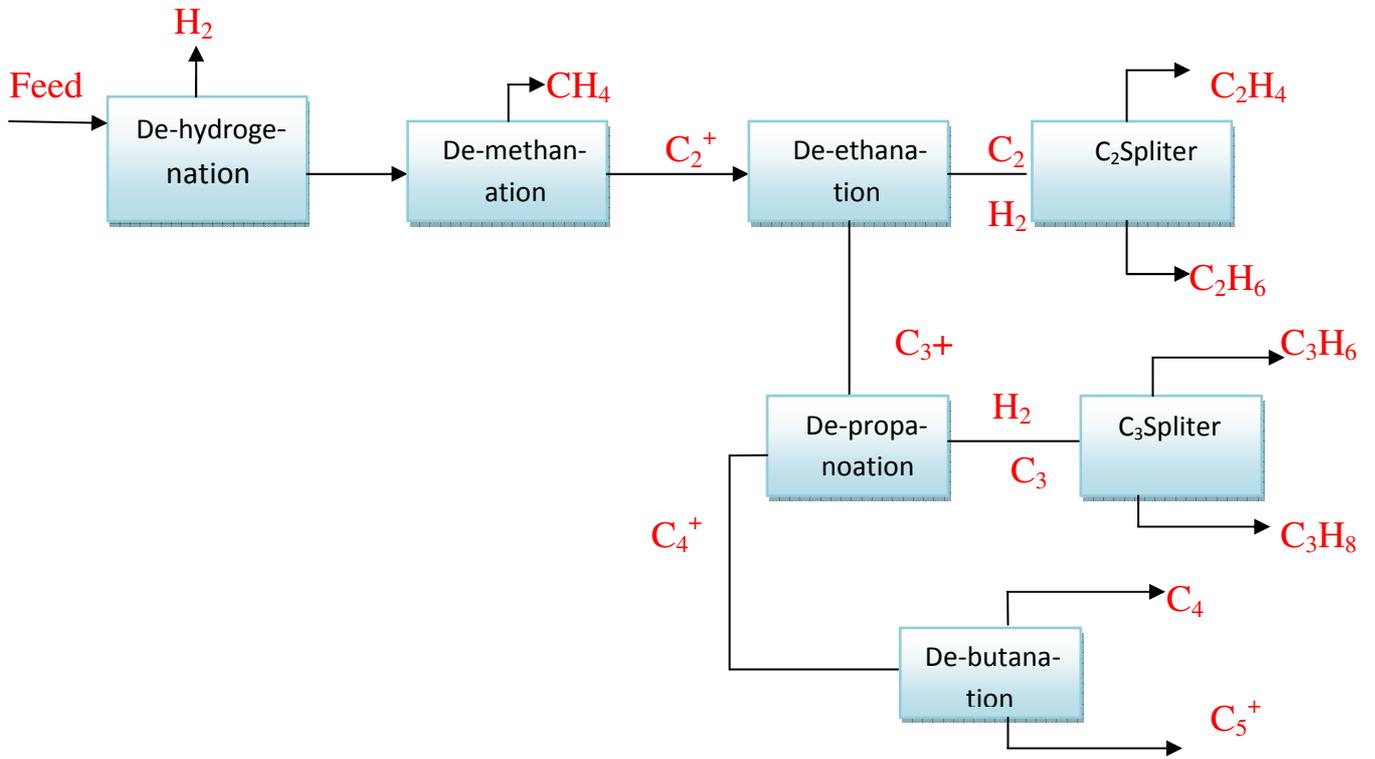
Tail end removal: Hydrogenation of pyro gas is carried out after product separation i.e. after directly after distillation processe and by using equivalent amount of hydrogen.Most recent units work by tail end removal especially when liquid feed is used.

Seventh:Product separation:

Pyro gas contains:LO(E,P,B)H₂,DO(diolefins)and acetylene.

Separation process :

To separate E and other LO from pyro gas ;distillation under pressure at low temp, using higher efficiency towers thus products with high purity are obtained.



Energy requirements:

Energy consumption:

- 1-Heating :vapourizing and cracking of raw material supplied to the furnace about 50%
- 2-Energy used to operate compressors to compress the gas to 40 atm. About 28-40%
- 3-Refrigeration energy in separation and purity units.
- 4- Thermal energy to produce medium pressure steam with feed.
- 5-Others :heating of recycle boiler,distillation towers, pumps,compressors operation furnace exhuasers.

Energy recovery:

- 1-Heat recovered from hot combustion gases emitted from thermal cracking furnace.
- 2-Heat from hot reaction product when they cooled in TLE to about 400⁰C and it produced as steam under medium pressure.
- 3-Final cooling for reaction product either in primary distilation tower or in heat exchanger and it produce as steam under low pressure or hot water.

Buytlenes and Butadienes:

Hydrocarbons with carbon no.4: C₄. Its include the followings:

Compound	Formula	Mwt.	Density
1- n-butane	CH ₃ CH ₂ CH ₂ CH ₃	58.12	0.600
2- Isobutane	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	58.12	0.603
3- Butylene-1	CH ₃ CH ₂ CH=CH ₂	56.1	0.668
4- Butylene-2 cis	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH} = \text{CH} \end{array}$	56.1	0.635
5- Butylene-2 Trans	$\begin{array}{c} \text{CH}_3 \quad \quad \quad \\ \quad \quad \quad \\ \text{CH} = \text{CH} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_3 \end{array}$	56.1	0.635
6- Isobutylene	$\begin{array}{c} \text{CH}_2=\text{CHCH}_3 \\ \\ \text{CH}_3 \end{array}$	56.1	0.611
7- 1,3-Butadiene	CH ₂ =CH.CH=CH ₂	54.1	-----

These chemical available as amixture with carbon no.-4. Also C₄ fraction contains some unsaturated comp. Such as acetylene also HCS with carbon no. (3,5) in low percentage.

Sources of butylene production:

- 1-By product in cracking unit of oil fractions.
- 2-Steam cracking unit in ethylene production.
- 3-Dehydrogenation processes and other synthesis processes.

Butylene consumption:

In 1985: Total Butylene consumption=28.09 MT

Linear Butylene =2/3 28.09 Iso=1/3 28.09 mt

Butylene Consumption for engine benzene.

BD consumption =8.3 mt in 2000 %growth=4.5% utilization of DO :in production of :rubber,solvent and other compounds.

Conversion processes-Dehydrogenation

It is used for production of:

1-LO(low olefins)from paraffins in a method similar to the production of ethylene.

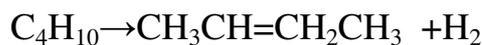
2-HO(higher olefins) from linear paraffins.

3-DO(diolefins)from paraffins and olefins.

Reactions:



n-butane 1-butene



n-butane 2-butene:cis



n-butane 2-butene:trans



Reaction characterization:

1-Reversible 2-Endothermic 3-Occur in gas phase :each vol.gives two vols.:i.e.increase in vol.

4-Takesplace in selective manner in presence of cata. And T=600-800⁰C.

Catalyst used:

Commercial catalyst :consists of 10-20%Cr₂O₃+80-90%Al₂O₃ .The catalyst loses its activity in presence of steam.

Note: Dehydrogenation reaction of low paraffin's is a difficult reaction thus 1-Sever conditions must be used 2-Catalyst must activated periodically.

Catalyst characterization:

1-Higher activity 2-Higher selectivity at higher temp.

BD Separation:

Classical method:

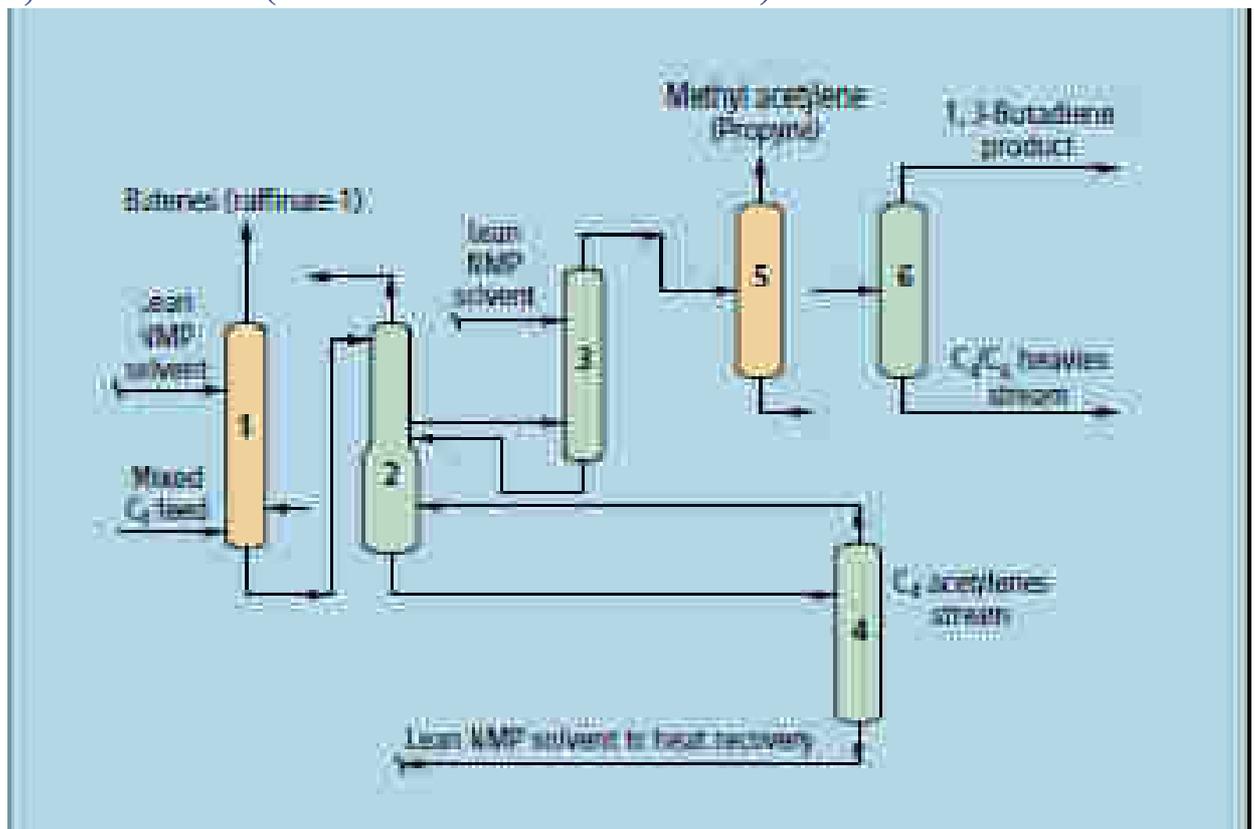
1-Absorption of BD in ammoniac copper acetate solution.

2-Separation:in multi-stages extraction-settling rig.

3-Displacement:BD is displaced from solution when temp.is raised and pressure is lowered.

4-Purification:by distillation.

1,3 Butadiene (Extraction from mixed C₄)



Application: To produce high-purity butadiene from a mixed C4 stream typically a byproduct stream from an ethylene plant using liquid feeds (liquids cracker). The BASF/ Lummus process uses n-methylpyrrolidone (NMP) as the solvent.

Description: The mixed C4 feed stream is fed into the first extractive distillation column (1), which produces an overhead butenes stream (raffinate-1) that is essentially free of butadiene and acetylenes.

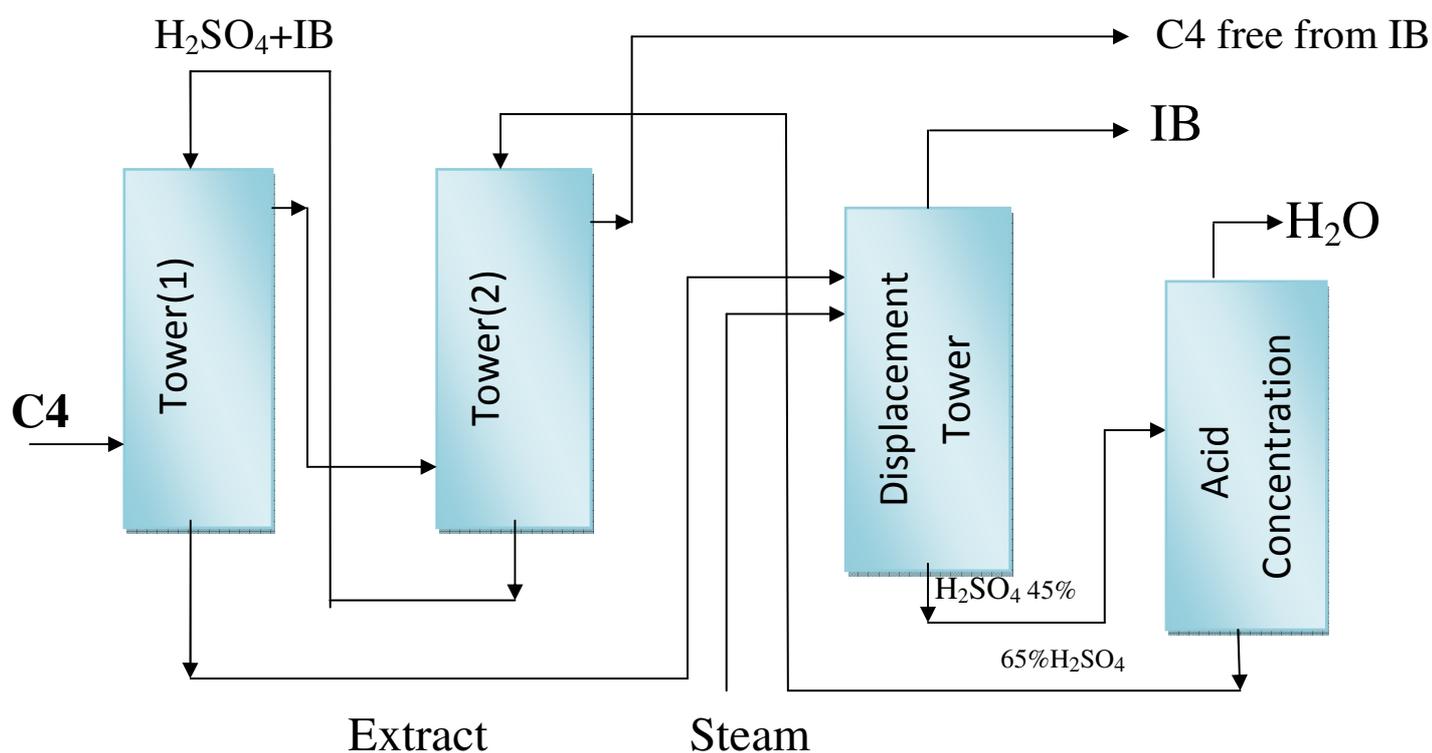
The bottoms stream from this column is stripped free of butenes in the top half of the rectifier (2). A side stream containing butadiene and a small amount of acetylenic compounds (vinyl and ethyl-acetylene) is withdrawn from the rectifier and fed into the second extractive distillation column (3). The C4 acetylenes, which have higher solubilities in NMP than 1,3-butadiene, are removed by the solvent in the bottoms and returned to the rectifier. A crude butadiene (BD) stream, from the overhead of the second extractive distillation column, is fed into the BD purification train. Both extractive distillation columns have a number of trays above the solvent addition point to allow for the removal of solvent traces from the overheads. The bottoms of the rectifier, containing BD, C4 acetylenes and C5 hydrocarbons in NMP, is preheated solvent stripping column (4)). In this column, solvent vapors are used as the stripping medium to remove all light hydrocarbons from NMP. The hot-stripped solvent from the bottom of the degasser passes through the heat economizers (a train of heat exchangers) and is fed to the extractive distillation columns. The hydrocarbons leaving the top of the degasser are cooled in a column by direct contact with solvent (NMP and water) and fed to the solvent than 1,3-butadiene accumulate in the middle zone of the degasser and are drawn off as a side stream. This side stream, after dilution with raffinate-1, is fed to a water scrubber to remove a small amount of NMP from the exiting gases. The scrubbed gases, containing the C4 acetylenes, are purged to disposal. In the propyne column (5), the propyne (C3 acetylene) is removed as overhead and sent to disposal. The bottoms are fed to the second

distillation column (the 1,3-butadiene column (6)), which BD as overhead and a small stream containing 1,2-butadiene and C5hydrocarbons as bottoms.

Yield: Typically, more than 98% of the 1,3-butadiene contained in the feed is recovered as product.

Isobutylene Separation:

Extraction of Isobutylene from C4 with H₂SO₄:



1-C4 is supplied to the bottom of tower (1).To the top of tower (1)H₂SO₄ (conc.65%) +(IB) is supplied from tower(2) to tower(1).

2-Extract from T(1) flow to displacement tower where there the conc. of acid is lowered to 45% And heating by steam.

3-From the bottom of displacement tower H₂SO₄

(45%) flows to concentrated tower .in which the conc. of acid is raised to 65% then it is resupply to Upper of tower 2.

Other methods:

- 1-Dilute H₂SO₄ is used. 2- HCl + metal's salt
- 3-Adsorption(molecular sieve):Union carbide
- 4-IB is converted to secondary & tertiary IB in presence of ion exchange with 96% conv. Bayer Company.

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

Products.HO Is classified in to:

- 1-Olefins with C₁₂-18:Use in production of active Material in detergent.
- 2-Olefins with C₉-15 and particularly C₁₁-12:is used in production of alkyl benzene :i.e :alkylation of B+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.

Uses: 1-Detergent 2-Synthetic oils 3- Solvent 4-Intermediate.

Production of HO

1-Steam cracking of petroleum waxes.

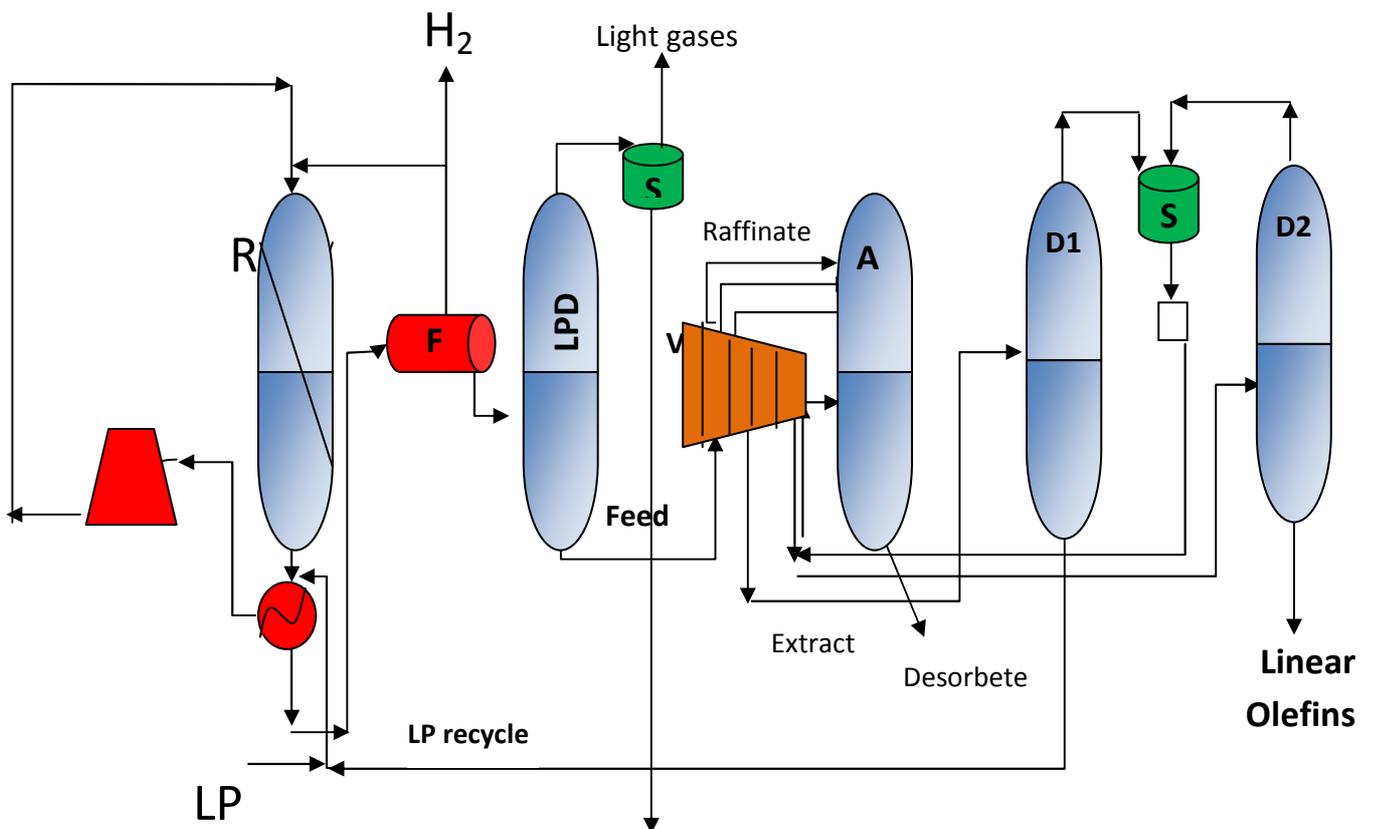
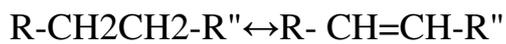
2-Dehydrogenation of n-paraffin's.

3-Selective polymerization (Oligomerization).

4-Metathesis.

Dehydrogenation of n-paraffin U.O.P:

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



Liquids

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 cata.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 .

LDP: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.

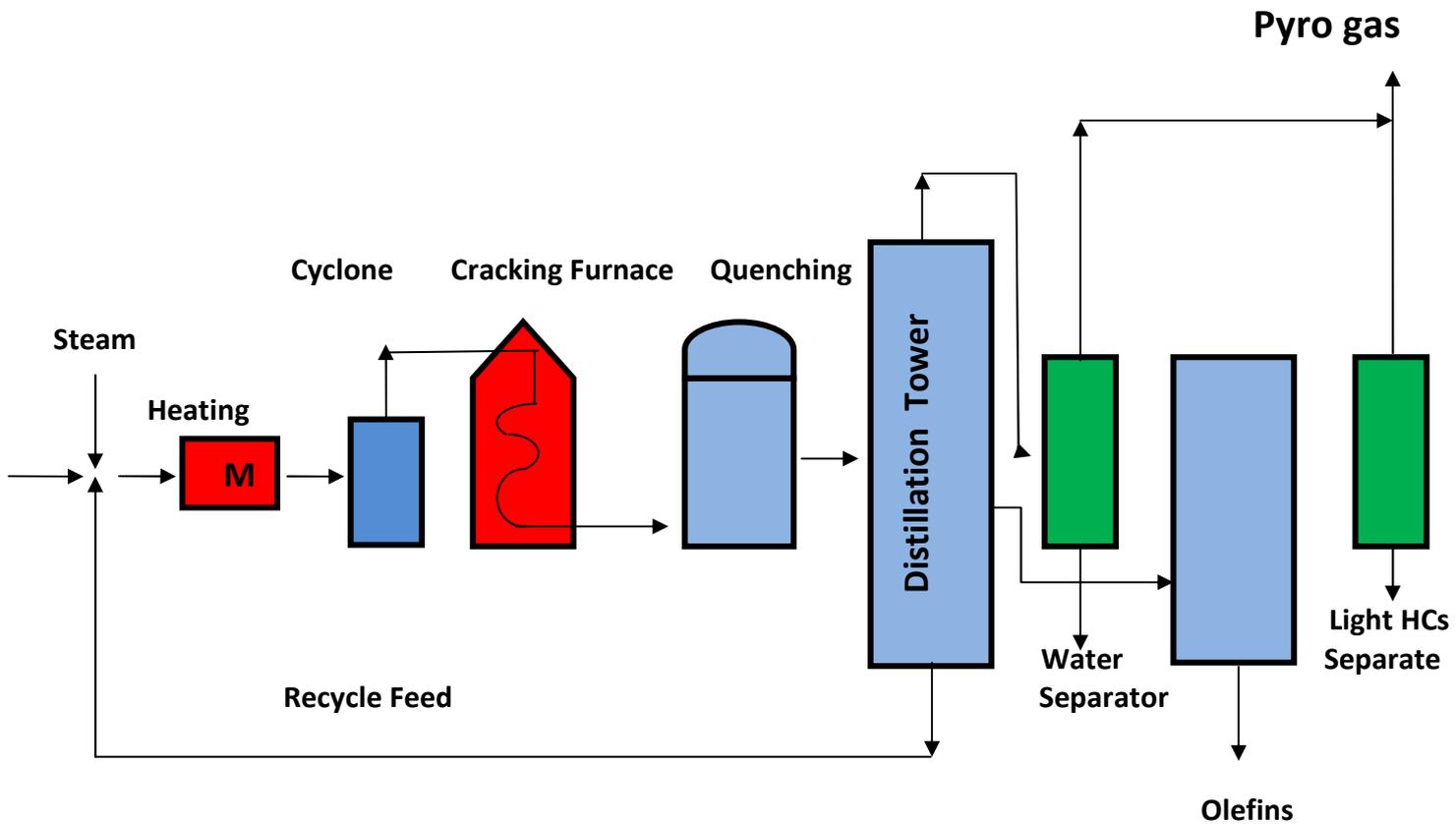
A:Adsorption of product .**D1**:Distillation of product. **S**:Stoage **D2**:Distillaton.

Conditions of Dehydrogenation= $420-520^{\circ}C$ 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 $\approx 90\%$.

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:



$T=550-650^{\circ}\text{C}$ $RT=10\text{ Sec.}$ $\text{Conv.}=25-35\%$

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+H₂ 40% C5-C9 15% C10-C13
15%

C14-C20 30% HO Liquid 60% α-olefin.

This process is considered to be economic if LO-HO is utilized

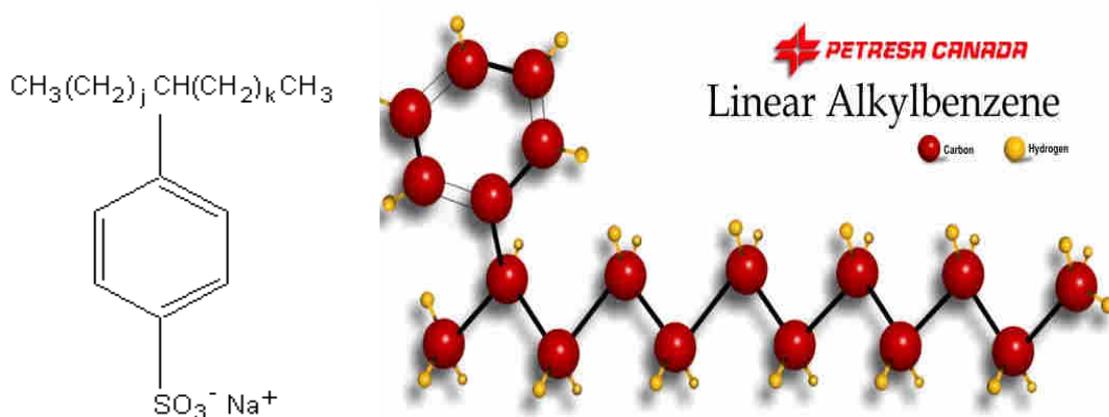
Linear Alkyl Benzene Complex LAB

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.



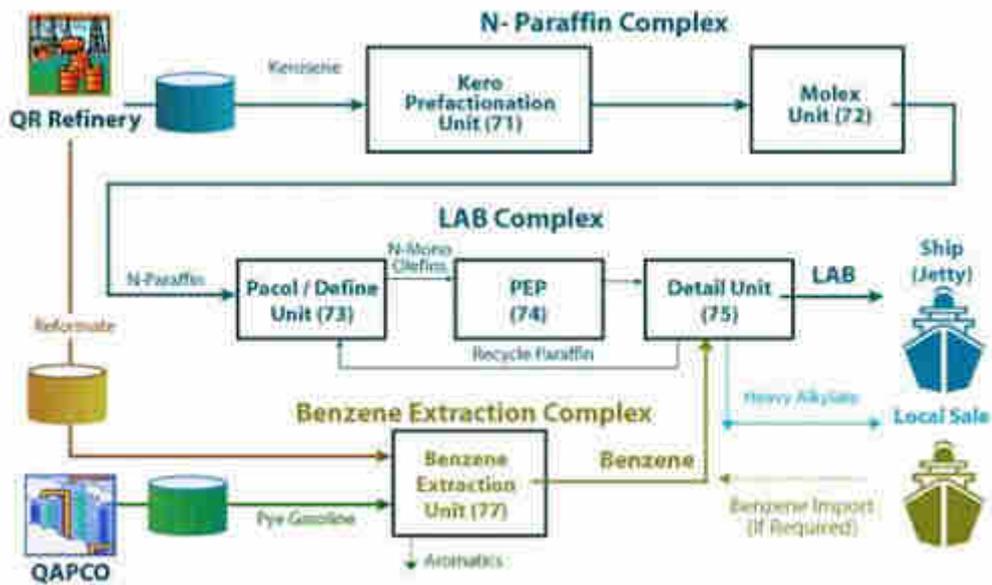
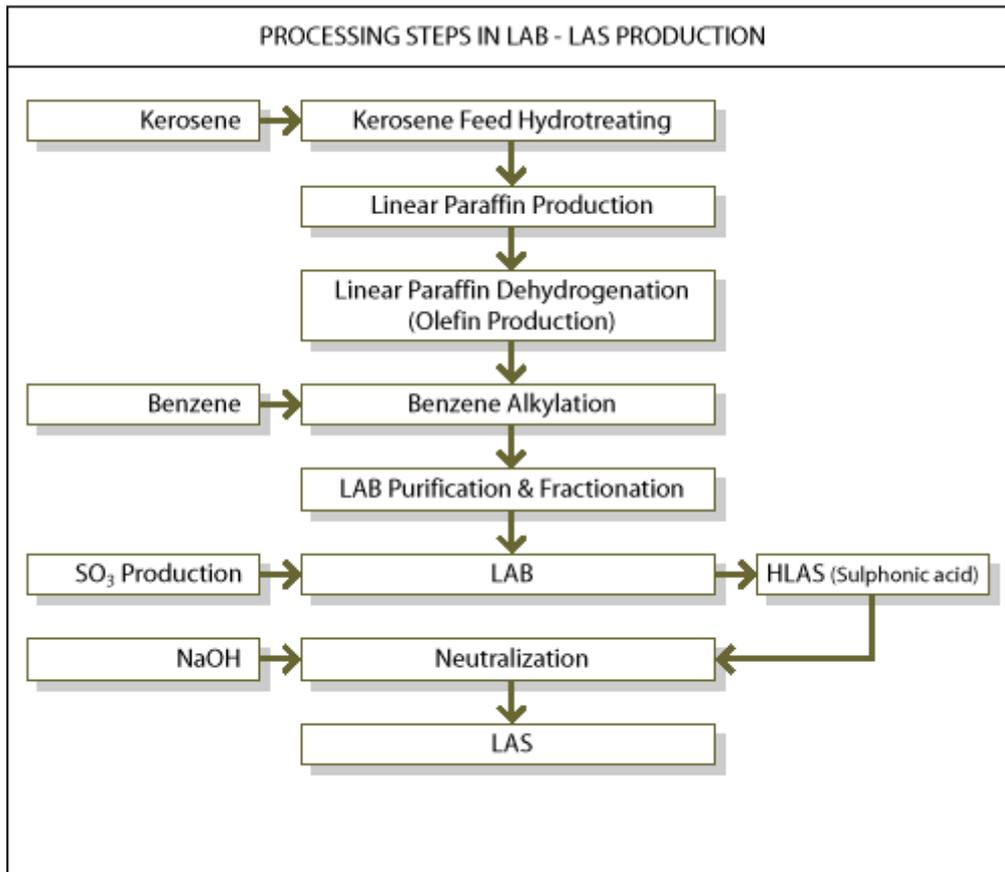
Chemical equation of preparation:

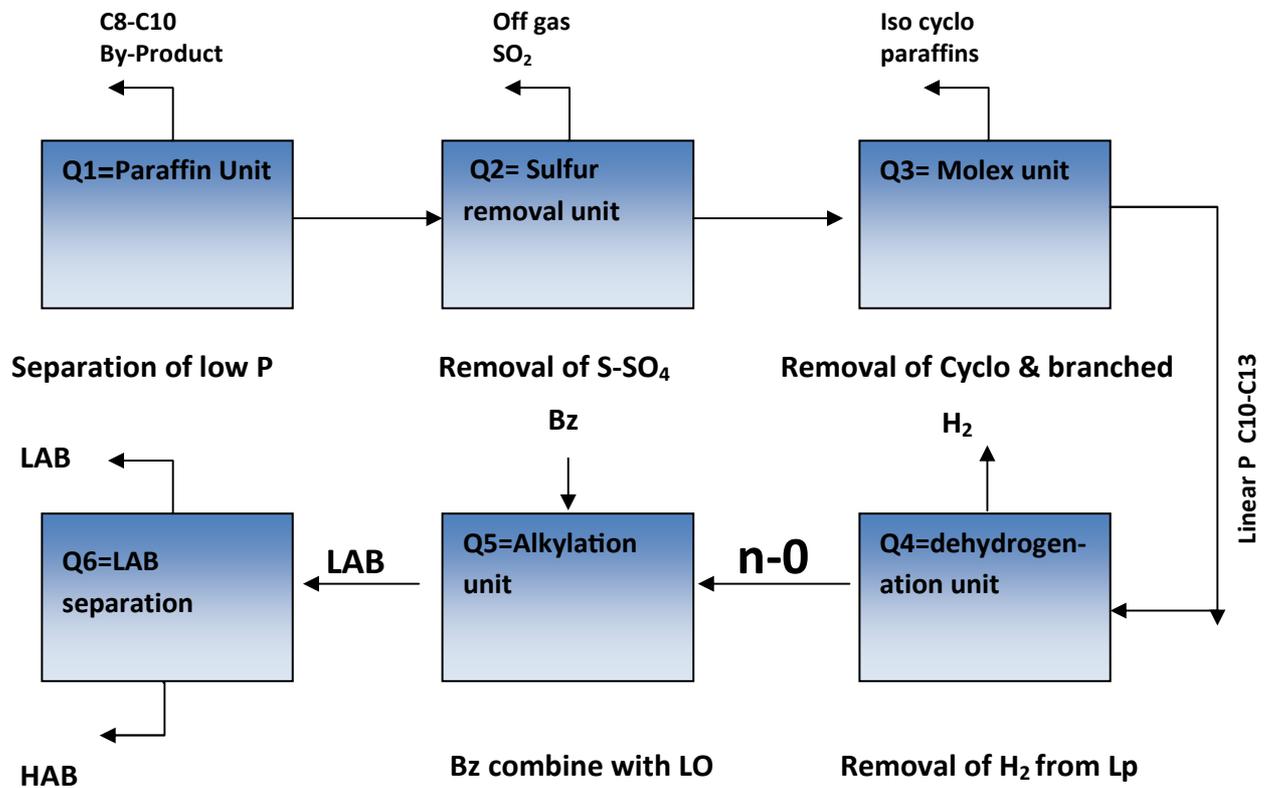
Reaction of LO with Bz(Alkylation)→Alkylbenzene:

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





Main units in LAB complex:

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

Paraffin unit:

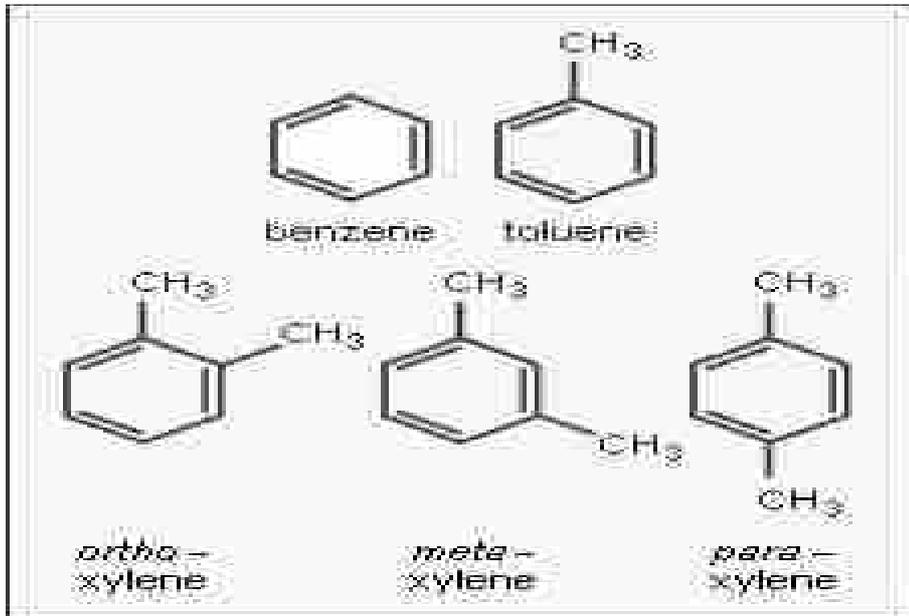
Q1:Paraffin unit Q2:Sulfur removal Q3:Molex unit.

Alkylation unit:

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

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.

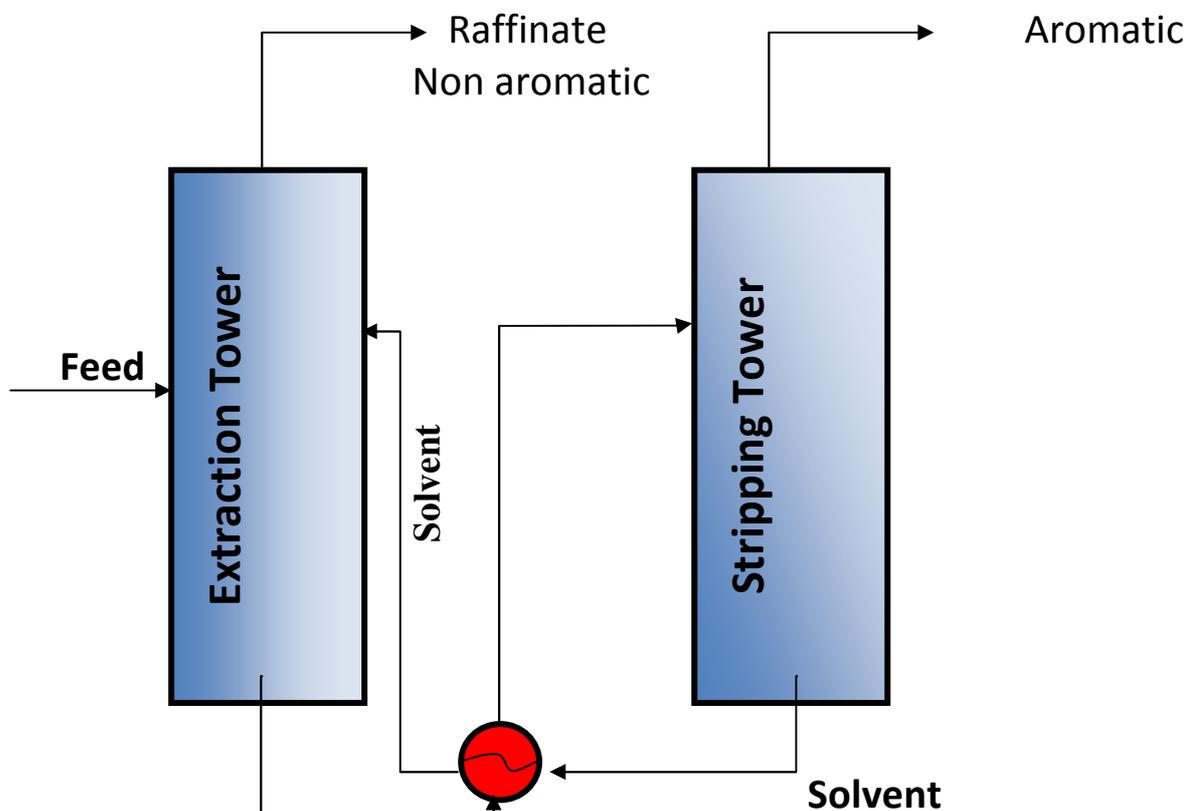
Catalytic reforming usually utilizes a feedstock naphtha that contains non-aromatic hydrocarbons with 6 to 11 or 12 carbon atoms and typically produces a *reformate* product containing C₆ to C₈ aromatics (benzene, toluene, xylenes) as well as paraffins and heavier aromatics containing 9 to 11 or 12 carbon 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 C₆ to C₈ 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 reformat 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 or a complex matrix.

Solvent: from the top of extractor.

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

Properties of solvent:

1-Density higher than feed.

2-Higher boiling point than aromatics.

3-Hidher dissolving properties.

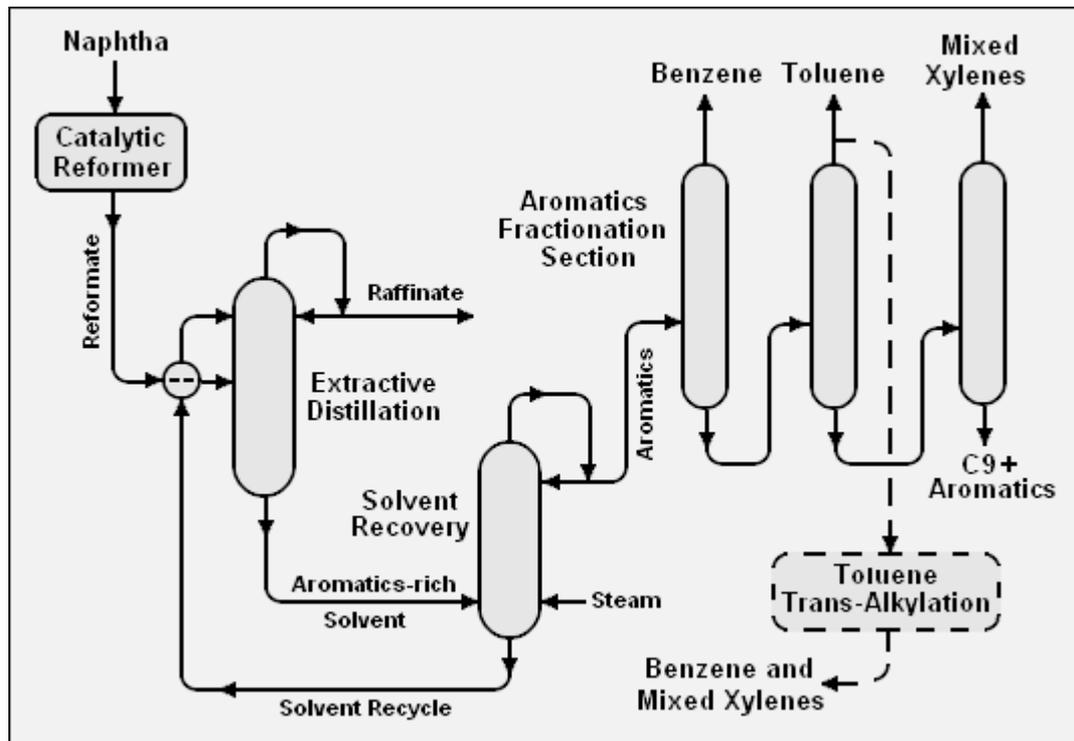
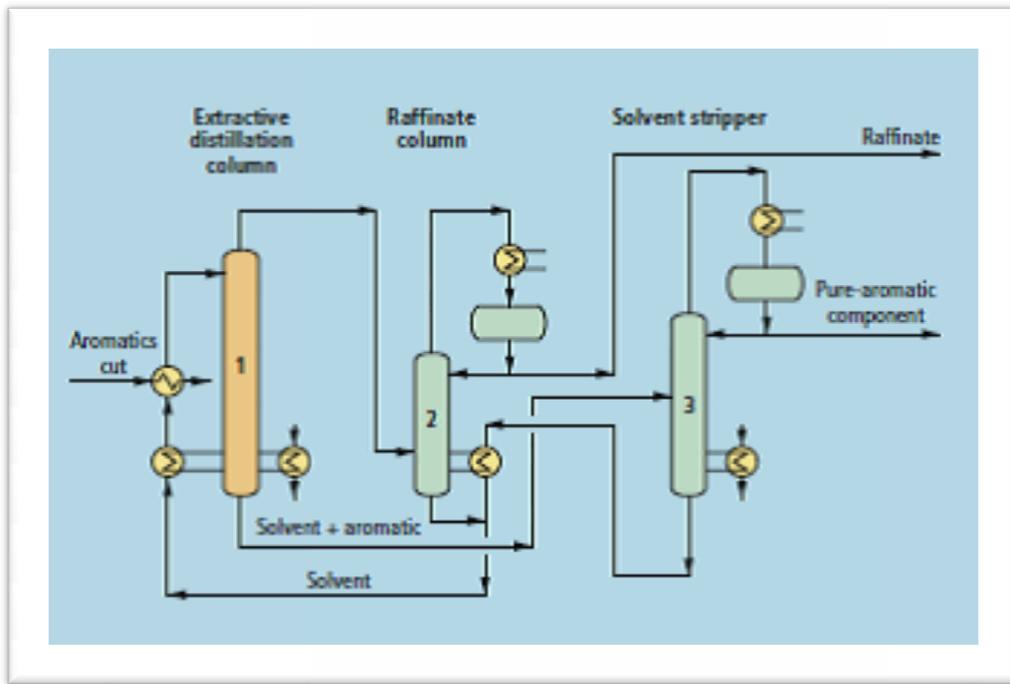
4-Higher thermal stability.

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 reformat:



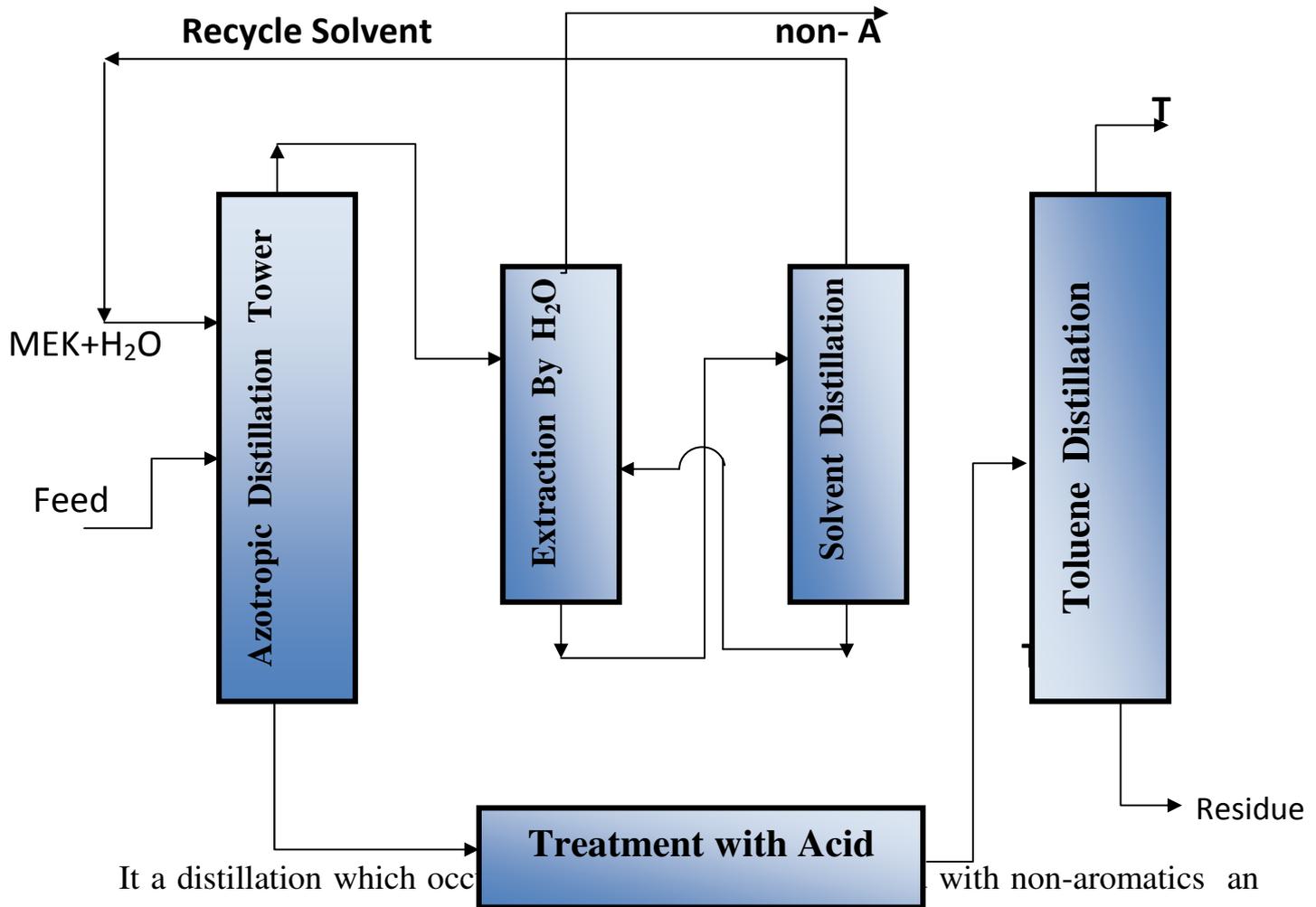
Schematic flow diagram for the extraction of BTX aromatics from a catalytic reformat.

Distillation occur in 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 65-92⁰C is separated and supply to Extractive distillation tower with 102 tower at 90 .tray. On-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 occ 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

The clay then distillate to required purity.

3-From the top of ADT ,mixture of non-aromaics+solvent (MEK)

+H₂O to extractive and distillation towers where the solvent is extracted ,wash and concentrated and recycled.

Comprism between Extractive and Azotropic distillation;

<u>Extractive</u>	<u>Azotropic</u>
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 ₂ O,N-methyl pyrrolidine,Formal morpholine	Acetone+H ₂ O for Bz Methanol+H ₂ O for T MEK+H ₂ O fot T
Fraction: need fraction with narrow range of b.pt	Fraction: need fraction with narrow range of b.pt

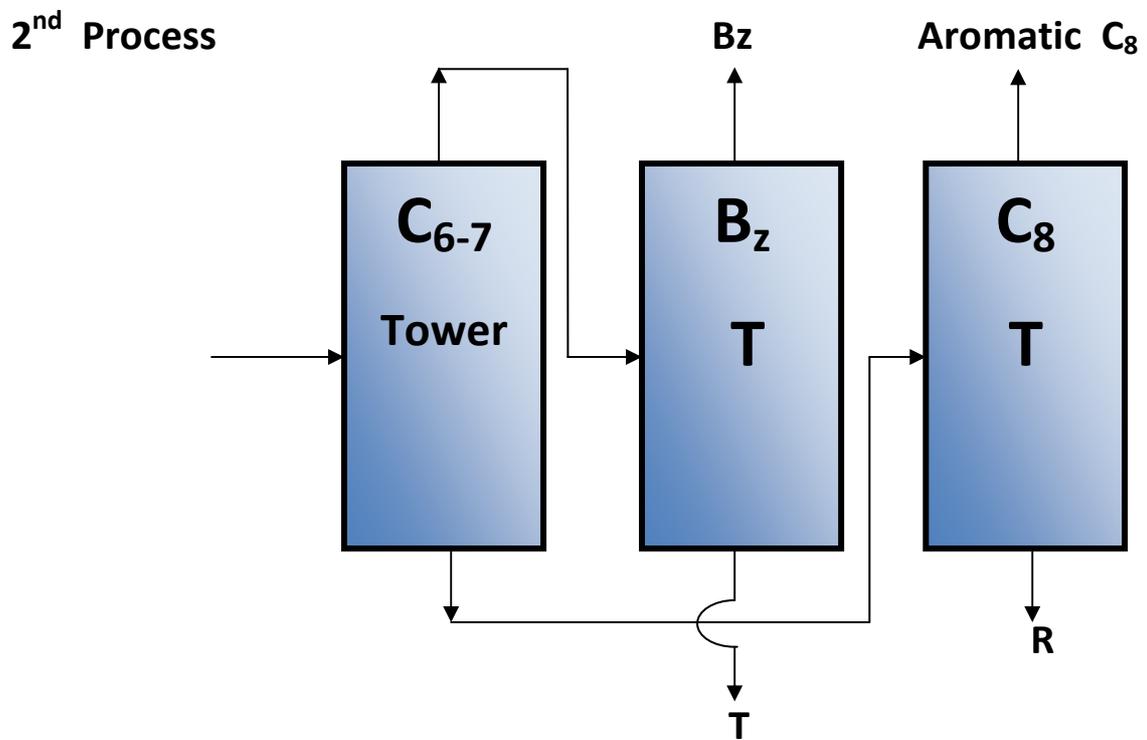
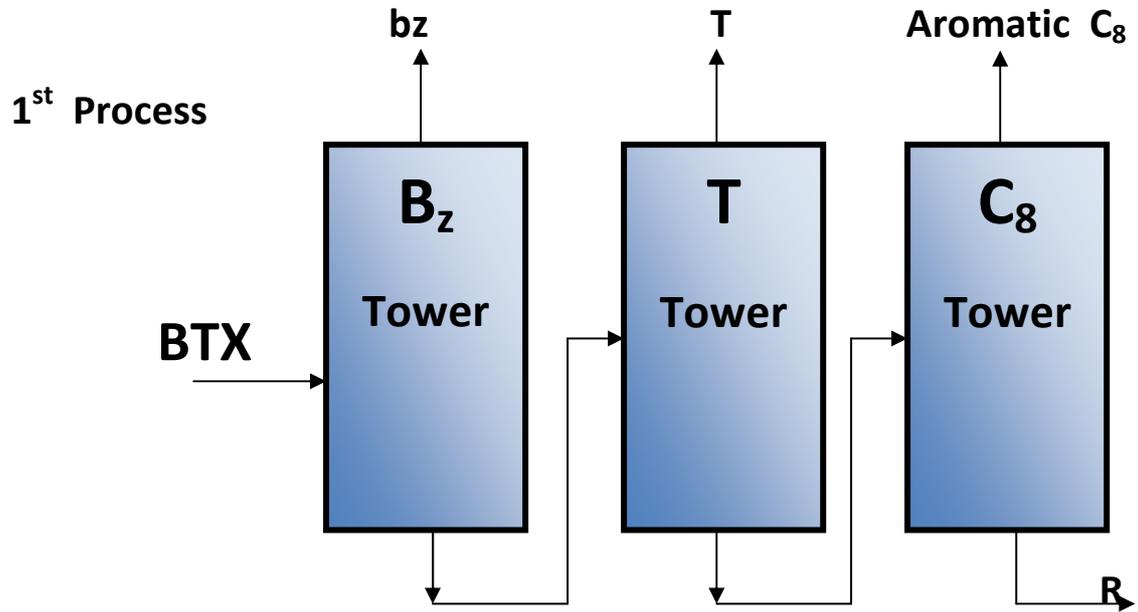
BTX Separation:

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 Naptha.

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.

Catalyst used in Isomerization:

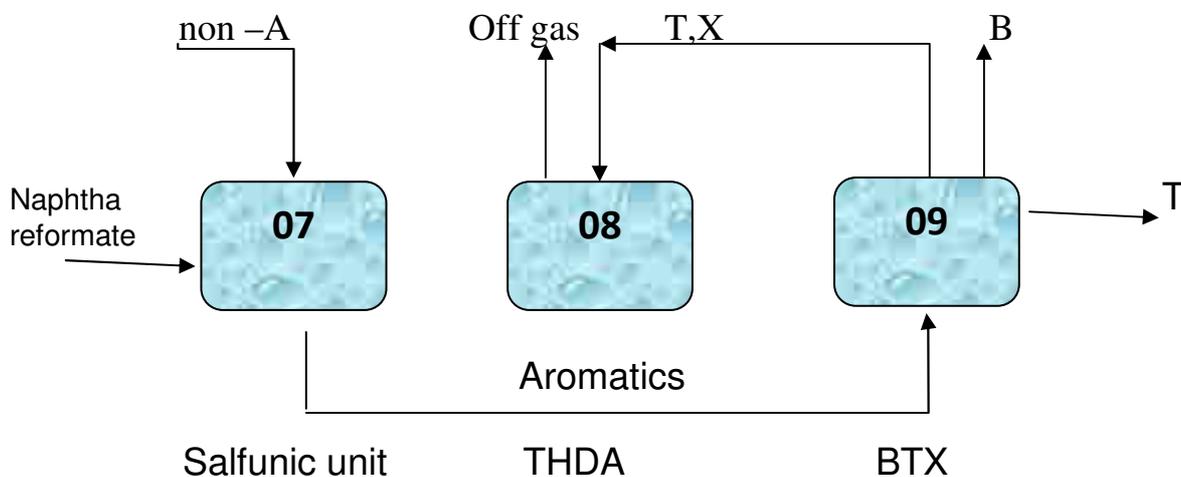
1-Gas phase catalyst: a-compose of metal such as

Mo,W over Al_2O_3 or b- pt over Al_2O_3 .

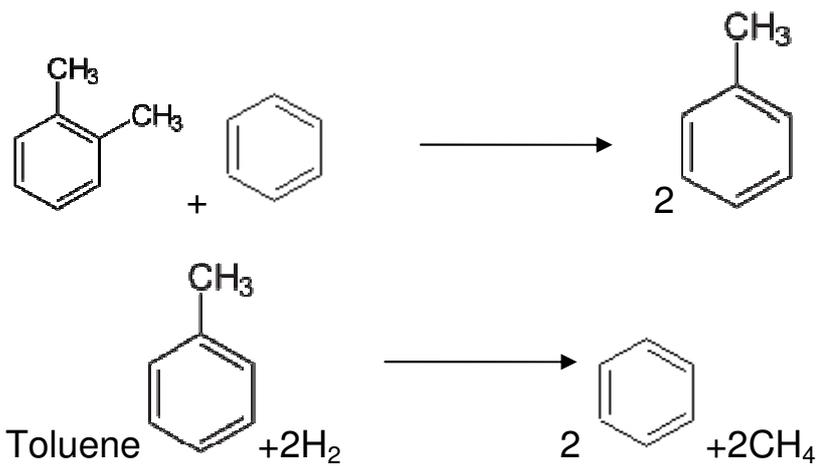
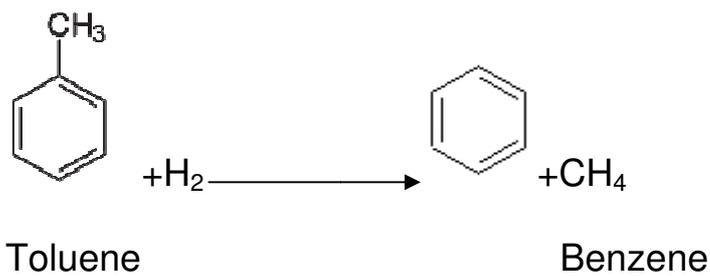
2-Liquid phase cata.

Compose of dry $AlCl_3$ or HF on BF_3 .

Aromatics unit in LAB Complex:



- Sulfonic unit: Separation of aromatics from non-aromatics by extraction with sulfonic solvent.
- THDA: Thermal hydrogenation dealkylation
- Aim: Chang T,X to B thus more benzene is formed.
- Chemical Equation for THDA:
-



09:BTX:Separation

Separation of B from T and X.

Synthetic gas(syn gas): H₂+CO

Importance:

1-Raw material and basic for production of a lot of

Materials such as methanol.

2-Used in process where H₂ is required.

Syn gas production:

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

Coke steam

Now: from petroleum fraction or natural gas

H₂ feed: 1-NG 2-Pet.fraction

Syn.gas: CO+H₂ IF H₂ is required only CO \rightarrow CO₂

Source of H₂:

1-Cata.reforming 80-85%

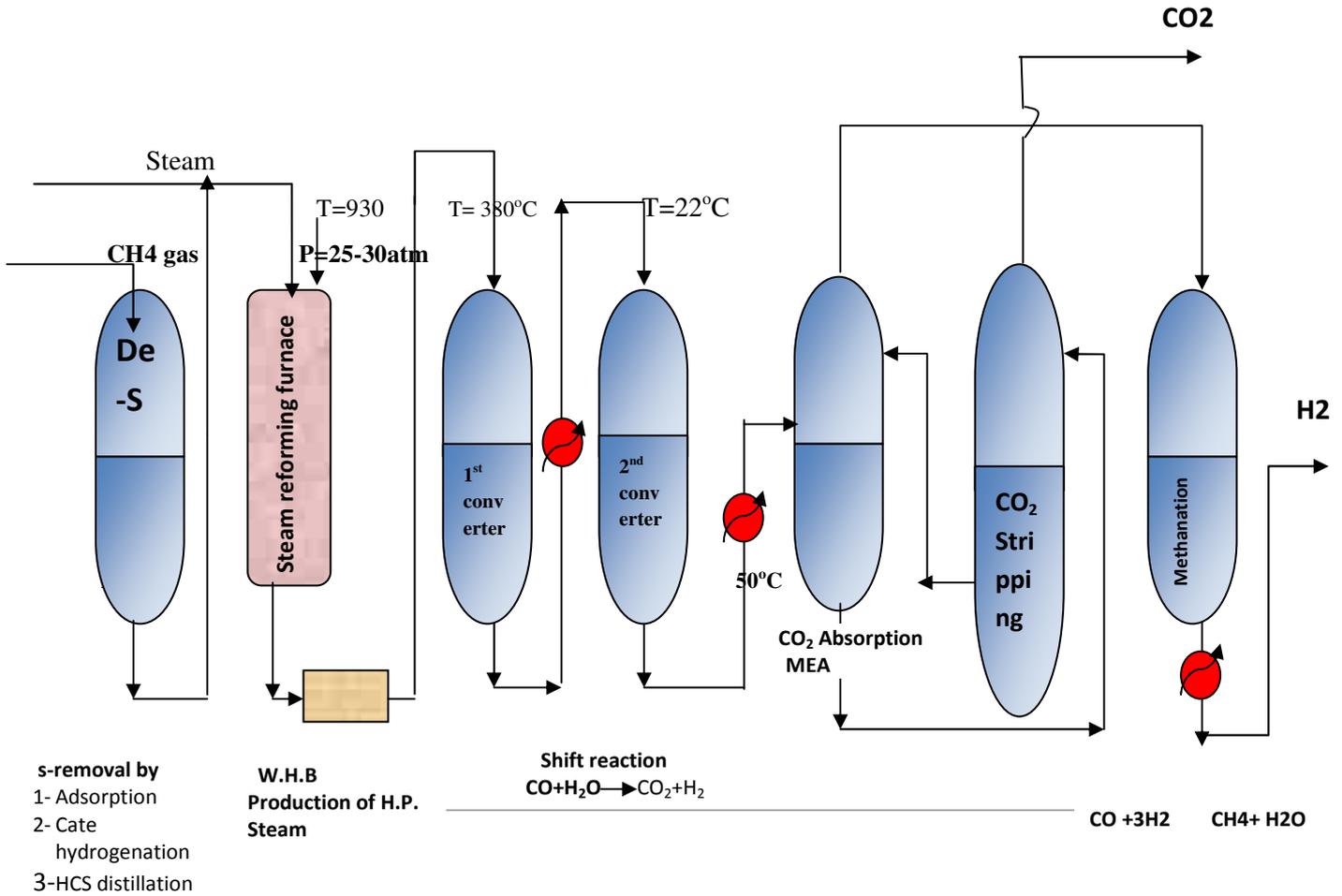
2-Cata. Cracking 60-80%

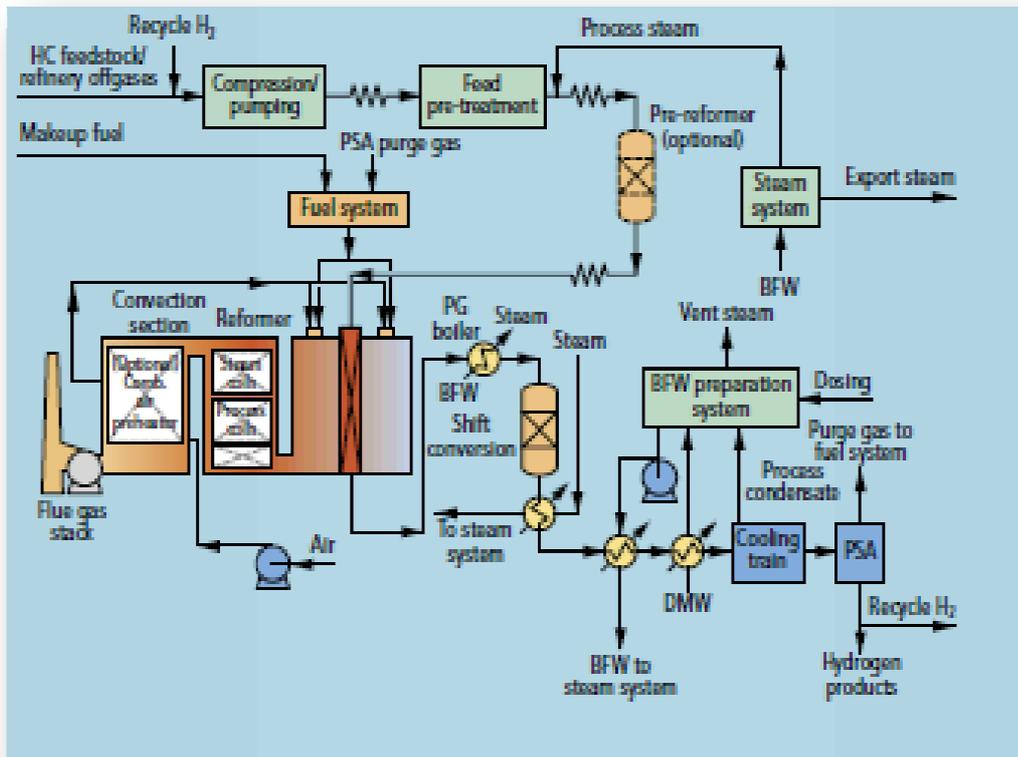
3-Dehydrogenation 90%

4-Electrolysis of water high purity 1m³ required 4940 Kw of electricity.

Hydrogen production from HCs feed

Hydrogen by steam reforming





Application: Production of hydrogen (H₂) from hydrocarbon (HC) feed stocks by steam reforming.

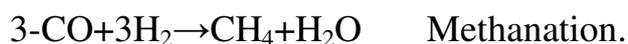
Feed stocks: Ranging from natural gas to heavy naphtha as well as potential refinery off gases. Many recent refinery hydrogen plants have multiple feedstock flexibility, either in terms of backup or alternative or mixed feed. Automatic feedstock change-over has also successfully been applied by Technip in several modern plants with multiple feed stock flexibility.

Description: The generic flow sheet consists of feed pre-treatment, pre reforming (optional), steam-HC reforming, shift conversion and hydrogen purification by pressure swing adsorption (PSA). However, it is often tailored to satisfy specific requirements. Feed pre-treatment normally involves removal of sulfur, chlorine and other catalyst poisons after preheating to 350 – 400°C. The treated feed gas mixed with process steam is reformed in a fired reformer (with adiabatic pre-reformer upstream, if used) after necessary super-heating. The net reforming

reactions are strongly endothermic. Heat is supplied by combusting PSA purge gas, supplemented by makeup fuel in multiple burners in a top-fired furnace. Reforming severity is optimized for each specific case. Waste heat from reformed gas is recovered through steam generation before the water-gas shift conversion. Most of the carbon monoxide (CO) is further converted to hydrogen. Process condensate resulting from heat recovery and cooling is separated and generally reused in the steam system after necessary treatment. The entire steam generation is usually on natural circulation, which adds to higher reliability. The gas flows to the PSA unit that provides high-purity hydrogen product (up to < 1 ppm CO) at near inlet pressures. Typical specific energy consumption based on feed + fuel – export steam ranges between 3 Gcal/KNm³ and 3.5 Gcal/KNm³ (330 – 370 Btu/scf) LHV, depending upon the feedstock, plant capacity, optimization criteria and steam export requirements. Recent advances include integration of hydrogen recovery and generation and recuperative (post-) reforming, also for capacity retrofits.

Commercial plants: Technip has been involved in over 240 hydrogen plants worldwide.

Reactions:



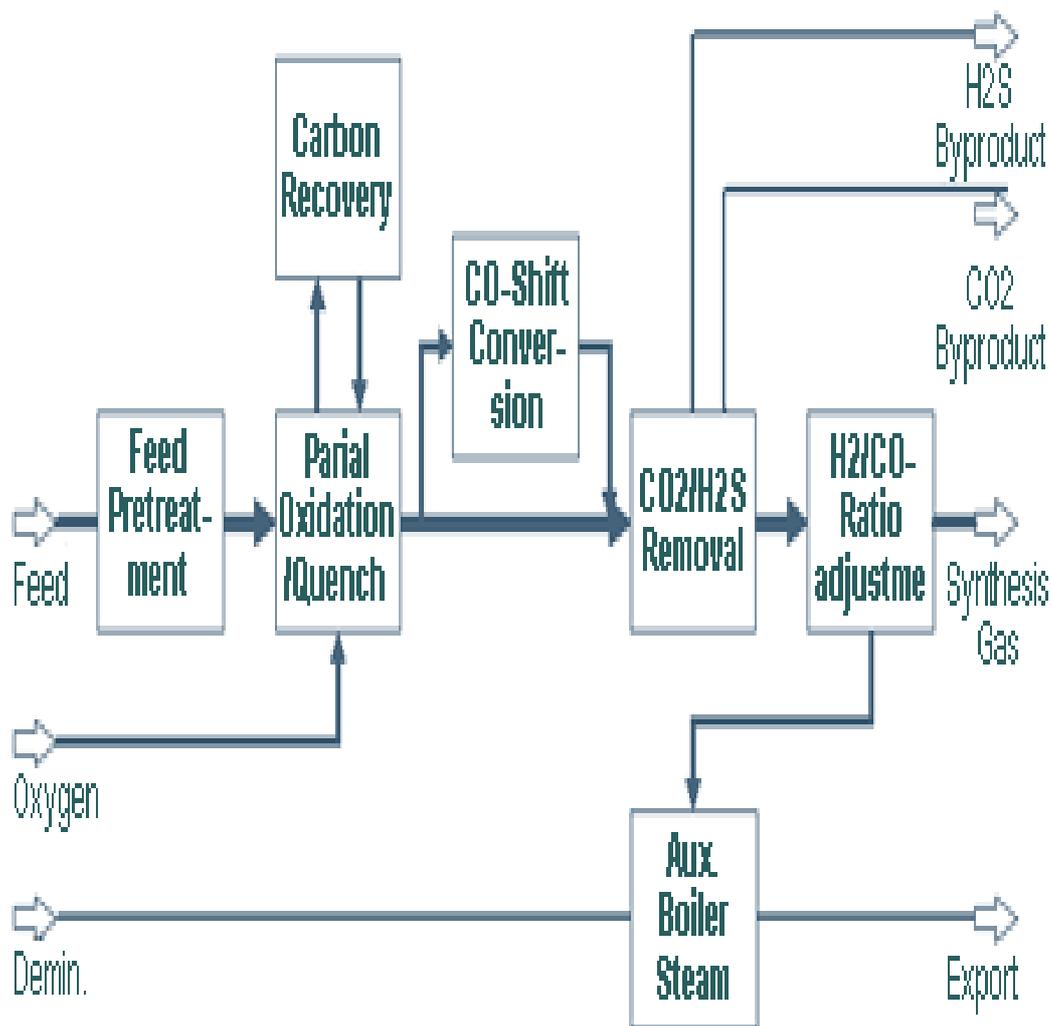
Operating conditions:

T=800-900^oC P=25-30 atm. Cata.=Ni(SRF)

H₂O/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:

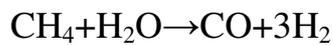
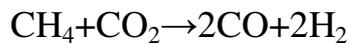
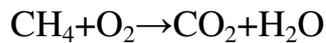
1-Flexibility of use of HCs fuel,pet.fraction,crude oil with high sulfur content and residue.

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:



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 CO₂ 5-Removal of CO₂,H₂S.

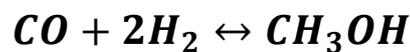
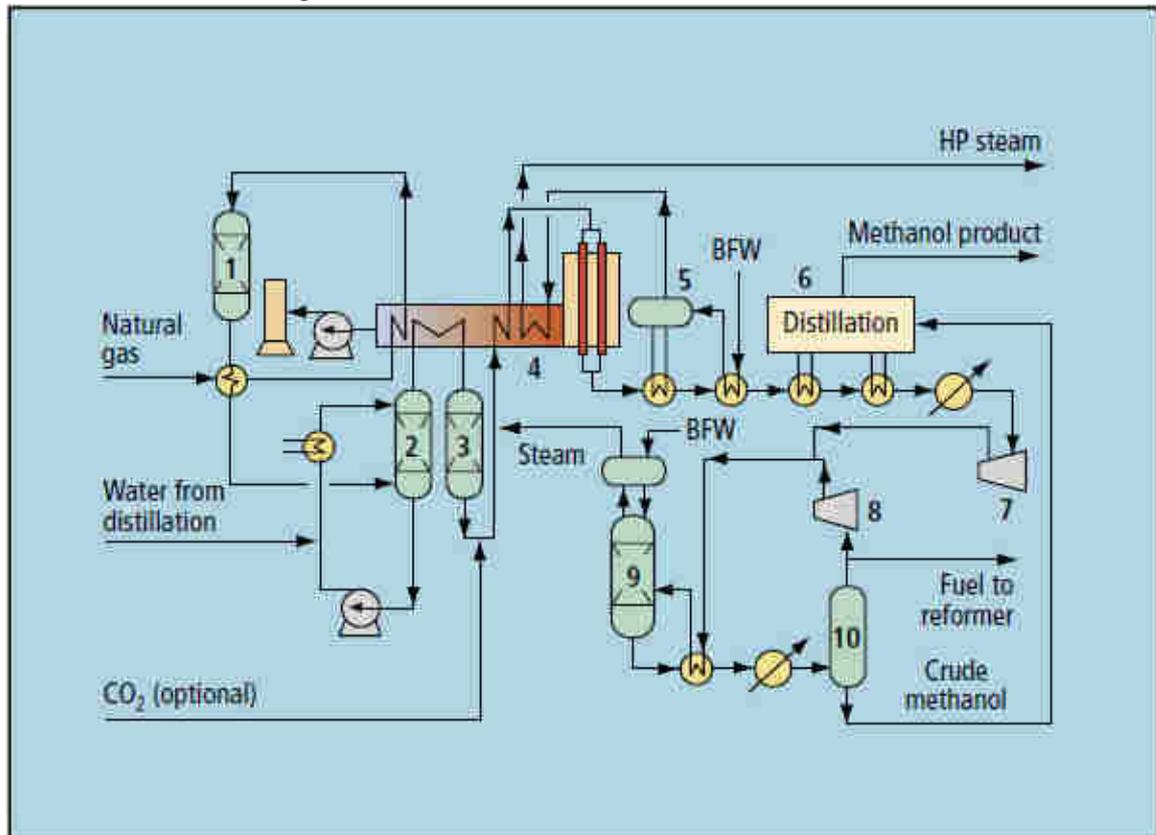
6-Removal of inert gases like Ar,CO.

7-Compression of resultant gases(H₂) or mixture(CO,H₂)

Comprism between Steam reforming(SR)and Parital oxidation(PO)

Properties	SR	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.

1-Methanol CH₃OH



Application: The One Synergy process is improved low-pressure methanol process to produce methanol. The new method produces methanol from natural or associated gas using two-stage steam reforming followed by compression, synthesis and distillation. Capacities, ranging from 5,000 to 7,000 mtpd, are practical in a single stream. Carbon dioxide (CO₂) can be used as a supplementary feedstock to adjust the stoichiometric ratio of the synthesis gas.

Description: Gas feedstock is compressed (if required), desulfurized (1) and sent to the optional saturator (2) where some process steam is generated. The saturator is used where maximum water recovery is important. Further process steam is added, and the mixture is preheated and sent to the pre-reformer (3), using the Catalytic-Rich-Gas process.

Steam raised in the methanol converter is added, along with available CO_2 , and the partially reformed mixture is preheated and sent to the reformer (4). High-grade heat in the reformed gas is recovered as high-pressure steam (5), boiler feed water preheat, and for reboil heat in the distillation system (6). The high-pressure steam is used to drive the main compressors in the plant.

After final cooling, the synthesis gas is compressed (7) and sent to the synthesis loop. The loop can operate at pressures between 70 to 100 bar. The converter design does impact the loop pressure, with radial-flow designs enabling low loop pressure even at the largest plant size. Low loop pressure reduces the total energy requirements for the process.

The synthesis loop comprises a circulator (8) and the converter operates around 200°C to 270°C , depending on the converter type. Reaction heat from the loop is recovered as steam, and is used directly as process steam for the reformer.

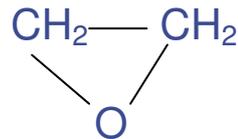
A purge is taken from the synthesis loop to remove inerts (nitrogen, methane), as well as surplus hydrogen associated with non-stoichiometric operation. The purge is used as fuel for the reformer. Crude methanol from the separator contains water, as well as traces of ethanol and other compounds. These impurities are removed in a two-column distillation system (6). The first column removes the light ends such as ethers, esters, acetone and dissolved noncondensable gases. The second column removes water, higher alcohols and similar organic heavy ends.

Economics: Recent trends have been to build methanol plants in regions offering low-cost gas (such as Chile, Trinidad and the Arabian Gulf). In these regions, total economics favor low investment rather than low-energy consumption. Recent plants have an energy efficiency of 7.2

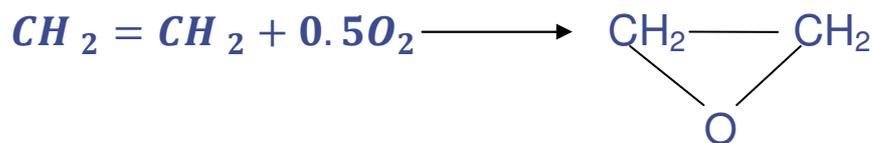
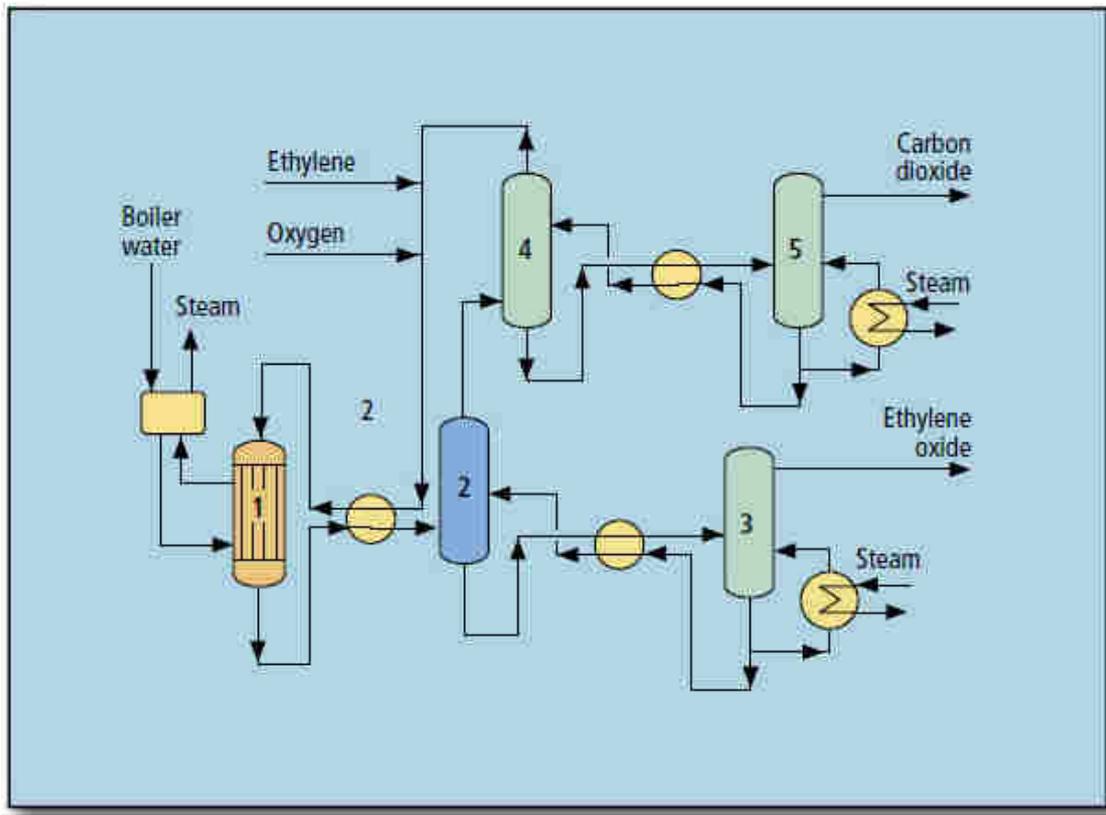
-7.8 Gcal/ton. A guideline figure to construct a 5,000-mtpd plant is US\$370 – 400 million.

Q: Explain why %methanol decrease with temp. increase?

2-Ethylene oxide



⇒



Application: To produce ethylene oxide (EO) from the direct oxidation of ethylene using the Dow Meteor process.

Description: The Meteor Process, a technology first commercialized in 1994, is a simpler, safer process for the production of EO, having lower capital investment requirements and lower operating costs. In the Meteor Process, a-ethylene and oxygen are mixed with methane-ballast recycle gas and passed through a single-train, multi tubular catalytic reactor (1) to selectively oxidize ethylene. The process is a simpler, safer technology with lower facility investment costs. The special high-productivity Meteor EO catalyst provides very high efficiencies while operating at high loadings. b- Heat generated by the reaction is removed and recovered by the direct boiling of water to generate steam on the shell side of the reactor. Heat is recovered from the reactor outlet gas before it enters the EO absorber (2) where EO is scrubbed from the gas by water. The EO-containing water from the EO absorber is concentrated by stripping (3). The cycle gas exiting the absorber is fed to the CO₂ removal section (4,5) where CO₂, which is co-produced in the EO reactor, is removed via activated, hot potassium carbonate treatment. The CO₂ lean cycle gas is recycled by compression back to the EO reactor. Most EO plants are integrated with glycol production facilities. When producing glycols, the EO stream (3) is suitable for feeding directly to a Meteor glycol process. When EO is the desired final product, the EO stream (3) can be fed to a single purification column to produce high-purity EO. This process is extremely flexible and can provide the full range of product mix between glycols and purified EO.

Economics: The process requires a lower capital investment and has lower fixed costs due to process simplicity and the need for fewer equipment items. Lower operating costs are also achieved through the

high productivity Meteor EO catalyst, which has very high efficiencies at very high loadings.

Commercial plants: Union Carbide was the first to commercialize the direct oxidation process for EO in the 1930s. Since 1954, 18 Union Carbide- designed plants have been started up or are under construction. Three million tons of EO equivalents per year (approximately 20% of total world capacity) are produced in Union Carbide-designed plants.

Advantages:

Plant with one reactor work with high selectivity with low conversion for each cycle. Reactants used with high concentration which reduced the capital cost.

Disadvantages:

- 1- The demand for additional units e.g. oxygen separation unit (high purity).
- 2- The need of CO₂removal from recycle gas.
- 3- N₂ must be removed from recycle gas; additional units.

However oxidation by O₂ is more economic when high capacity production is used.

EO Uses:

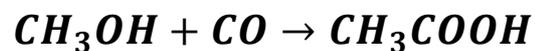
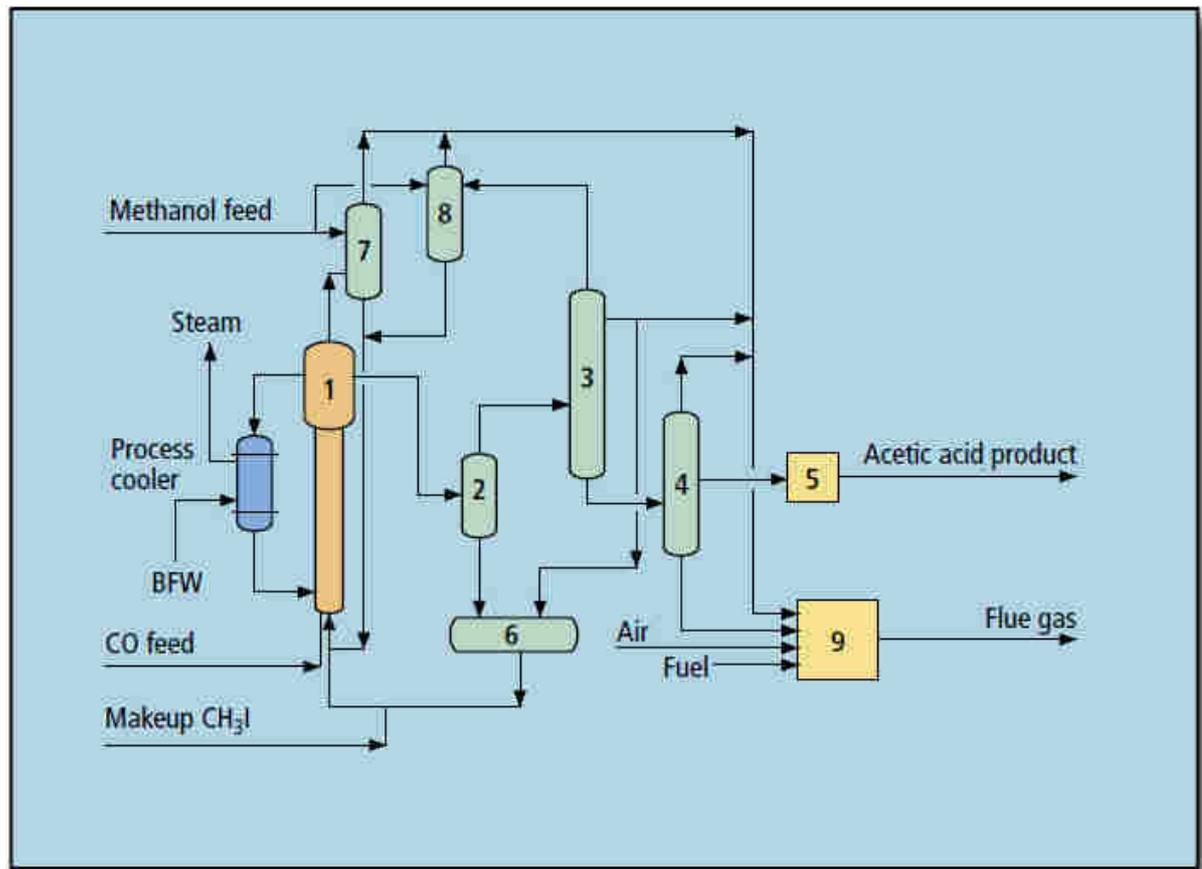
- 1-In production of ethylene glycol(anti freeze agent).
- 2-Used as surfactant. 3-In production of polyester.
- 4-In manufacture of Hydraulic fluid.

Other old method utilized air for oxidation:

- 1-Two reactors and two absorber to complete oxidation of E to produce EO. T=260-290OC, P=10-13 atm.

Cata: Ag/Al₂O₃ + Promotor: Ba, K + Inhibitor AgCl ,NaI ,used as sphere to reduce pressure drop.

3-Acetic acid CH₃COOH



Application: To produce acetic acid using the process, ACETICA. Methanol and carbon monoxide (CO) are reacted with the carbonylation reaction using a heterogeneous Rh catalyst.

Description: Fresh methanol is split into two streams and is contacted with reactor offgas in the high-pressure absorber (7) and light gases in the low-pressure absorber (8). The methanol, exiting the absorbers, are

recombined and mixed with the recycle liquid from the recycle surge drum (6). This stream is charged to a unique bubble-column reactor (1).

Carbon monoxide is compressed and sparged into the reactor riser. The reactor has no mechanical moving parts, and is free from leakage/maintenance problems. The ACETICA Catalyst is an immobilized Rh complex catalyst on solid support, which offers higher activity and operates under less water conditions in the system due to heterogeneous system, and therefore, the system has much less corrosivity.

Reactor effluent liquid is withdrawn and flash-vaporized in the Flasher (2). The vaporized crude acetic acid is sent to the dehydration column (3) to remove water and any light gases. Dried acetic acid is routed to the finishing column (4), where heavy byproducts are removed in the bottom draw off. The finished acetic-acid product is treated to remove trace iodide components at the iodide removal unit (5).

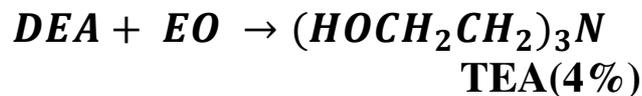
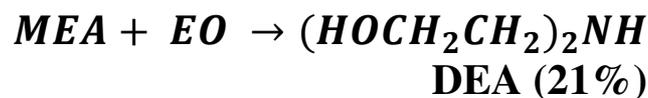
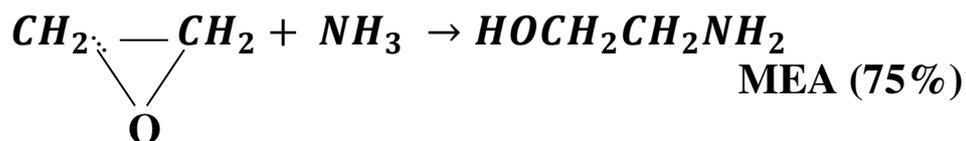
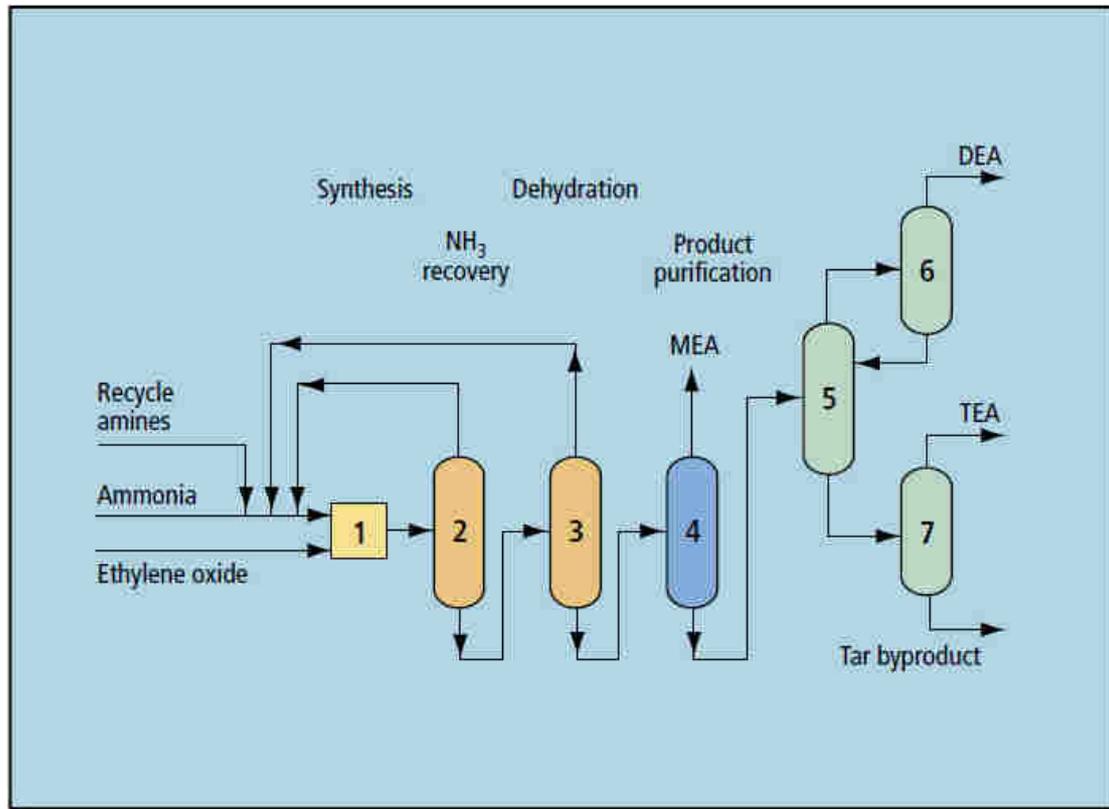
Vapor streams from the dehydration column overhead contacted with methanol in the low-pressure absorber (8). Unconverted CO, methane, other light byproducts exiting in the vapor outlets of the high- and low-pressure absorbers and heavy byproducts from the finishing column are sent to the incinerator with scrubber (9).

Feed and utility consumption:

Methanol, mt/mt	0.539
CO, mt/mt	0.517
Power (@CO Supply 0 K/G), kWh/mt	129
Water, cooling, m ³ /mt	137
Steam @100 psig, mt/mt	1.7

Commercial plant: One unit is under construction for a Chinese client.

4-Ethanolamines,MEA,DEA &TEA



Application: To produce mono-(MEA), di-(DEA) and triethanolamines (TEA) from ethylene oxide and ammonia.

Description: Ammonia solution, recycled amines and ethylene oxide are fed continuously to a reaction system (1) that operates under mild conditions and simultaneously produces MEA, DEA and TEA. Product ratios can be varied to maximize MEA, DEA or TEA production. The

correct selection of the NH_3 / EO ratio and recycling of amines produces the desired product mix. The reactor products are sent to a separation system where ammonia (2) and water are separated and recycled to the reaction system. Vacuum distillation (4,5,6,7) is used to produce pure MEA, DEA and TEA. A saleable heavies tar byproduct is also produced. Technical grade TEA (85 wt%) can also be produced if required.

Yields: Greater than 98% on raw materials.

Economics: Typical performance data per ton amines MEA/DEA/TEA product ratio of 1/3 : 1/3 : 1/3

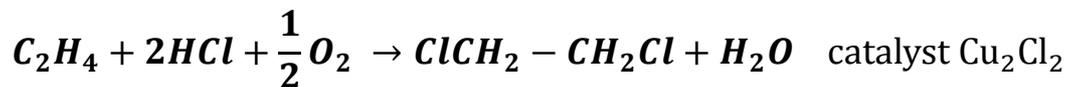
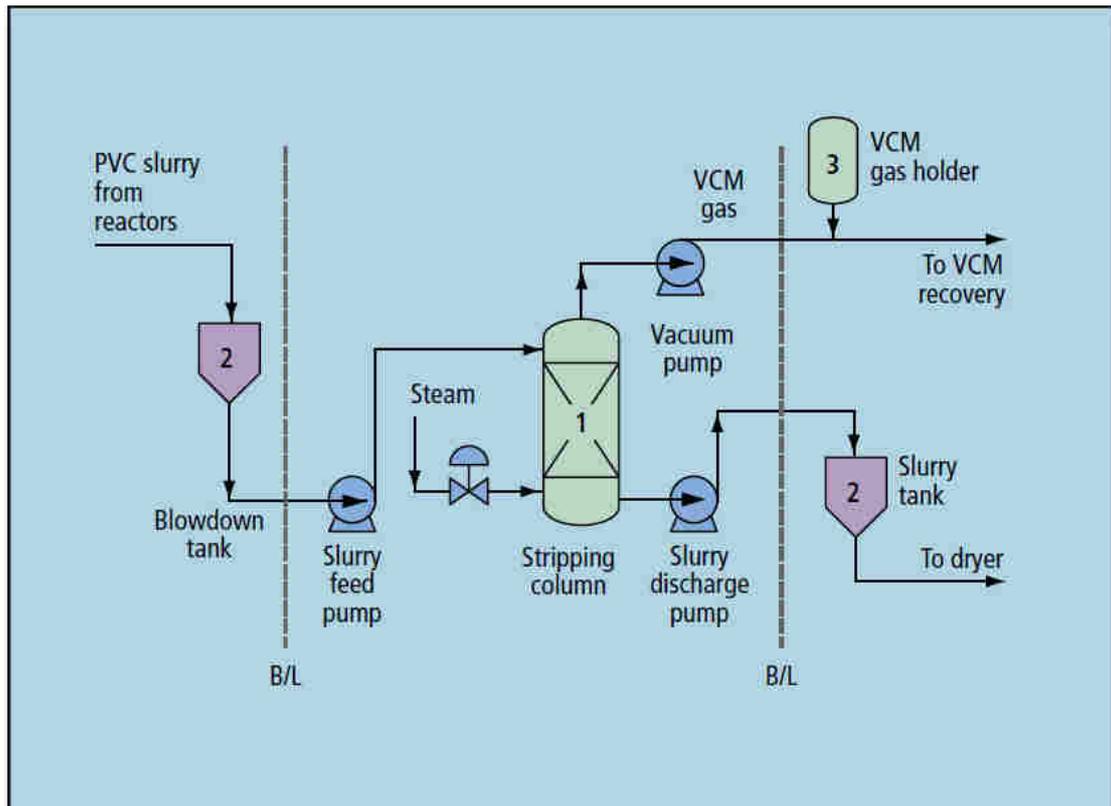
Ethylene oxide, t	0.82
Ammonia, t	0.19
Steam, t	5
Water, cooling , m ³	300
Electricity, kWh	30

Commercial plants: One 20,000-mtpy original capacity facility.

Uses:

- 1-Gases softening.
- 2-Detergent production.
- 3-Corrosion stabilizers
- 4- Chlorinated HCs stabilizers :decrease its decomposition.

5-Vinylchloride monomer VCM $\text{CH}(\text{Cl})=\text{CH}_2$



Application: Adding a stripping column to existing polyvinyl chloride (PVC) plants to remove vinyl chloride monomer (VCM) from PVC slurry. The recovered VCM can be reused in the PVC process, without any deterioration of PVC polymer quality.

Description: PVC slurry discharged from reactors contains significant amounts of VCM (>30,000 ppm) even after initial flashing. This process effectively removes the remaining VCM so that the monomer is recovered and reused. Recycling of raw materials drastically reduces VCM emissions from the following dryer. There is no significant change in PVC quality after stripping. Residual VCM level in the PVC product can be lowered below 1 ppm, and, in some cases, below 0.1 ppm.

The PVC slurry, containing VCM, is continuously fed to the stripping column (1). The slurry passes counter-currently to steam, which is fed into the base of the column. The proprietary internals of the column are specially designed to ensure intimate contact between the steam and the PVC slurry and to ensure that no PVC particles remain inside the column. All process operations, including grade change, are automatically done in a completely closed system.

While steam stripping is widely used, this proprietary technology, which involves sophisticated design and know-how of the column, offers attractive benefits to existing PVC plant sites.

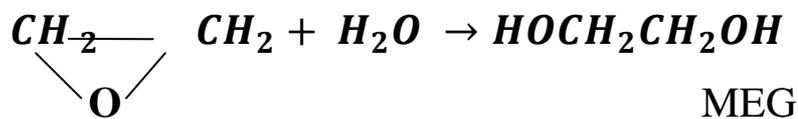
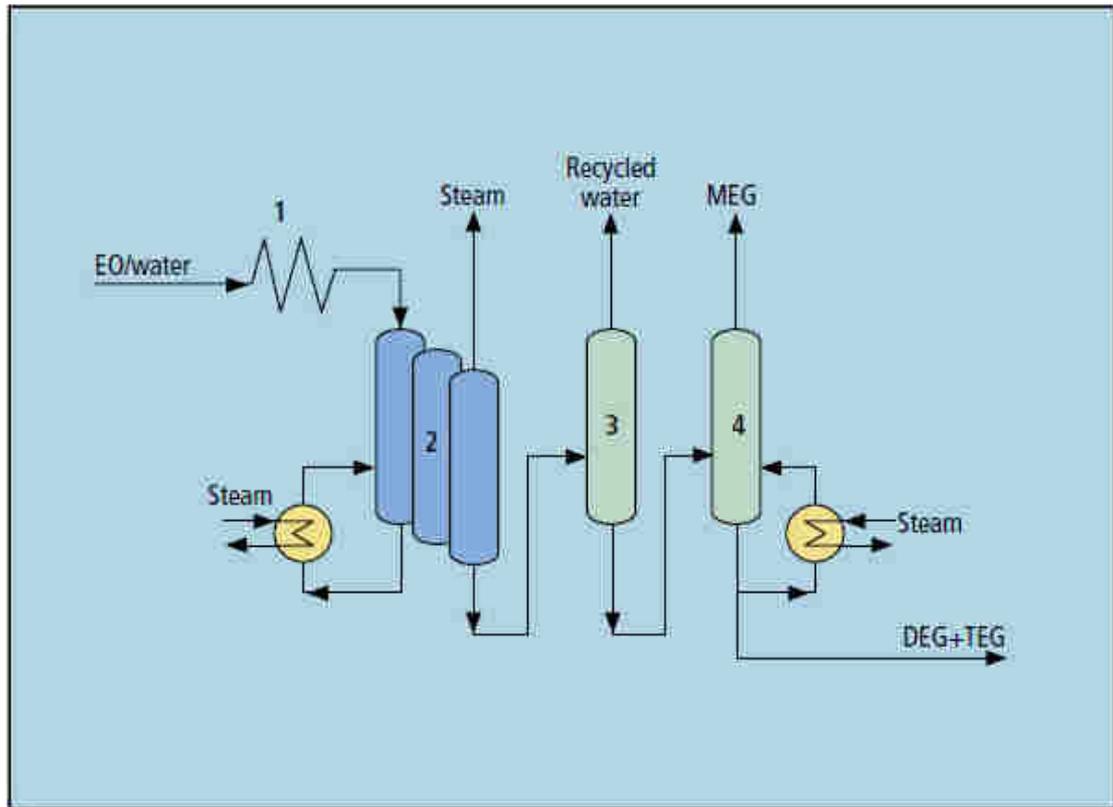
The process design is compact with a small area requirement and low investment cost. The size of the column is 2.5 t / h to 30 t / h.

Economics:

Steam 130 kg/t of PVC

Commercial plants: Chisso has licensed the technology to many PVC producers worldwide. More than 100 columns of the Chisso process are under operation or construction, and total capacity exceeds 5 million tpy of PVC.

6-Ethylene glycol $HOCH_2CH_2OH$



Application: To produce ethylene glycols (MEG, DEG, TEG) from ethylene oxide (EO) using Dow's Meteor process.

Description: In the Meteor Process, an EO/water mixture is preheated and fed directly to an adiabatic reactor (1), which can operate with or without a catalyst. An excess of water is provided to achieve high selectivities to monoethylene glycol (MEG). Diethylene (DEG) and triethylene (TEG) glycols are produced as coproducts. In a catalyzed mode, higher selectivities to MEG can be obtained, thereby reducing DEG production to one-half that produced in the uncatalyzed mode. The

reactor is specially designed to fully react all of the EO and to minimize back-mixing, which promotes enhanced selectivity to MEG.

Excess water from the reactor effluent is efficiently removed in a multi-effect evaporation system (2). The last-effect evaporator overhead produces low-pressure steam, which is a good low-level energy source for other chemical units or other parts of the EO/MEG process. The concentrated water/glycols stream from the evaporation system is fed to the water column (3) where the remaining water and light ends are stripped from the crude glycols. The water-free crude glycol stream is fed to the MEG refining column (3) where polyester-grade MEG, suitable for polyester fiber and PET production, is recovered. DEG and TEG exiting the base of the MEG refining column can be recovered as high-purity products by subsequent fractionation.

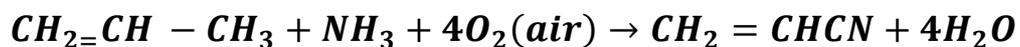
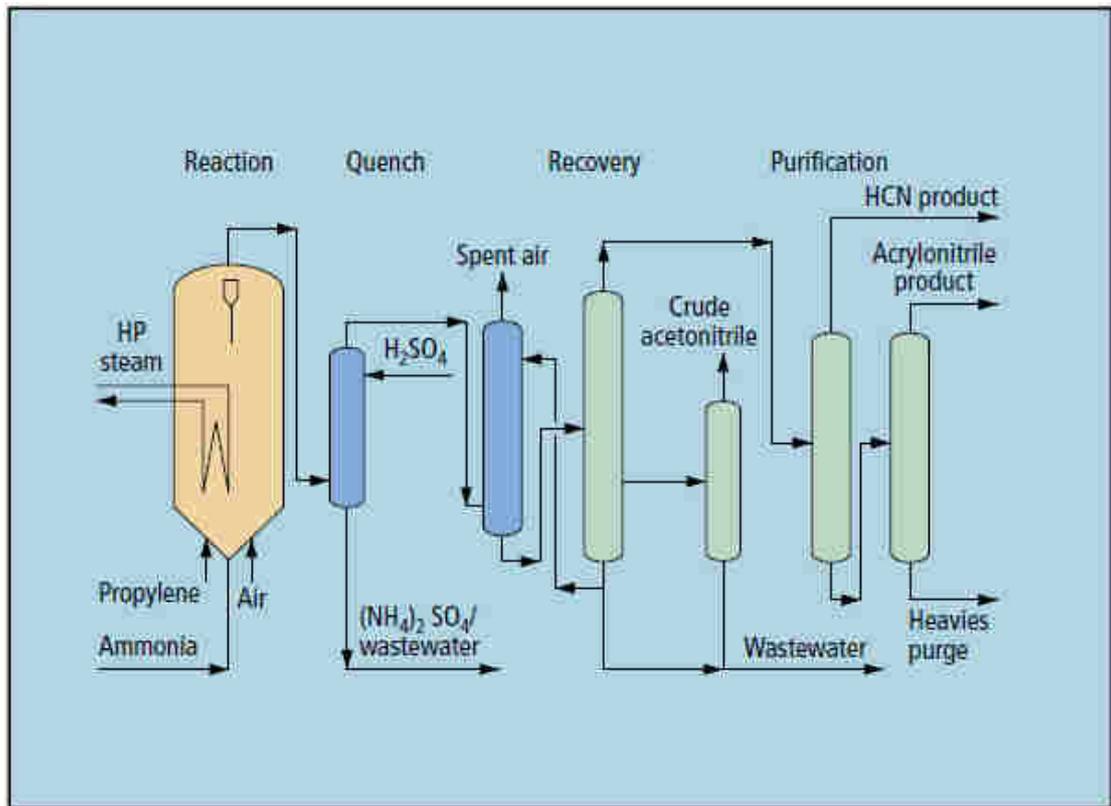
Economics: The conversion of EO to glycols is essentially complete. The reaction not only generates the desired MEG, but also produces DEG and TEG that can be recovered as coproducts. The production of more DEG and TEG may be desirable if the manufacturer has a specific use for these products or if market conditions provide a good price for DEG and TEG relative to MEG. A catalyzed process will produce less heavy glycols. The ability to operate in catalyzed or uncatalyzed mode provides flexibility to the manufacturer to meet changing market demands.

Commercial plants: Since 1954, 18 UCC-designed glycol plants have been started up or are under construction.

Uses:

- 1-Polyester(fibers and films).
- 2-Anti freeze agent.
- 3-Gas drying.
- 4-Manufacturing of plastizers.

7-Acrylonitrile $CH_2 = CHCN$



Application: A process to produce high-purity acrylonitrile and high-purity hydrogen cyanide from propylene, ammonia and air. Recovery of byproduct acetonitrile is optional.

Description: Propylene, ammonia, and air are fed to a fluidized bed reactor to produce acrylonitrile (ACRN) using DuPont's proprietary catalyst system. Other useful products from the reaction are hydrogen cyanide (HCN) and acetonitrile (ACE). The reaction is highly exothermic and heat is recovered from the reactor by producing high-pressure steam. The reactor effluent is quenched and neutralized with a sulfuric solution to remove the excess ammonia.

The product gas from the quench is absorbed with water to recover the ACRN, HCN, and ACE. The aqueous solution of ACRN, HCN, and

ACE is then fractionated and purified into high-quality products. The products' recovery and purification is a highly efficient and low-energy consumption process.

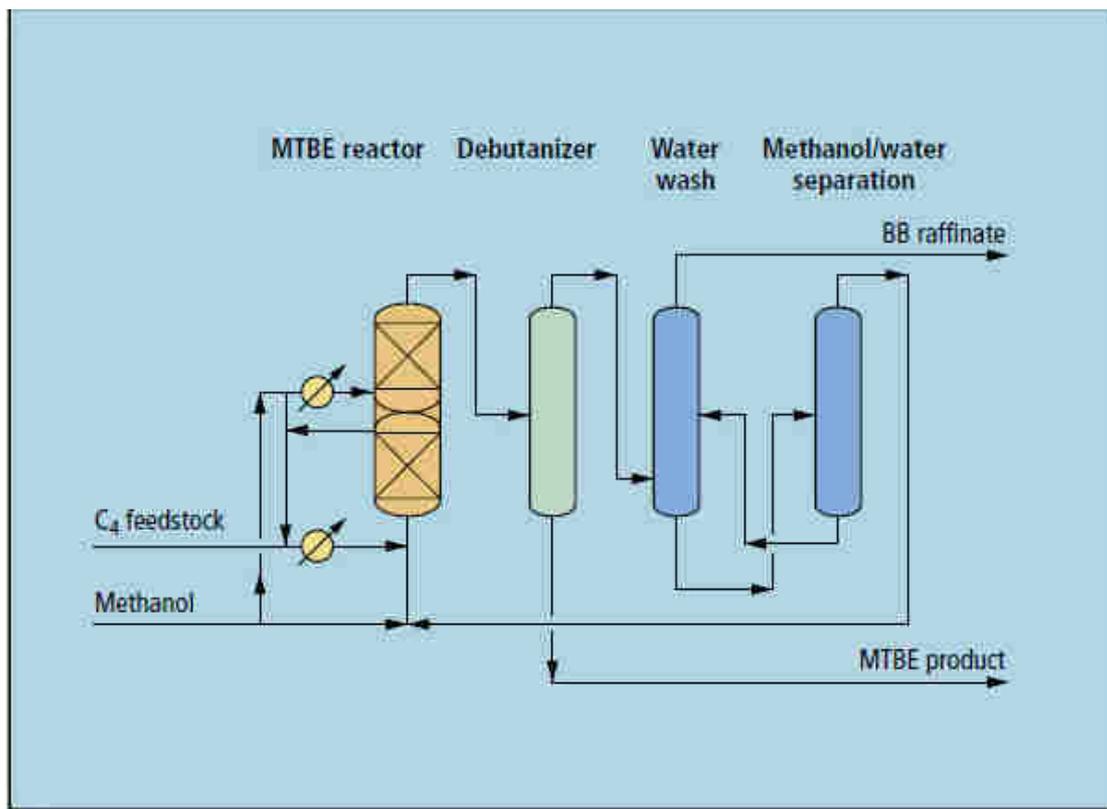
This ACRN technology minimizes the amount of aqueous effluent, a major consideration for all acrylonitrile producers. This ACRN technology is based on a high-activity, high-throughput catalyst. The propylene conversion is 99% with a selectivity of 85% to useful products of ACRN, HCN, and ACE. The DuPont catalyst is a mechanically superior catalyst, resulting in a low catalyst loss. DuPont has developed a Catalyst Bed Management Program (CBMP) to maintain the properties of the catalyst bed inside the reactor at optimal performance throughout the operation. The catalyst properties, the CBMP and proprietary reactor internals provide an optimal performance of the ACRN reactor, resulting in high yields.

With over 30 years of operating experience, DuPont has developed know-how to increase the onstream factor of the plant. This knowhow includes the effective use of inhibitors to reduce the formation of cyanide and nitrile polymers and effective application of an antifoulant system to increase onstream time for equipment.

Commercial plants: DuPont Chemical Solution Enterprise, Beaumont, Texas (200,000 mtpy).

Uses: For production of Acrylic fibers ,flexible plastic ,Rubber And resins.

8-Methyl-Tetra-Butyl-Ether (MTBE) ($(CH_3)_3COCH_3$)



Application: The Uhde (Edeleanu) MTBE process combines methanol and isobutene to produce the high-octane oxygenate—methyl tertiary butyl ether (MTBE).

Feeds: C₄-cuts from steam cracker and FCC units with isobutene contents range from 12% to 30%.

Products: MTBE and other tertiary alkyl ethers are primarily used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency.

Description: The technology features a two-stage reactor system of which the first reactor is operated in the recycle mode. With this method, a slight expansion of the catalyst bed is achieved which ensures very

uniform concentration profiles within the reactor and, most important, avoids hot spot formation. Undesired side reactions, such as the formation of dimethyl ether (DME), are minimized.

The reactor inlet temperature ranges from 45°C at start-of-run to about 60°C at end-of-run conditions. One important factor of the two stage system is that the catalyst may be replaced in each reactor separately, without shutting down the MTBE unit.

The catalyst used in this process is a cation-exchange resin and is available from several catalyst manufacturers. Isobutene conversions of 97% are typical for FCC feedstocks. Higher conversions are attainable when processing steam-cracker C4 cuts that contain isobutene concentrations of 25%.

MTBE is recovered as the bottoms product of the distillation unit. The methanol-rich C4 distillate is sent to the methanol-recovery section. Water is used to extract excess methanol and recycle it back to process. The isobutene-depleted C4 stream may be sent to a raffinate stripper or to a molsieve-based unit to remove other oxygenates such as DME, MTBE, methanol and tert-butanol.

Very high isobutene conversion, in excess of 99%, can be achieved through a debutanizer column with structured packings containing additional catalyst. This reactive distillation technique is particularly suited when the raffinate-stream from the MTBE unit will be used to produce a high-purity butene-1 product.

For a C4 cut containing 22% isobutene, the isobutene conversion may exceed 98% at a selectivity for MTBE of 99.5%.

Utility requirements, (C4 feed containing 21% isobutene; per metric ton of MTBE):

Steam, LP, kg	900
Steam, MP, kg	100

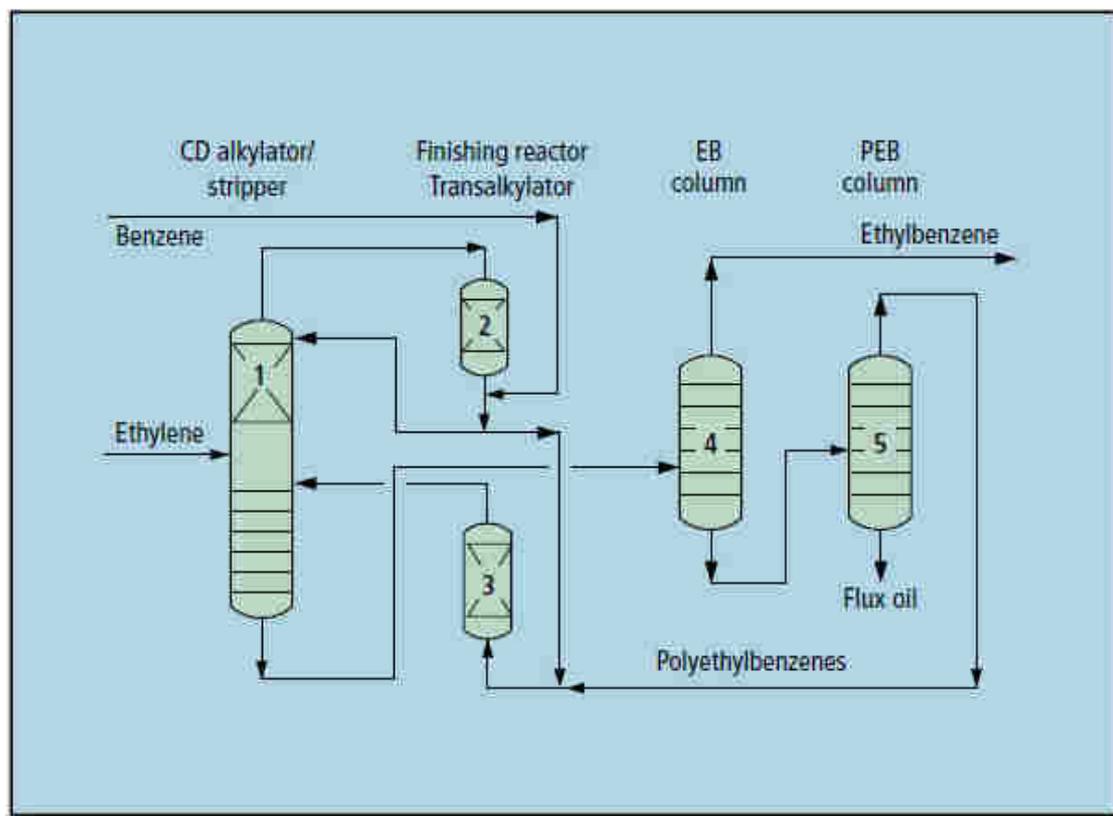
Electricity, kWh 35

Water, cooling, m³ 15

Commercial plants: The Uhde (Edeleanu) proprietary MTBE process has been successfully applied in five refineries. The accumulated licensed capacity exceeds 1 MMtpy.

Uses: Octane booster.

9-Ethylbenzene C₆H₅CH₂CH₃



Application: Advanced technology to produce high-purity ethylbenzene (EB) alkylating benzene with ethylene using patented catalytic distillation (CD) technology. The CDTECH EB process uses a specially formulated zeolite alkylation catalyst packaged in a proprietary

CD structure. The process is able to handle a wide range in ethylene feed composition— from 10% to 100% ethylene.

Description: The CD alkylator stripper (1) operates as a distillation column. Alkylation and distillation occur in the alkylator in the presence of a zeolite catalyst packaged in patented structured packing. Unreacted ethylene and benzene vapor from the alkylator top are condensed and fed to the finishing reactor (2) where the remaining ethylene reacts over zeolite catalyst pellets. The alkylator stripper bottoms is fractionated (4, 5) into EB product, polyethylbenzenes and flux oil. The polyethylbenzenes are transalkylated with benzene over zeolite catalyst pellets in the transalkylator (3) to produce additional EB. The ethylene can be polymer grade or, with only minor differences in the process scheme, dilute ethylene containing as little as 10 mol% ethylene as in FCC offgas. Reactors are designed for 3 to 6 years of uninterrupted runlength. The process does not produce any hazardous effluent. Low operating temperatures allow using carbon steel for all equipment.

Yields and product quality: Both the alkylation and trans-alkylation reactions are highly selective—producing few byproducts. The EB product has high purity (99.9 wt% minimum) and is suitable for styrene-unit feed. Xylene make is less than 10 ppm. The process has an overall yield of 99.7%.

Economics: The EB process features consistent product yields, highproduct purity, low-energy consumption, low investment cost and easy, reliable operation.

Investment (500,000 tpy, ISBL Gulf Coast), US\$: 17 million

Raw materials and utilities, based on one metric ton of EB:

Ethylene, kg	265
Benzene, kg	738

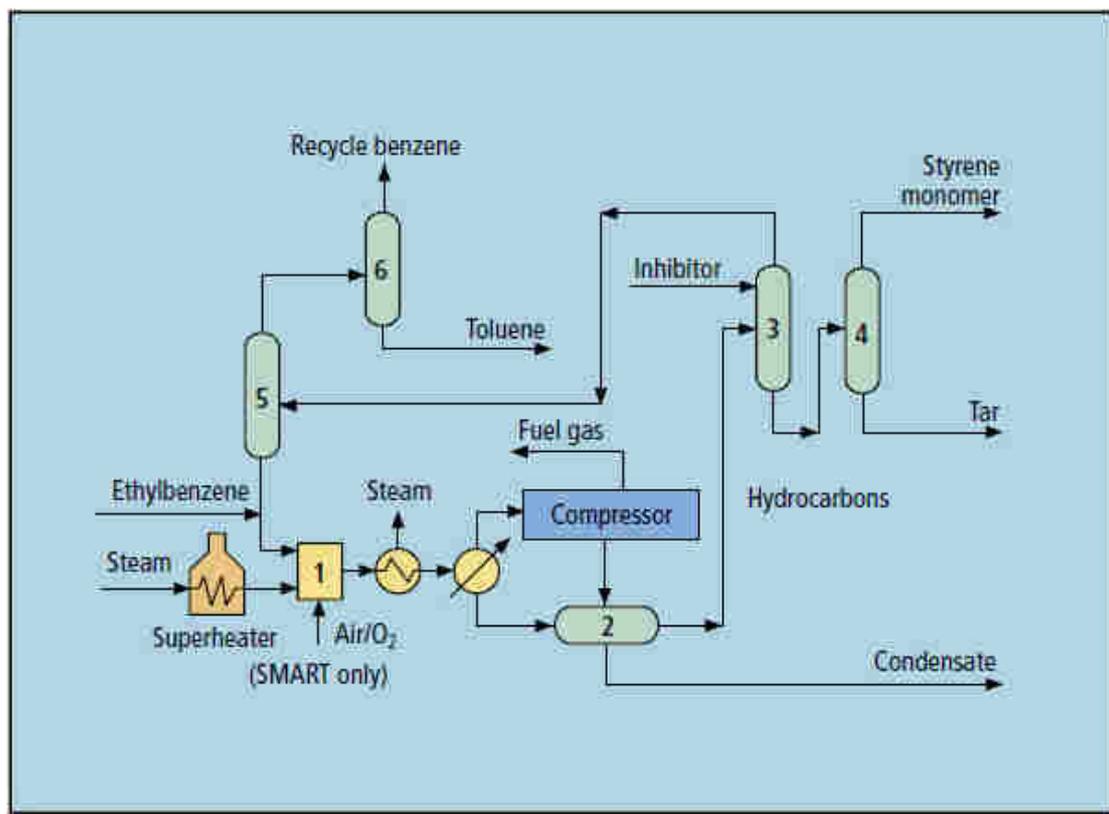
Electricity, kWh	20
Water, cooling m ³	3
Steam, mtons (export)	1.3
Hot oil, 10 ⁶ kcal	0.6

Commercial plants: Three commercial plants are in operation in Argentina and Canada with capacities from 140,000 to 816,000 mtpy. They process ethylene feedstocks with purities ranging from 75% ethylene to polymer-grade ethylene. An 850,000-mtpy unit using dilute ethylene is currently under construction.

Uses:

0.5 consumption of B:in EB production: which is used in production of styrene.

10-Styrene $C_6H_5CH = CH_2$



EB

S

Application: To produce polymer-grade styrene monomer (SM) by dehydrogenating ethylbenzene (EB) to form styrene using the Lummus/UOP “Classic” styrene process for new plants and the Lummus/UOP SMART process for revamps involving plant capacity expansion.

Description: In the Classic SM process, EB is catalytically dehydrogenated to styrene in the presence of steam. The vapor phase reaction is carried out at high temperature under vacuum. The EB (fresh and recycle) is combined with superheated steam, and the mixture is dehydrogenated in a multistage reactor system (1). A heater reheats the process gas between stages. Reactor effluents are cooled to recover waste heat and condense the hydrocarbons and steam. Uncondensed offgas—containing mostly hydrogen— is compressed and is used as fuel. Condensed hydrocarbons from an oil/water separator (2) are sent to the distillation section. Process condensate is stripped to remove dissolved aromatics.

A fractionation train (3,4) separates high-purity styrene product, unconverted EB, which is recycled, and the relatively minor byproduct tar, which is used as fuel. Toluene is produced (5,6) as a minor byproduct and benzene (6) is normally recycled to the upstream EB process.

Typical SM product purity ranges from 99.85% to 99.95%. The process provides high-product yield due to a unique combination of catalyst and operating conditions used in the reactors and the use of a highly effective polymerization inhibitor in the fractionation columns.

The SMART SM process is the same as Classic SM except that oxidative reheat technology is used between the dehydrogenation stages of the multistage reactor system (1). Specially designed reactors are used

to achieve the oxidation and dehydrogenation reactions. In oxidative reheat, oxygen is introduced to oxidize part of the hydrogen produced over a proprietary catalyst to reheat the process gas and to remove the equilibrium constraint for the dehydrogenation reaction. The process achieves up to about 80% EB conversion per pass, eliminates the costly interstage reheater, and reduces superheated steam requirements. For existing SM producers, revamping to SMART SM may be the most cost-effective route to increased capacity.

Economics: (Classic) 500,000 mtpy, ISBL, US Gulf Coast:

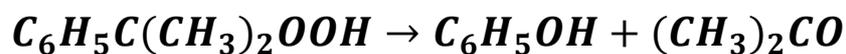
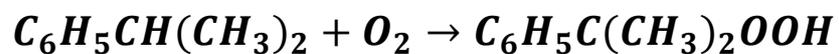
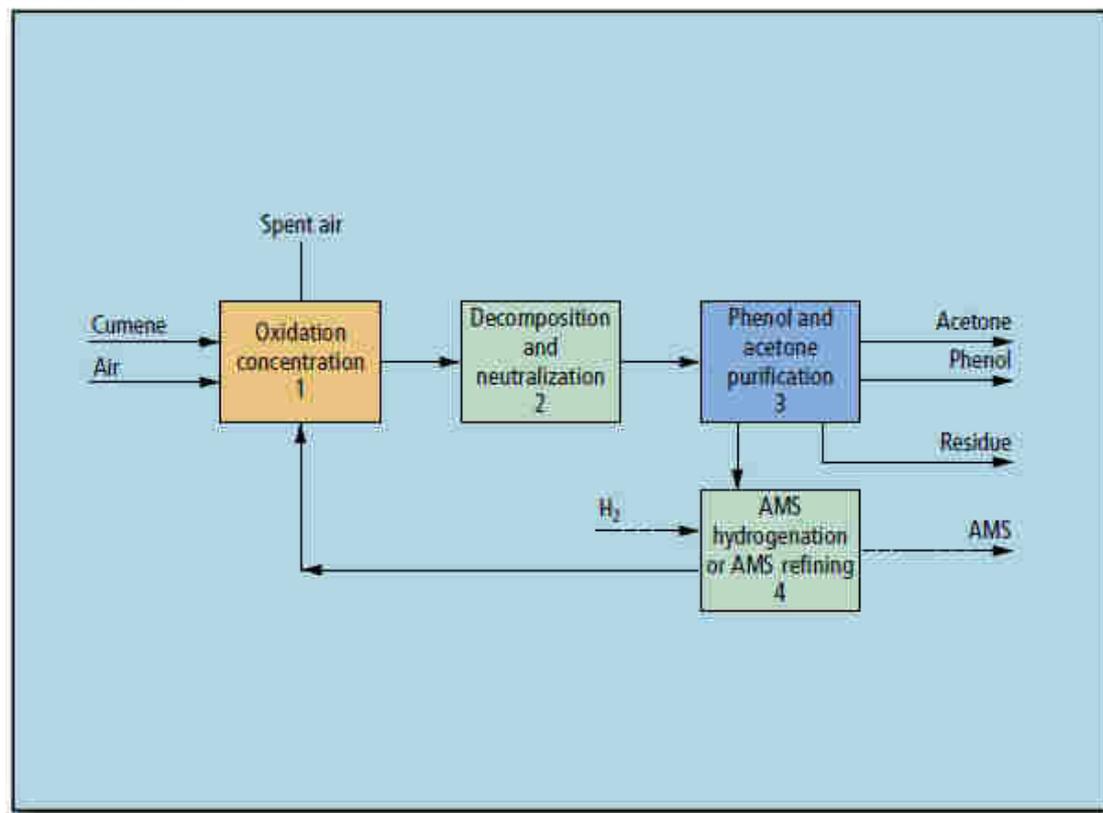
Investment, US\$ million 78

Ethylbenzene, ton/ton SM 1.055

Utilities, US\$/mton SM 29

Commercial plants: Currently, 36 operating plants incorporate the Lummus / UOP Classic Styrene technology. Seven operating facilities are using the SMART process technology. Many future units using the SMART process are expected to be retrofits of conventional units, since the technology is ideally suited for revamps.

11-Phenol



Phenol acetone

Application: The Sunoco/UOP phenol process produces high-quality phenol and acetone by liquid-phase peroxidation of cumene.

Description: Key process steps:

Oxidation and concentration (1): Cumene is oxidized to cumene hydroperoxide (CHP). A small amount of dimethylphenylcarbinol (DMPC) is also formed, but low-pressure and low-temperature oxidation results in very high selectivity of CHP. CHP is then concentrated and unreacted cumene is recycled back to the oxidation section.

Decomposition and neutralization (2): CHP is decomposed to phenol and acetone, accompanied by dehydration of DMPC to

alphanethylstyrene (AMS), catalyzed by mineral acid. This unique design achieves a very high selectivity to phenol, acetone and AMS without using recycle acetone. The high total yields from oxidation and decomposition combine to achieve 1.31 wt cumene/wt phenol without tar cracking. Decomposed catalyst is neutralized.

Phenol and acetone purification (3): Phenol and acetone are separated and purified. A small amount of byproduct is rejected as heavy residue.

AMS hydrogenation or AMS refining (4): AMS is hydrogenated back to cumene and recycled to oxidation, or AMS is refined for sale. Cumene peroxidation is the preferred route to phenol, accounting for more than 90% of world production. The Sunoco/UOP Phenol process features low feedstock consumption (1.31 wt cumene/wt phenol) without tar cracking, avoiding the expense and impurities associated with tar cracking. High phenol and acetone product qualities are achieved through a combination of minimizing impurity formation and efficient purification techniques. Optimized design results in low investment cost along with low utility and chemicals consumption for low variable cost of production. Design options for byproduct alphanethylstyrene (AMS) allow producers to select the best alternative for their market: hydrogenate AMS back to cumene, or refine AMS for sale. No acetone recycle to the decomposition (cleavage) section, simplified neutralization, and no tar cracking make the Sunoco/UOP Phenol process easier to operate.

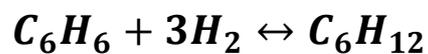
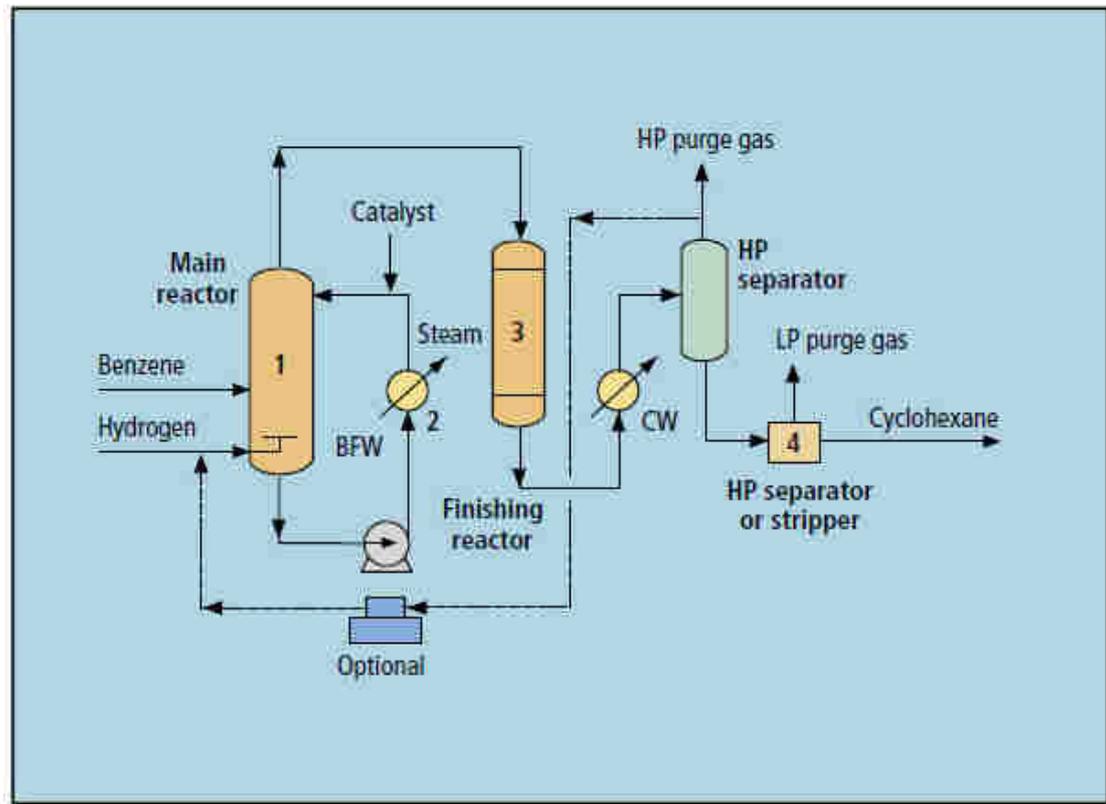
Commercial plants: The Sunoco/UOP Phenol process is currently used in 11 plants worldwide having total phenol capacity of more than 1

million mtpy. Four additional process units, with a total design capacity of 600,000 mtpy, are in design and construction.

Uses: Raw materials or intermediate for production of:

- 1- Phenol-formaldehyde resins
- 2- Bisphenol(for production of epoxy)
- 3-Caprolactum(for production of Nylon6 monomer)
- 4-Adipic acid (for production of Nylon 66 monomer)
- 5- Salicylic acid(Aspirin production)
- 6-Phenol alkyl (Rubber chemical) or(production of Detergent).

12-Cyclohexane



Application: Produce high-purity cyclohexane by liquid-phase catalytic hydrogenation of benzene.

Description: The main reactor (1) converts essentially all the feed isothermally in the liquid phase at a thermodynamically-favorable low temperature using a continuously-injected soluble catalyst. The catalyst's high activity allows use of low hydrogen partial pressure, which results in fewer side reactions, e.g., isomerization or hydrocracking. The heat of reaction vaporizes cyclohexane product and, using pumparound circulation through an exchanger, also generates steam (2). With the heat of reaction being immediately removed by vaporization, accurate temperature control is assured. A vapor-phase fixed-bed finishing reactor (3) completes the catalytic hydrogenation of any residual benzene. This step reduces residual benzene in the cyclohexane product to very low levels. Depending on the purity of the hydrogen make-up gas, the stabilization section includes either an LP separator (4) or a small stabilizer to remove the light ends.

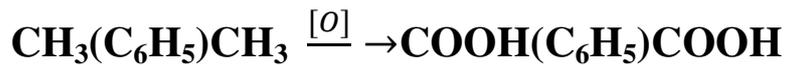
A prime advantage of the liquid-phase process is its substantially lower cost compared to vapor phase processes: investment is particularly low because a single, inexpensive main reactor chamber is used compared to multiple-bed or tubular reactors used in vapor phase processes. Quench gas and unreacted benzene recycles are not necessary and better heat recovery generates both the cyclohexane vapor for the finishing step and a greater amount of steam. These advantages result in lower investment and operating costs. Operational flexibility and reliability are excellent; changes in feedstock quality and flows are easily handled. Should the catalyst be deactivated by feed quality upsets, fresh catalyst can be injected without shutting down.

Yield: 1.075 kg of cyclohexane is produced from 1 kg of benzene.

Economics: Basis: 200,000-tpy cyclohexane complex, ISBL 2005 Gulf Coast location with PSA hydrogen is US\$8 million. Catalyst cost is US\$ 1.2/metric ton of product.

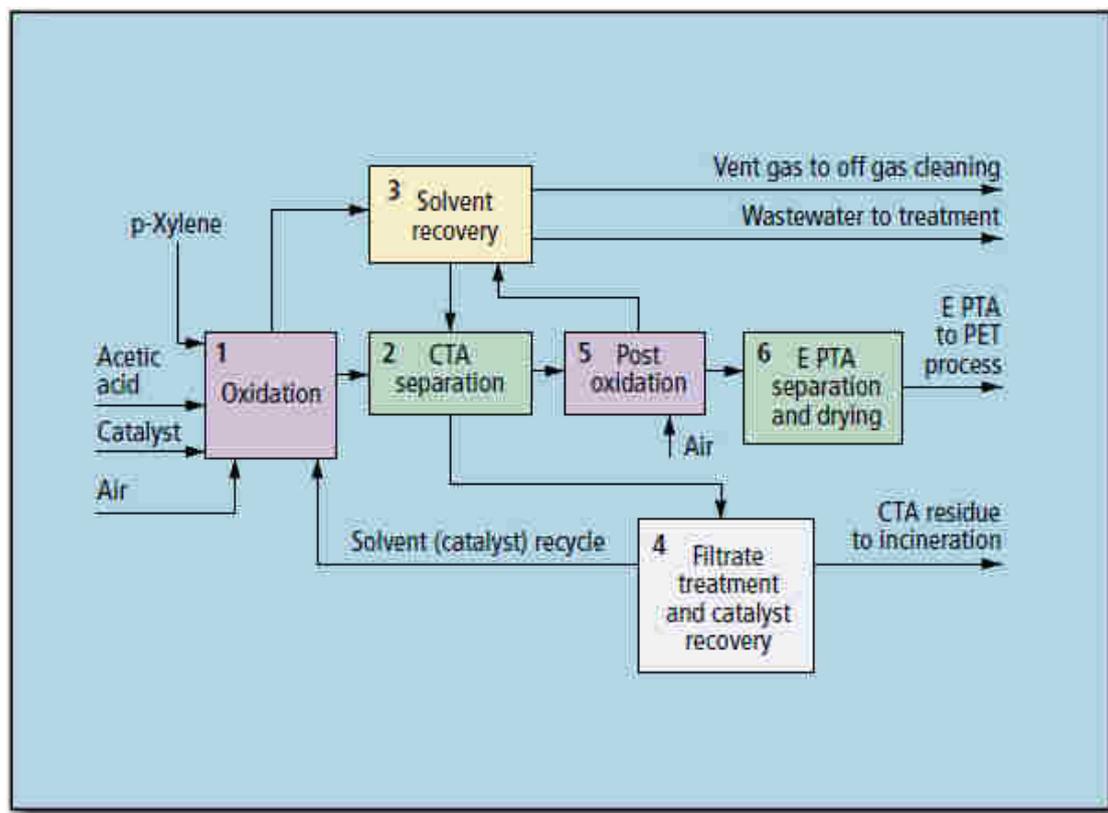
Commercial plants: Thirty-three cyclohexane units have been licensed.

13-Terephthalic acid (EPTA) $\text{COOH}(\text{C}_6\text{H}_5)\text{COOH}$



P-xylene

TPA



Application: EPTA (Eastman polymer-grade terephthalic acid) is an excellent raw material for engineering plastics and packaging materials, bottles, other food containers including hot fill, as well as films. The process is proven to be suitable for the production of all kinds of polyester fibers and containers without limitation, at international first-grade quality.

Description: The general flow diagram to produce E PTA using Eastman Chemical's proprietary process comprises three different main sections — crude terephthalic acid (CTA), polymer-grade terephthalic acid (EPTA) and catalyst recovery.

Crude terephthalic acid (1,2,3): CTA is produced by the catalytic oxidation of p-xylene with air in the liquid phase using acetic acid as a solvent (1). The feed mix— p-xylene, solvent and catalyst— together with compressed air is continuously fed to the reactor, which is a bubble-column oxidizer. It operates at moderate temperature and offers an extremely high yield. The oxidizer product is known as crude terephthalic acid (CTA) due to the high level of impurities contained. Many impurities are fairly soluble in the solvent. In the CTA separation step (2), impurities can be effectively removed from the product by exchanging the reaction liquor with lean solvent from the solvent recovery system. The reactor overhead vapor, mainly reaction water, acetic acid and nitrogen is sent to the solvent-recovery system (3), where water is separated from the solvent by distillation. After recovering its energy, the offgas is sent to a regenerative thermal oxidation unit for further cleaning.

Polymer-grade terephthalic acid (5,6): The crude acid is purified to obtain EPTA in a post-oxidation step, at elevated temperature conditions. The post oxidizers serve as reactors to increase conversion of the partially oxidized compounds to terephthalic acid. The level of 4-carboxy benzaldehyde (4-CBA) ptoluic acid (p-TA) the main impurities in terephthalic acid is significantly lowered. In a final step (6), E PTA is separated from the solvent and dried for further processing in the polyester-production facilities.

Catalyst recovery (4): After exchanging the liquor in the CTA separation, the suspended solids are separated and removed as CTA residue, which can be burned in a fluidized-bed incinerator or, if

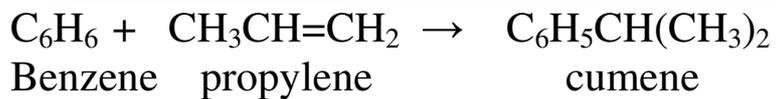
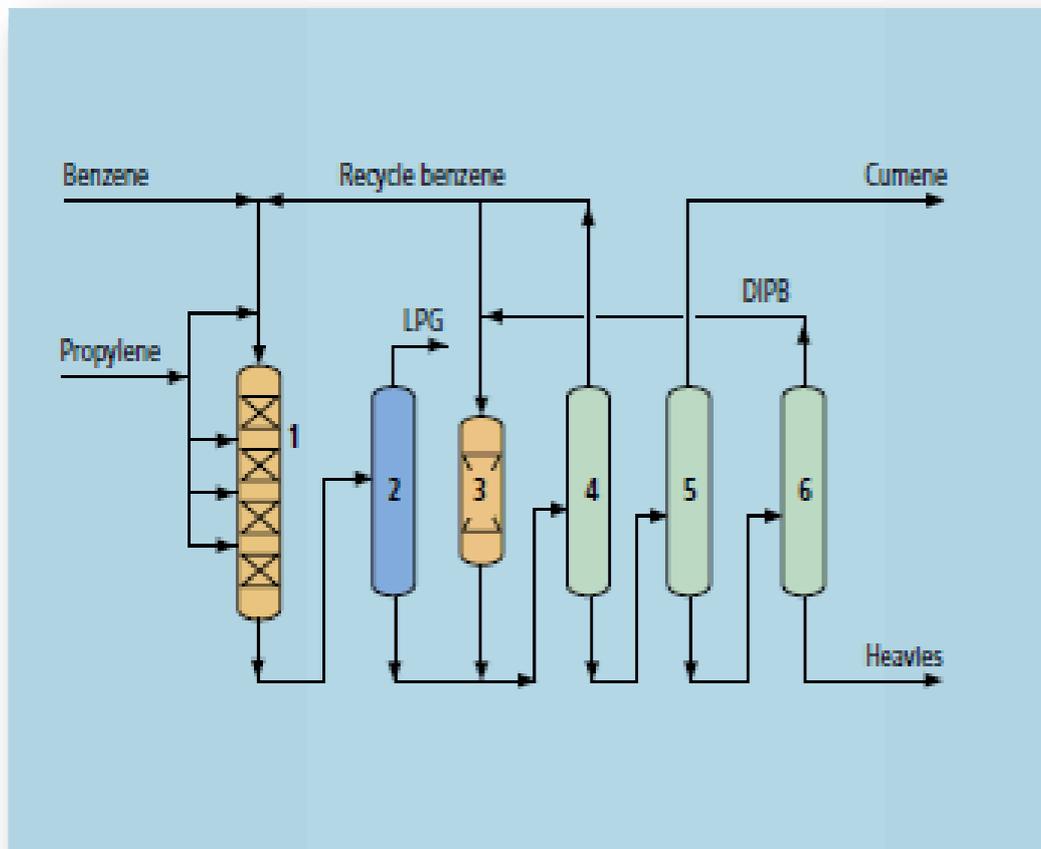
desirable, used as land fill. The soluble impurities are removed from the filtrate within the filtrate treatment section, and the dissolved catalyst is recycled.

Economics: The advanced Eastman E PTA technology uses fewer processing steps. In combination with the outstanding mild-oxidation technology, this technology leads to considerable capital cost savings and lower production cost than in other technologies.

Commercial plants: Commercial plants are operating in the US, Europe and Asia Pacific.

The latest plant with a capacity of 660,000 tpy for Zhejiang Hualian Sunshine Petro-Chemical Co. Ltd. in Shaoxing, China, is under construction and will be started up in April 2005, increasing the worldwide capacity to 2.1 million tpy.

14- Cumene



Application: To produce high-quality cumene (isopropylbenzene) by alkylating benzene with propylene (typically refinery or chemical grade) using liquid-phase Q-Max process based on zeolitic catalyst technology.

Description: Benzene is alkylated to cumene over a zeolite catalyst in a fixed-bed, liquid-phase reactor. Fresh benzene is combined with recycle benzene and fed to the alkylation reactor (1). The benzene feed flows in series through the beds, while fresh propylene feed is distributed equally between the beds. This reaction is highly exothermic, and heat is removed by recycling a

portion of reactor effluent to the reactor inlet and injecting cooled reactor effluent between the beds. In the fractionation section, propane that accompanies the propylene feedstock is recovered as LPG product from the overhead of the depropanizer column (2), unreacted benzene is recovered from the overhead of the benzene column (4) and cumene product is taken as overhead from the cumene column (5). Di-isopropylbenzene (DIPB) is recovered in the overhead of the DIPB column (6) and recycled to the transalkylation reactor (3) where it is transalkylated with benzene over a second zeolite catalyst to produce additional cumene. A small quantity of heavy byproduct is recovered from the bottom of the DIPB column(6) and is typically blended to fuel oil. The cumene product has a high purity (99.96 – 99.97 wt%), and cumene yields of 99.7 wt% and higher are achieved. The zeolite catalyst is noncorrosive and operates at mild conditions; thus, carbon-steel construction is possible. Catalyst cycle lengths are two years and longer. The catalyst is fully regenerable for an ultimate catalyst life of six years and longer. Existing plants that use SPA or AlCl₃ catalyst can be revamped to gain the advantages of Q-Max cumene technology while increasing plant capacity

Economics: Basis: ISBL US Gulf Coast

Investment, US\$/tpy 40 – 90

Raw materials & utilities, per metric ton of cumene

Propylene, tons 0.35

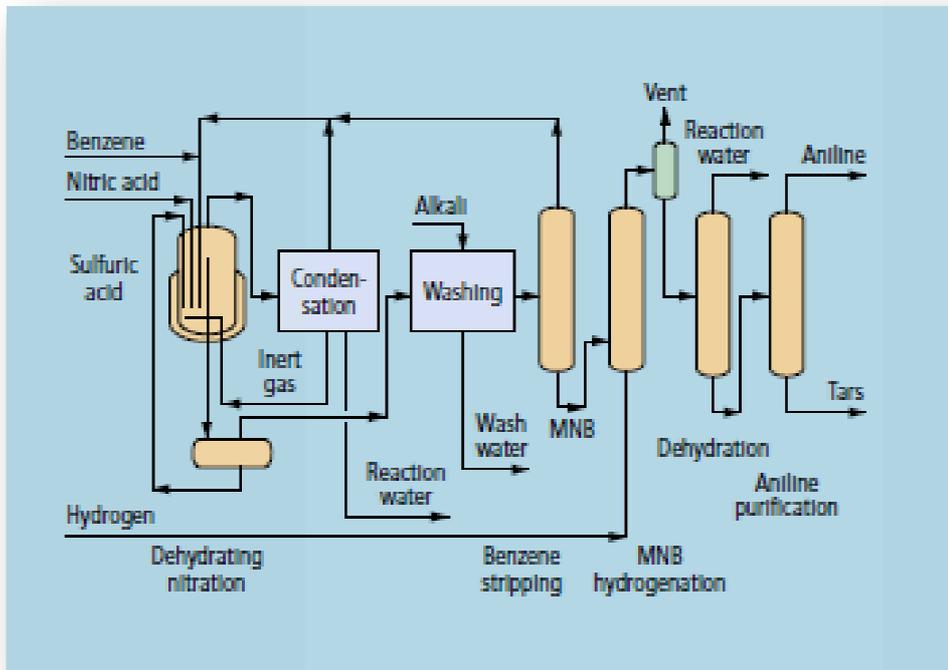
Benzene, tons 0.66

Electricity, kW 12

Steam, tons (import) 0.7

Water, cooling, m³ 3

The Q-Max design is typically tailored to provide optimal utility advantage for the plant site, such as minimizing heat input for standalone operation or recovering heat as steam for usage in a nearby phenol plant.

15- Aniline $C_6H_5NH_2$ 

Application: A process for the production of high-quality aniline from benzene and nitric acid.

Description: Aniline is produced by the nitration of benzene with nitric acid to mononitrobenzene (MNB) which is subsequently hydrogenated to aniline. In the DuPont/KBR process, benzene is nitrated with mixed acid (nitric and sulfuric) at high efficiency to produce mono nitrobenzene(MNB) in the unique dehydrating nitration (DHN) system.

The DHN system uses an inert gas to remove the water of nitration from the reaction mixture, thus eliminating the energy-intensive and high-cost sulfuric acid concentration system.

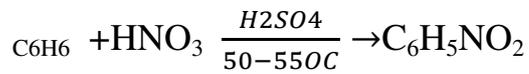
As the inert gas passes through the system, it becomes humidified, removing the water of reaction from the reaction mixture. Most of the energy required for the gas humidification comes from the heat of nitration. The wet gas is condensed and the inert gas is recycled to the nitrator. The condensed organic phase is recycled to the nitrator while the aqueous phase is sent to effluent treatment. The reaction mixture is phase separated and the sulfuric acid is returned to the nitrator. The crude MNB is washed to remove residual acid and the impurities formed during the nitration reaction. The product is then distilled and residual benzene is recovered and recycled. Purified MNB is fed, together with hydrogen, into a liquid phase plug-flow hydrogenation reactor that contains a DuPont proprietary catalyst. The supported noble metal catalyst has a high selectivity and the MNB conversion per pass is 100%.

The reaction conditions are optimized to achieve essentially quantitative yields and the reactor effluent is MNB-free. The reactor product is sent to a dehydration column to remove the water of reaction followed by a purification column to produce high-quality aniline product

Commercial plants: DuPont produces aniline using this technology for the merchant market with a total production capacity of 160,000 tpy at a plant located in Beaumont, Texas. In addition, DuPont's aniline technology is used in three commercial units and one new license was awarded in 2004 with a total aniline capacity of 300,000 tpy.

16-Nitrobenzene $C_6H_5NO_2$

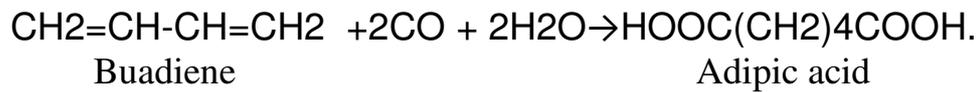
Raw materials: Benzene, nitric acid, sulphuric acid (cata.)



Reaction at liquid phase, Yield: 95-98%

17-Adipic acid $COOH(CH_2)_4COOH$

Raw materials: Butadiene, CO & H₂O.

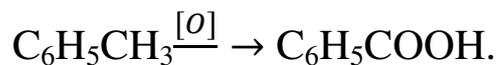


T=220°C P=75 atm. Cata: RdCl₂/CH₃I Yield: 49%

Uses: for production of Nylon 66 directly or through Hexamethyldiamine HMDA

18-Benzoic acid C_6H_5COOH

Raw materials: Toluene, oxygen



Toluene Benzoic acid

Oxidation of toluene in liquid phase

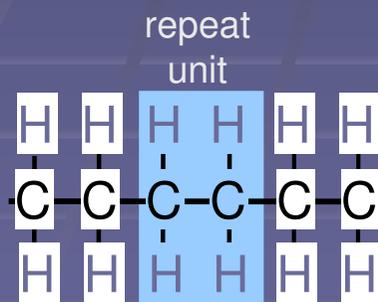
Cata.: Cobalt salt at T=165°C.
or Cobalt bromide at T=140-165°C
P=27 atm

Polymers

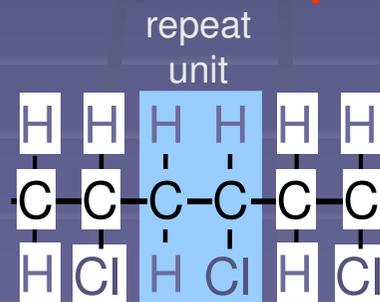
What is a polymer?

Very Large molecules structures chain-like in nature.

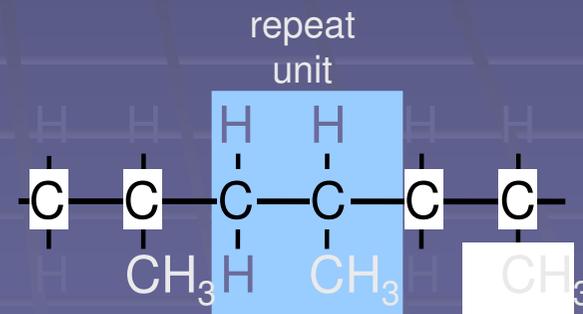
Poly **mer**
many **repeat unit**



Polyethylene (PE)



Polyvinyl chloride (PVC)



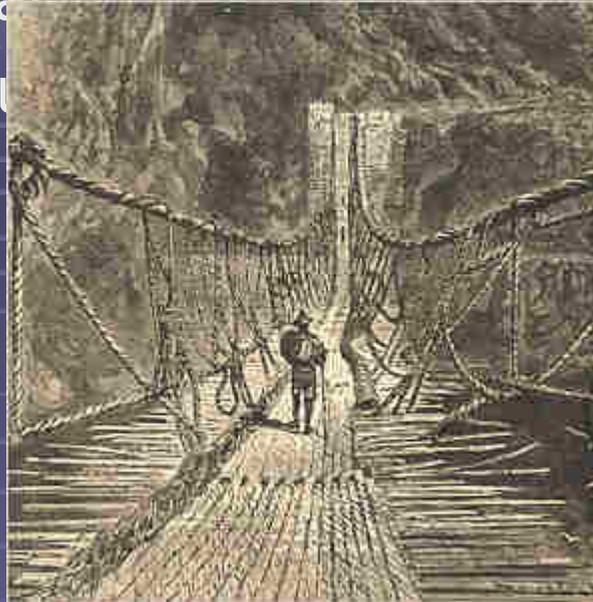
Polypropylene (PP)

Adapted from Fig. 14.2, *Callister 7e*.

4.1 Ancient Polymers

Originally natural
polymers were used

- Wood
- Rubber
- Cotton
- Wool
- Leather
- Silk



Noah's pitch

Genesis 6:14 "...and cover it inside and outside with pitch."

Oldest known use:

Rubber balls used by

Noah used pitch (a

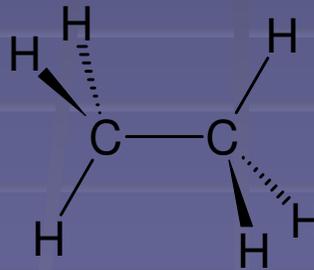


gum based resins
extracted from pine
trees

Polymer Composition

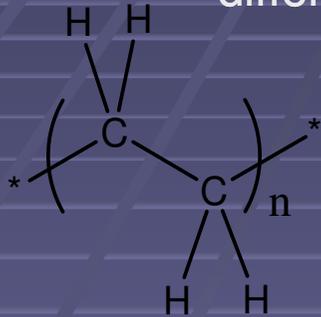
Most polymers are hydrocarbons
– i.e. made up of H and C

- **Saturated hydrocarbons**
 - Each carbon bonded to four other atoms

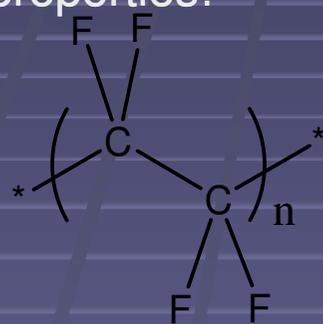


Polymer chemistry

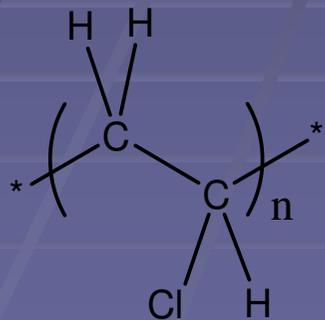
- In polyethylene (PE) synthesis, the monomer is ethylene
- Turns out one can use many different monomers
 - Different functional groups/chemical composition – polymers have very different properties!



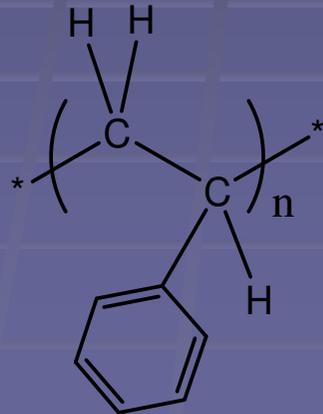
poly(ethylene)
(PE)



poly(tetrafluoroethylene)
(PTFE, teflon)

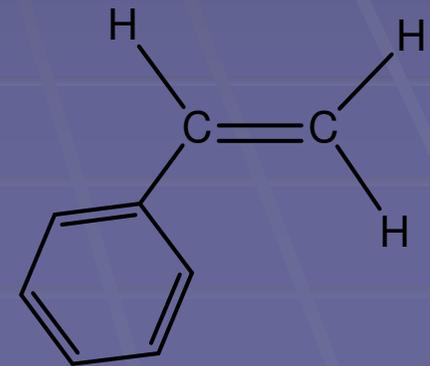
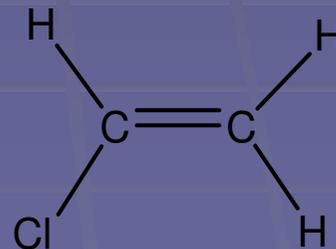
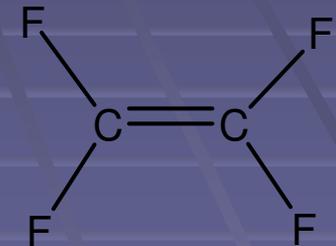
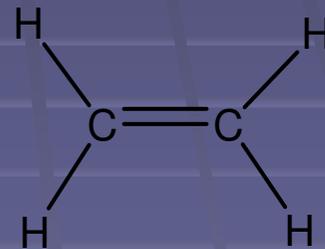


poly(vinylchloride)
(PVC)



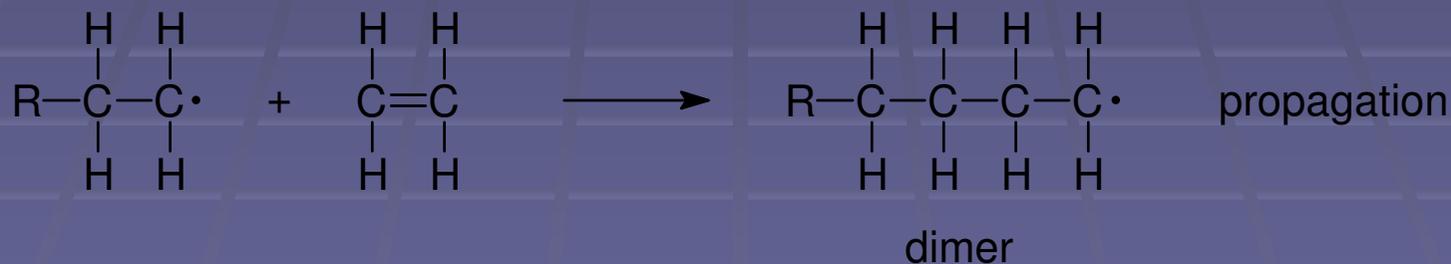
poly(styrene)
(PS)

Monomers

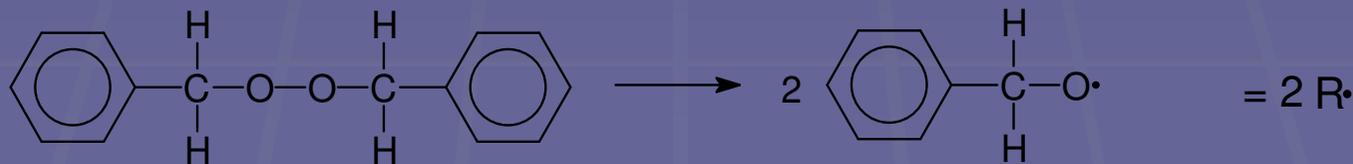


Chemistry of Polymers

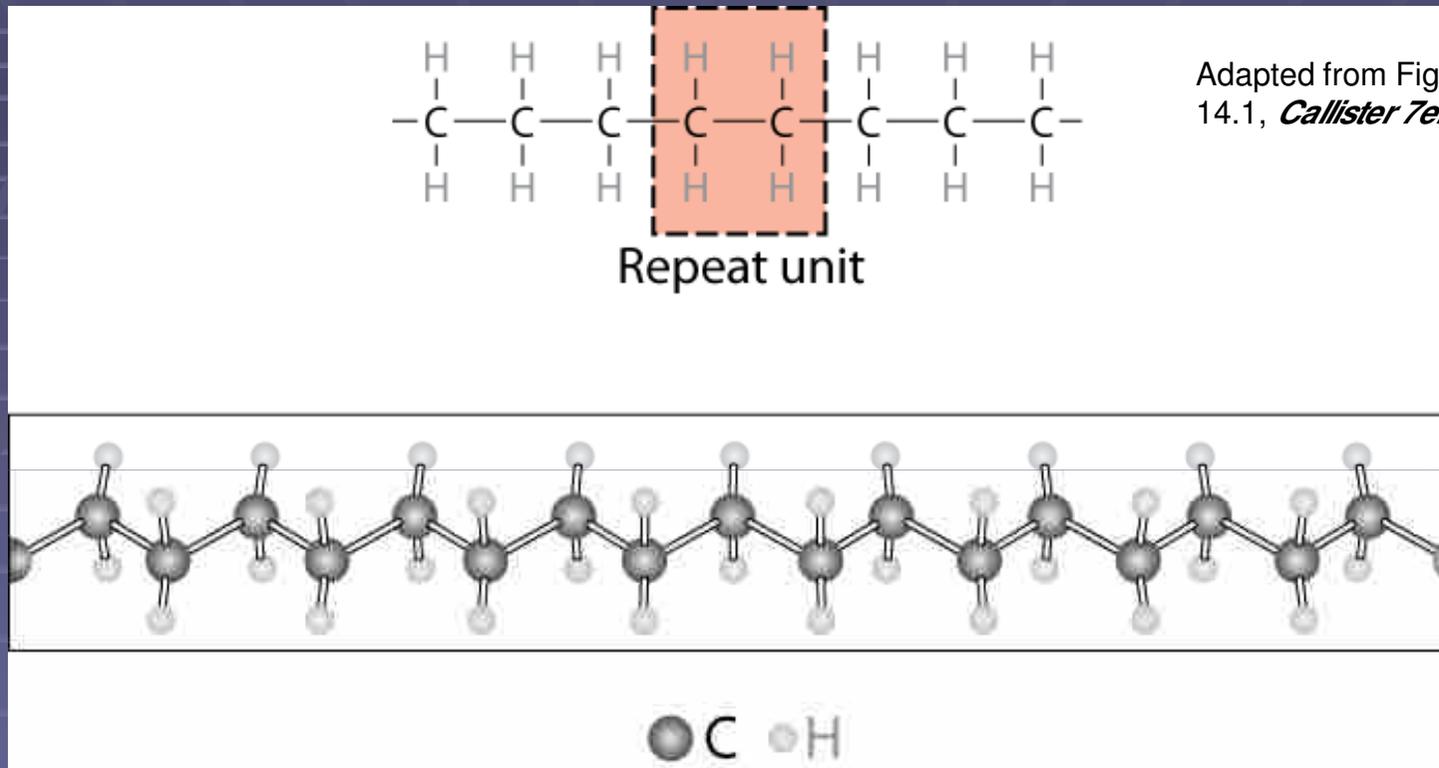
- Free radical polymerization



- Initiator: example - benzoyl peroxide



Chemistry of Polymers



Note: polyethylene is just a long HC
- paraffin is short polyethylene

Bulk or Commodity Polymers

Table 14.3 A Listing of Repeat Units for Polymeric Materials

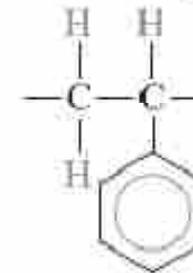
<i>Polymer</i>	<i>Repeat Unit</i>
 Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array}$
 Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{Cl} \end{array}$
 Polytetrafluoroethylene (PTFE)	$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array}$
 Polypropylene (PP)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array}$

Polymer

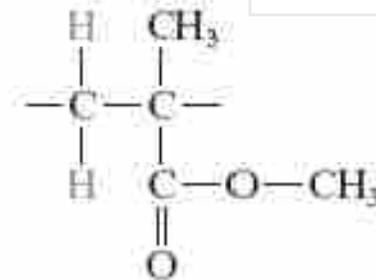
Repeat Unit



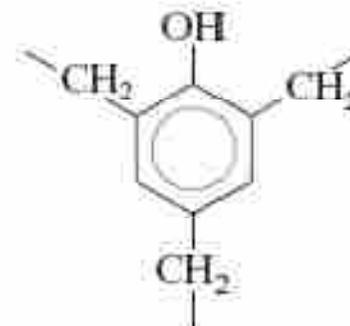
Polystyrene (PS)



Poly(methyl methacrylate) (PMMA)



Phenol-formaldehyde (Bakelite)



Polymer



Poly(hexamethylene adipamide) (nylon 6,6)

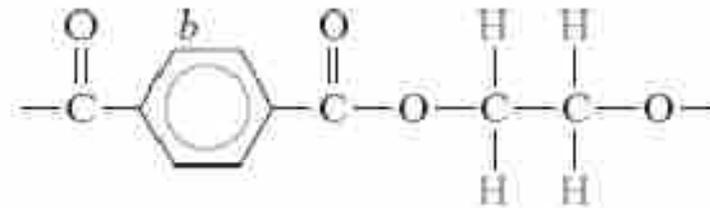
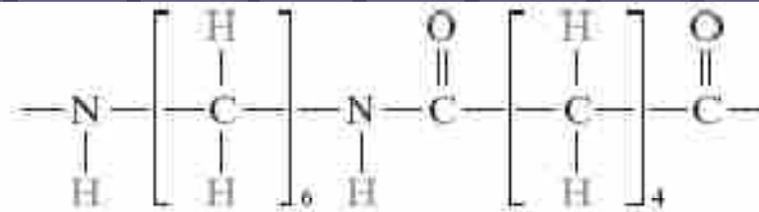


Poly(ethylene terephthalate) (PET, a polyester)



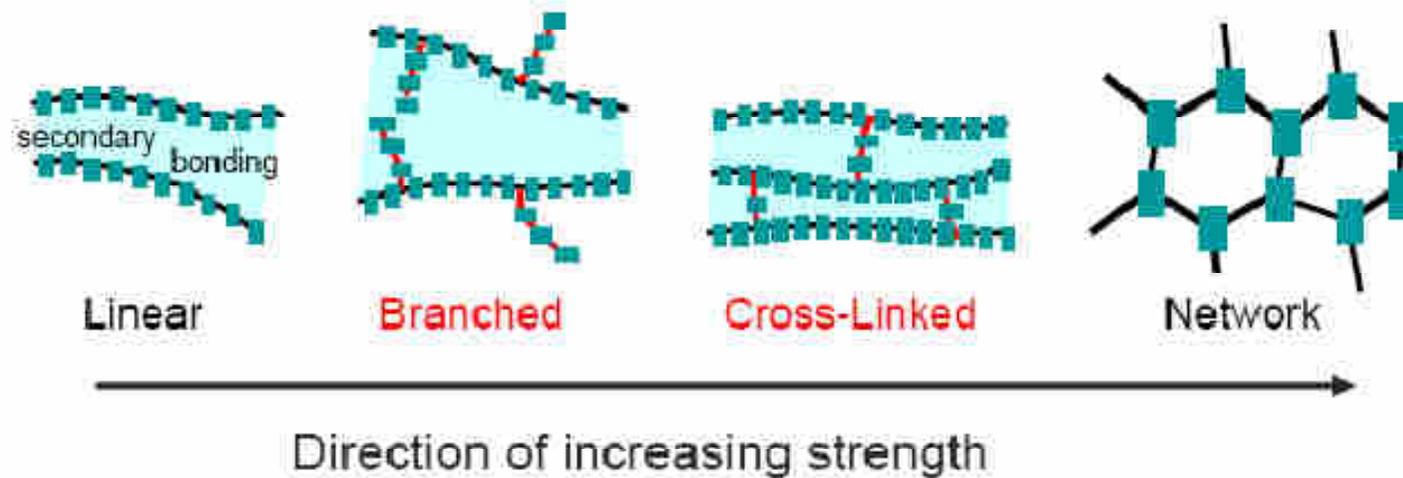
Polycarbonate (PC)

Repeat Unit



Molecular Structures

- Covalent **chain** configurations and strength:



Adapted from Fig. 14.7, Callister 7e.



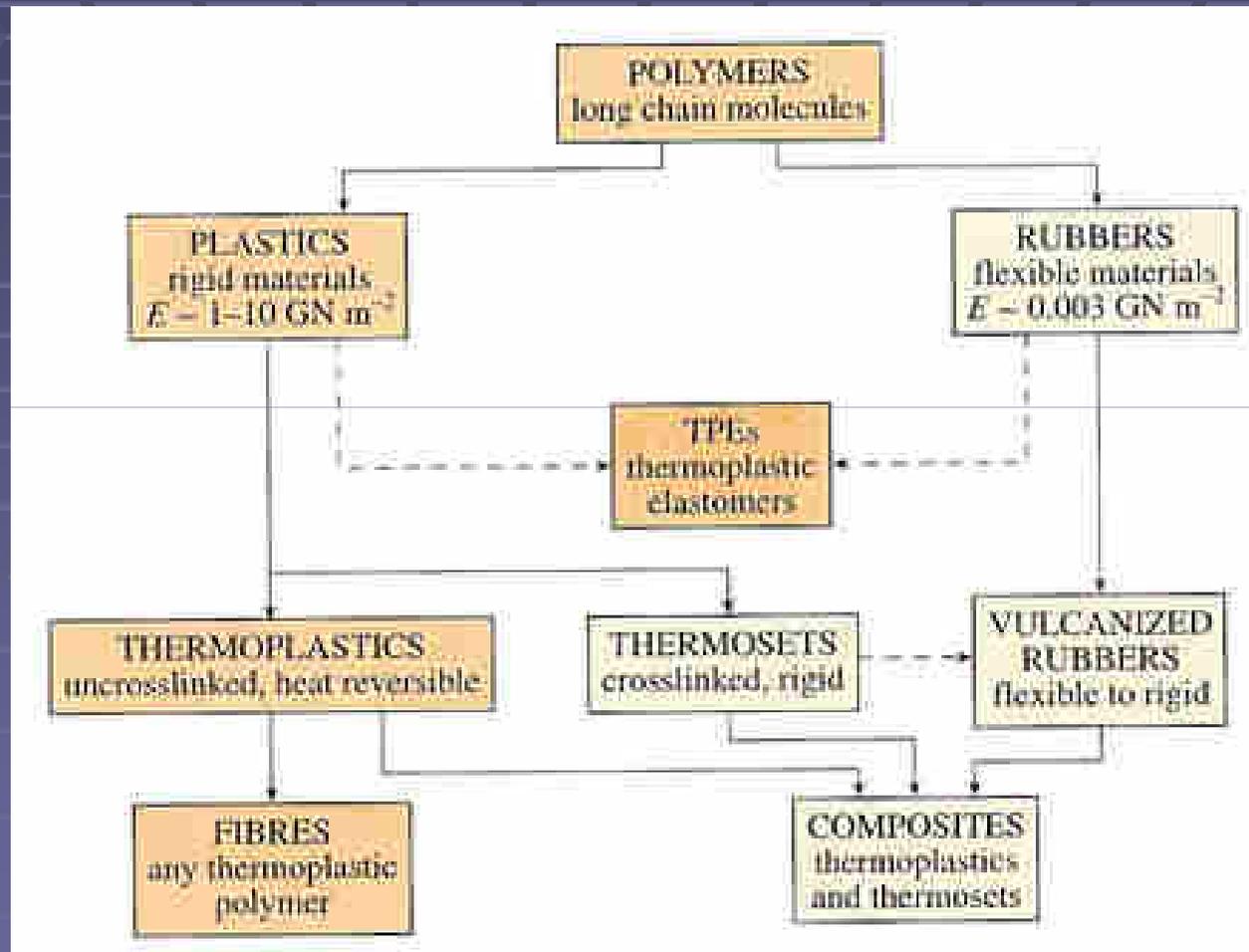
Range of Polymers

- Traditionally, the industry has produced two main types of synthetic polymer – plastics and rubbers.
- Plastics are (generally) rigid materials at service temperatures
- Rubbers are flexible, low modulus materials which exhibit long-range elasticity.

Range of Polymers

- Plastics are further subdivided into thermoplastics and thermosets

Range of Polymers

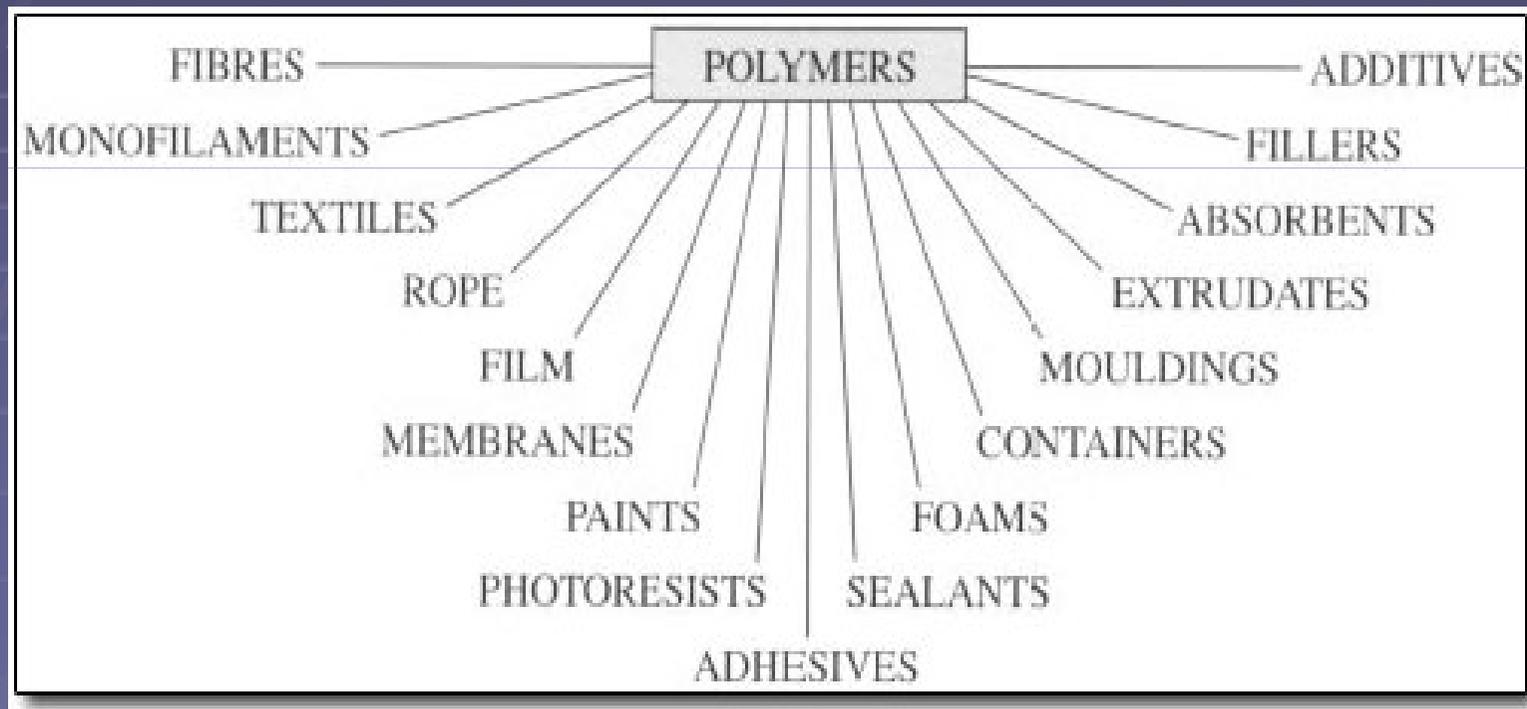


Thermoplastics & Thermosetting polymers

- **Thermoplastics** polymers: soften when heated and harden when cooled and vice versa
- Structure Example: linear, branched:
- Polyethylene, polystyrene, PVC, Poly (ethylene terephthalate)
- **Thermosetting** polymers: permanently hard (do not soften when heated)
- Made from network polymers: covalent bond resist motion at high temperature prevent.
- Epoxies, phenolics, and some polyester resins.

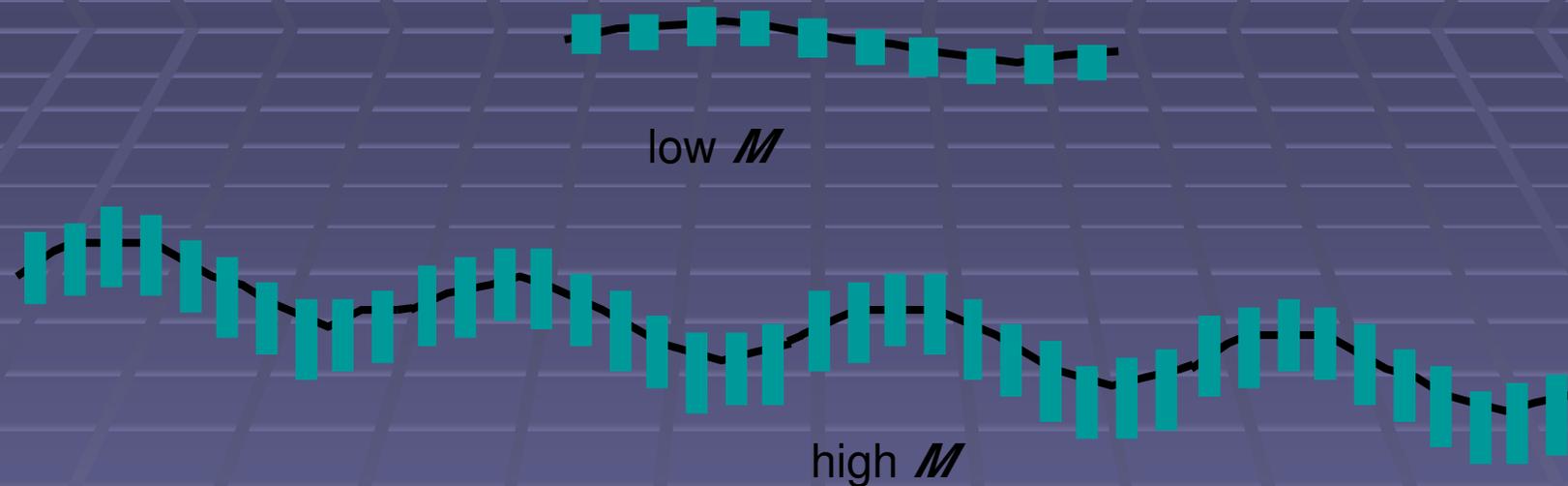
Range of Polymers

- Another way of classifying polymers is in terms of their form or function



4.5 MOLECULAR WEIGHT

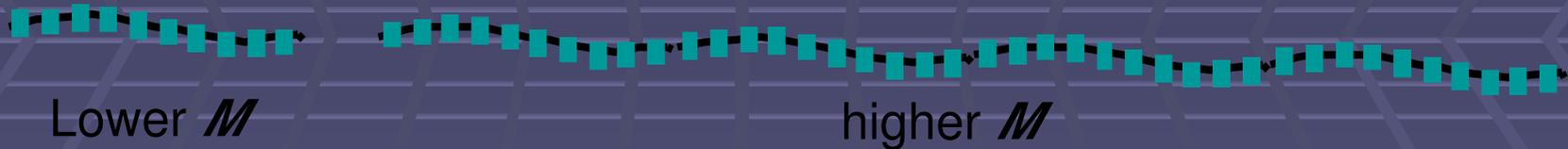
Molecular weight, M . Mass of a mole of chains.



Not all chains in a polymer are of the same length
i.e., there is a distribution of molecular weights

MOLECULAR WEIGHT

- Molecular weight, M_i : Mass of a *mole of chains*.

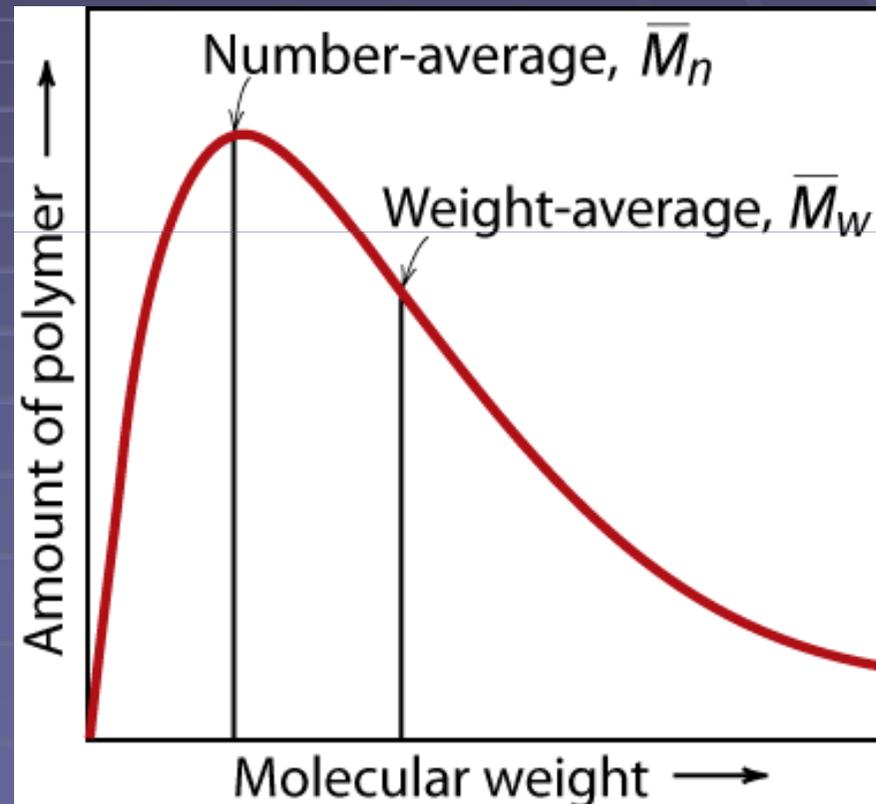


$$\bar{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

$$\bar{M}_n = \sum x_i M_i$$

$$\bar{M}_w = \sum w_i M_i$$

\bar{M}_w is more sensitive to higher molecular weights



Adapted from Fig. 14.4, *Callister 7e*.

Molecular Weight Calculation

Example: average mass of a class

N_i	M_i	x_i	w_i
# of students	mass (lb)		
1	100	0.1	0.054
1	120	0.1	0.065
2	140	0.2	0.151
3	180	0.3	0.290
2	220	0.2	0.237
1	380	0.1	0.204
		\bar{M}_n	\bar{M}_w
		186 lb	216 lb

$$\bar{M}_n = \sum x_i M_i$$

$$\bar{M}_w = \sum w_i M_i$$

$$x_i = \frac{N_i}{\sum_{all\ i} N_i}$$

$$w_i = \frac{N_i * M_i}{\sum_{all\ i} N_i * M_i}$$

Molecular weight

- The properties of a polymer depend on its length
- synthesis yields polymer distribution of lengths
- Define “average” molecular weight
 -
 -
- Two approaches are typically taken
 - Number average molecular weight (M_n)
 - Weight-average molecular weight (M_w)

Molecular weight of polymers

1-No. average Mwt M_n

$$M_n = \frac{\sum M_i N_i}{\sum N_i}$$

2-Weight average Mwt M_w

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$$

$$\eta_r = \frac{t}{t_0} = \frac{\eta}{\eta_0}$$

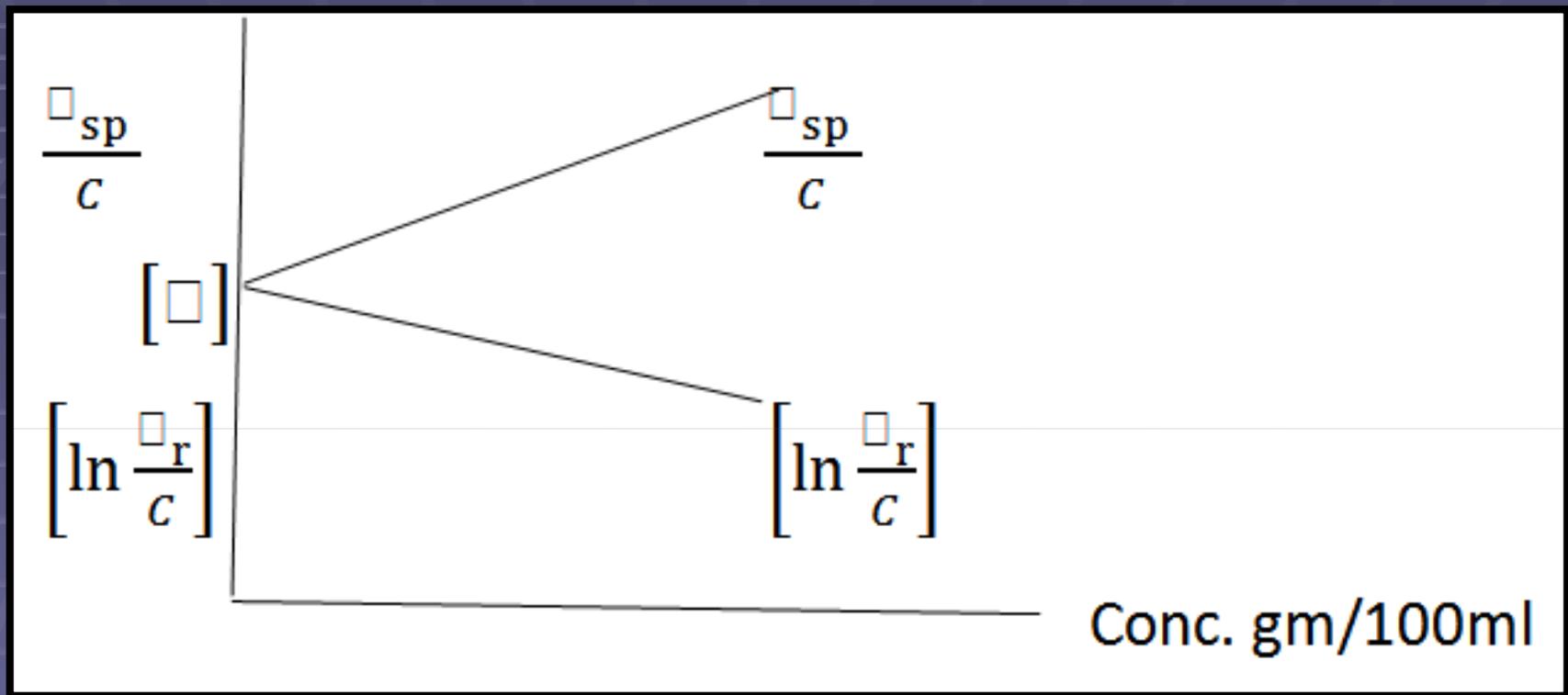
$$\eta_{sp} = \frac{t - t_0}{t_0} = \eta_r - 1$$

$$\left[\frac{\eta_{sp}}{c} \right]_{c \rightarrow 0} \quad \text{Or} \quad \left[\ln \frac{\eta_r}{c} \right]_{c \rightarrow 0} = [\eta]$$

$[\eta]$ = Intrinsic viscosity

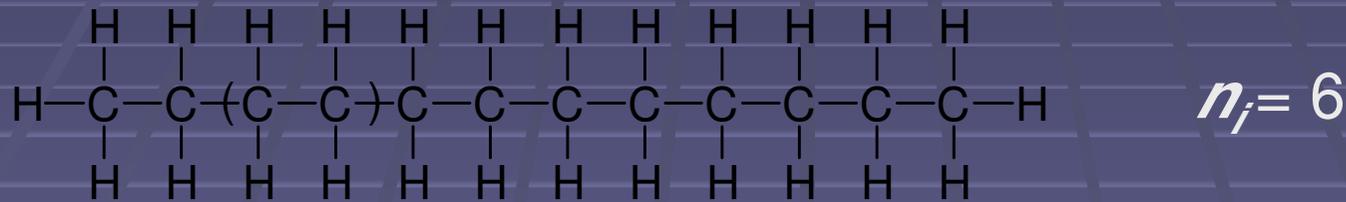
$[\eta] = KM^\alpha$ K, α : constants

$\log[\eta] = \log K + \alpha \log M$



Degree of Polymerization, n

n = number of repeat units per chain



$$n_n = \sum x_i n_i = \frac{\overline{M}_n}{\overline{m}}$$

$$n_w = \sum w_i n_i = \frac{\overline{M}_w}{\overline{m}}$$

where \overline{m} = average molecular weight of repeat unit

$$\overline{m} = \sum f_i m_i$$

Chain fraction

mol. wt of repeat unit i

Molecular Weight Calculation

Example: average mass of a class

N_i	M_i	x_i	w_i
# of students	mass (lb)		
1	100	0.1	0.054
1	120	0.1	0.065
2	140	0.2	0.151
3	180	0.3	0.290
2	220	0.2	0.237
1	380	0.1	0.204
		\overline{M}_n	\overline{M}_w
		186 lb	216 lb

$$\overline{M}_n = \sum x_i M_i$$

$$\overline{M}_w = \sum w_i M_i$$

$$x_i = \frac{N_i}{\sum_{all\ i} N_i}$$

$$w_i = \frac{N_i * M_i}{\sum_{all\ i} N_i * M_i}$$

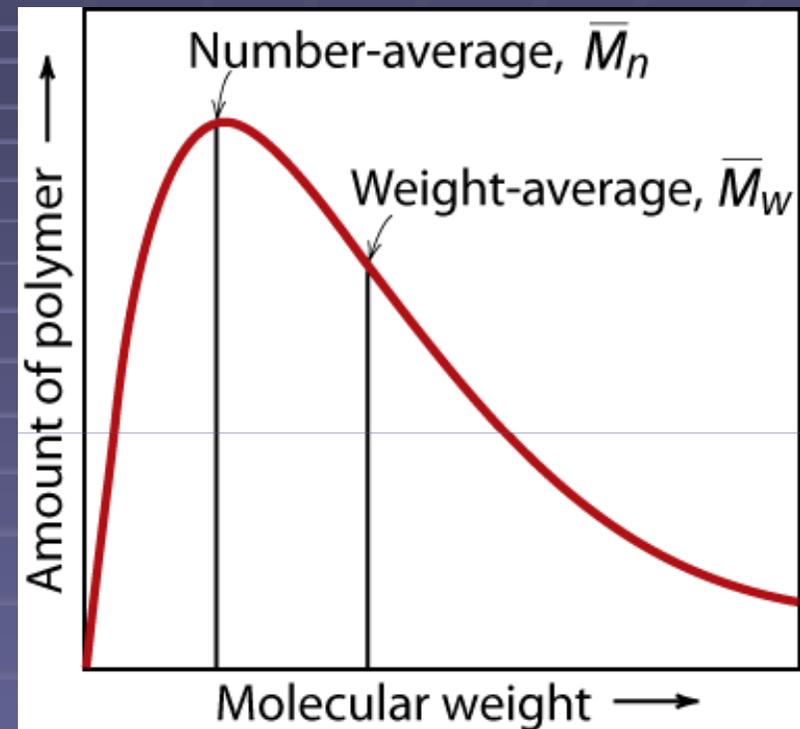
MOLECULAR WEIGHT DISTRIBUTION

Adapted from Fig. 4.4, *Callister & Rethwisch 3e*.

$$\bar{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

$$\bar{M}_n = \sum x_i M_i$$

$$\bar{M}_w = \sum w_i M_i$$



M_i = mean (middle) molecular weight of size range i

x_i = number fraction of chains in size range i

w_i = weight fraction of chains in size range i

Example Problem 4.1

- Given the following data determine the
 - Number average MW
 - Number average degree of polymerization
 - Weight average MW

How to find \overline{M}_n ?

1. Calculate $x_i M_i$
2. Sum these!

Number average MW (\overline{M}_n)

MW range (g/mol)			Mean (M_i)	
Min	Max	x_i	(g/mol)	$x_i M_i$ (g/mol)
5000	10000	0.05	7500	375
10000	15000	0.16	12500	2000
15000	20000	0.22	17500	3850
20000	25000	0.27	22500	6075
25000	30000	0.20	27500	5500
30000	35000	0.08	32500	2600
35000	40000	0.02	37500	750

$$\overline{M}_n = 21,150 \text{ g / mol}$$

Example Problem 4.1

Number average degree of polymerization

- (MW of H₂C=CHCl is 62.50 g/mol)

$$n_n = \frac{\overline{M}_n}{m} = \frac{21,150 \text{ g/mol}}{62.50 \text{ g/mol}} = 338$$

How to find \overline{M}_w ?

1. Calculate $w_i M_i$
2. Sum these!

Weight average molecular weight (\overline{M}_w)

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{23,200 \text{ g/mol}}{21,150 \text{ g/mol}} = 1.10$$

$$\overline{M}_w = 23,200 \text{ g/mol}$$

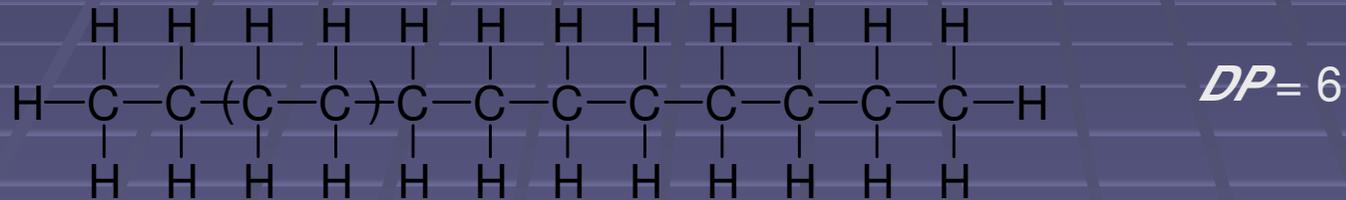
MW range (g/mol)			Mean (M _i)	
Min	Max	w _i	(g/mol)	w _i M _i (g/mol)
5000	10000	0.02	7500	150
10000	15000	0.10	12500	1250
15000	20000	0.18	17500	3150
20000	25000	0.29	22500	6525
25000	30000	0.26	27500	7150
30000	35000	0.13	32500	4225
35000	40000	0.02	37500	750

Table 4.4a Data Used for Number-Average Molecular Weight Computations in Example Problem 4.1

<i>Molecular Weight Range (g/mol)</i>	<i>Mean M_i (g/mol)</i>	x_i	$x_i M_i$
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750
			$\bar{M}_n = 21,150$

Degree of Polymerization, DP

DP = average number of repeat units per chain



$$DP = \frac{\overline{M}_n}{\overline{m}}$$

where \overline{m} = average molecular weight of repeat unit
for copolymers this is calculated as follows:

$$\overline{m} = \sum f_i m_i$$

Chain fraction

mol. wt of repeat unit i

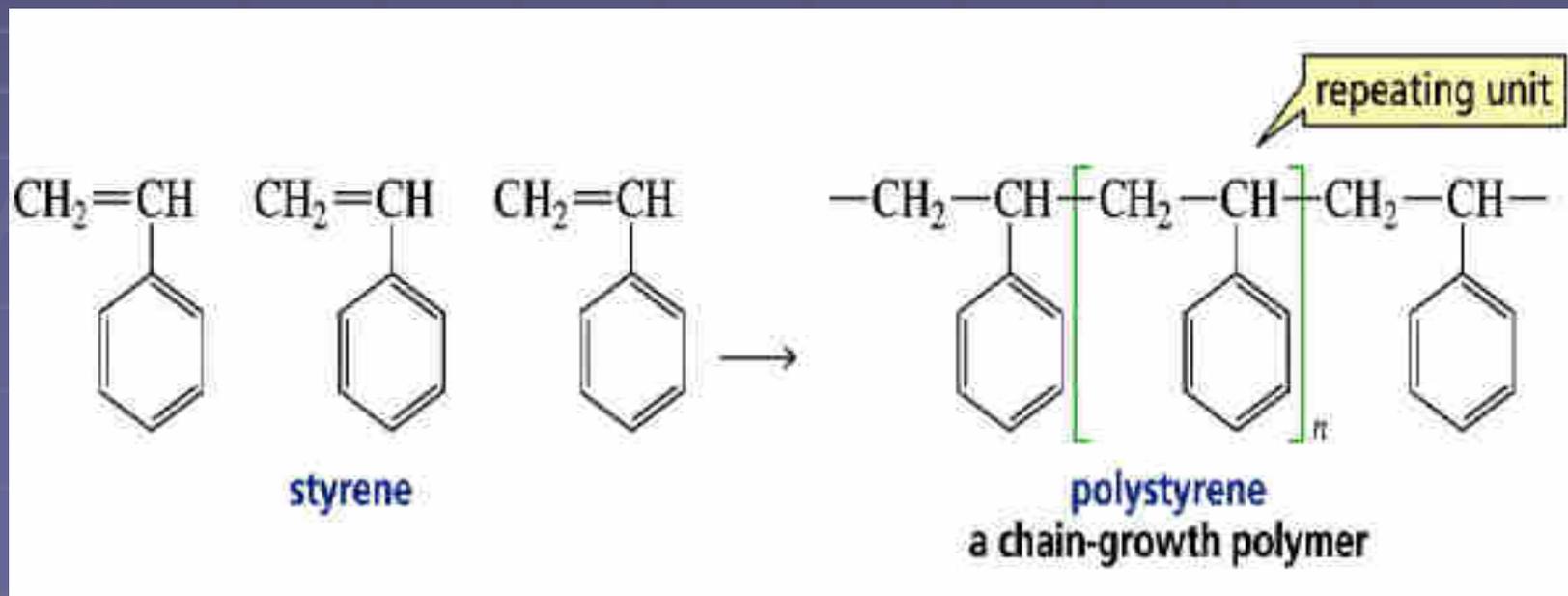
Synthesis of Polymers

Synthesis of Polymers

- There are a number different methods of preparing polymers from suitable monomers, these are
 - step-growth (or condensation) polymerisation
 - addition polymerisation
 - insertion polymerisation.

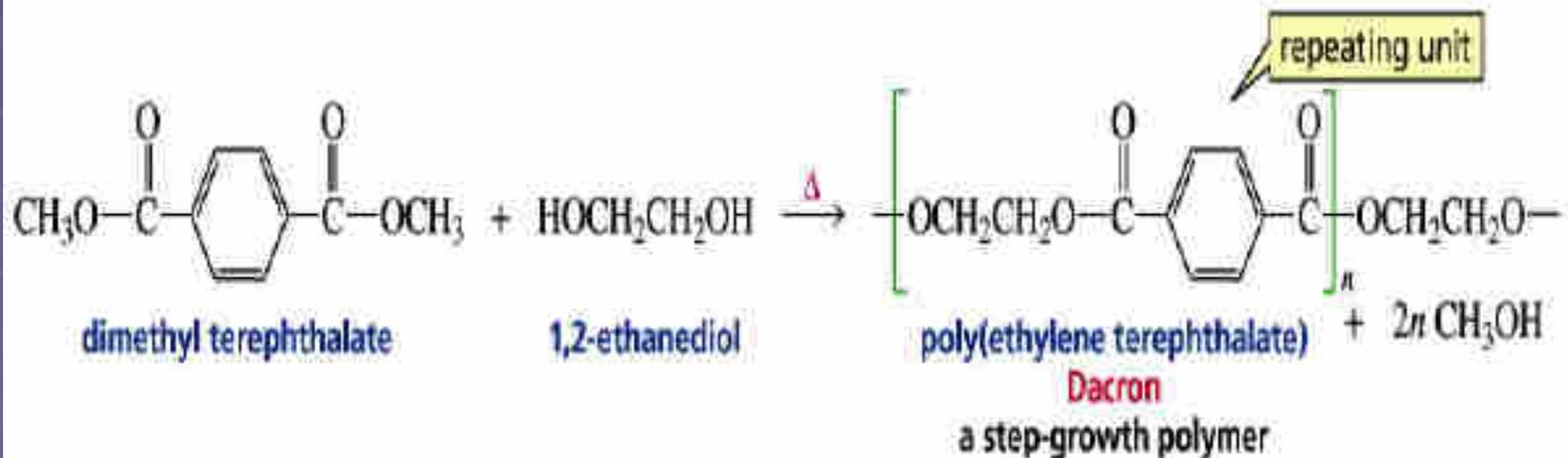
Types of Polymerization

- Chain-growth polymers, also known as addition polymers, are made by chain reactions



Types of Polymerization

- Step-growth polymers, also called condensation polymers, are made by combining two molecules by removing a small molecule



Addition Vs. Condensation Polymerization

- Polymerisation reactions can generally be written as



- In a reaction that leads to **condensation polymers**, x and y may assume any value
- i.e. chains of any size may react together as long as they are capped with the correct functional group

Addition Vs. Condensation Polymerization

- In **addition polymerization** although x may assume any value, y is confined to unity
- i.e. the growing chain can react only with a monomer molecule and continue its growth

Thermodynamics

- For polymerization to occur (i.e., to be thermodynamically feasible), the Gibbs free energy of polymerization $\Delta G_p < 0$.
- If $\Delta G_p > 0$, then depolymerization will be favored.

THERMOPLASTIC

Organic long chain polymer that usually unsaturated become soft when heated and can be molded under pressure. They are linear or branched polymers with little or no cross linking. Growth of thermoplastic is attributed to certain attractive properties:

- 1-Lightness in weight.
- 2-Chemical corrosion resistance.
- 3-Toughness.
- 4-Ease of handling.

1-Polyethylene

PE :The most commodity polymers ,and PCs final products(widely used)

Why PE is widely used?

1-Easy in producing monomer (E) from NG or petroleum fractions or Naphtha.

2-Low cost 3- PE posses especial properties such as resistance to corrosion and plastering.

Classification of PE;

Low density PE :**LDPE**

Density:0.915-0.935 gm/cm³ .

Mwt=30000-50000.

Branched chain polymer .

Degree of crystallization is low.

Low ability to absorb water.

High resistance to chemicals(acids and bases)

Resistances to impact and electricity thus it is used in insulating.

2-High density PE :HDPE

a-Density=0.95-0.96gm/cm³ .

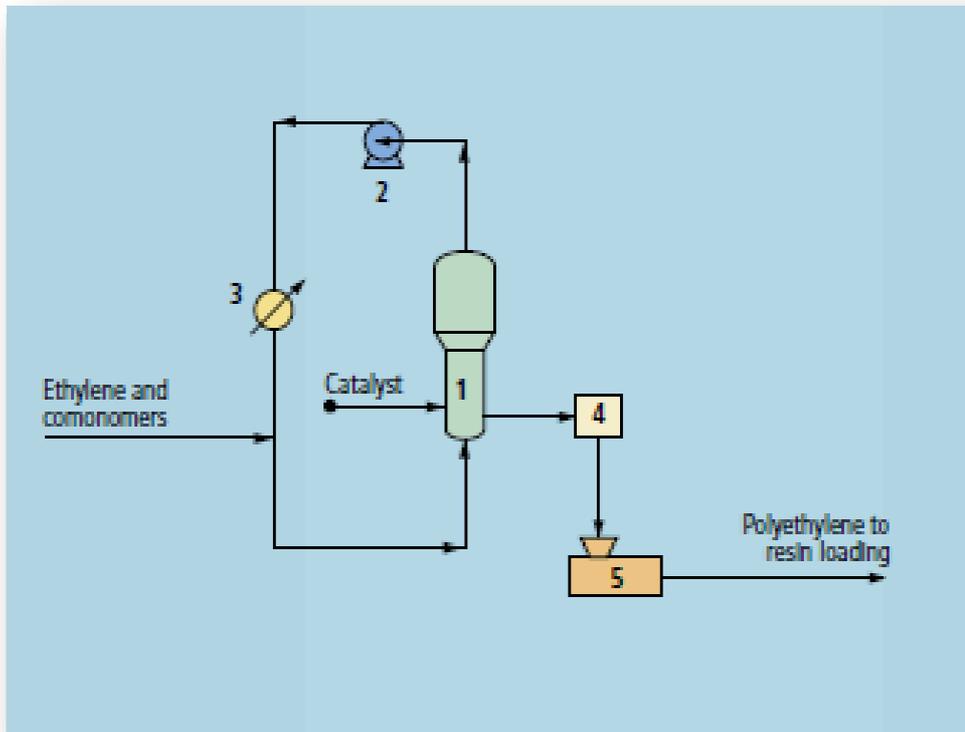
b- Linear polymer(no branches).

c-Highly crystalline.

d-Highly packed molecule, less permeable to gases.

3-Linear low density:LLDPE

It posses good physical and mechanical properties



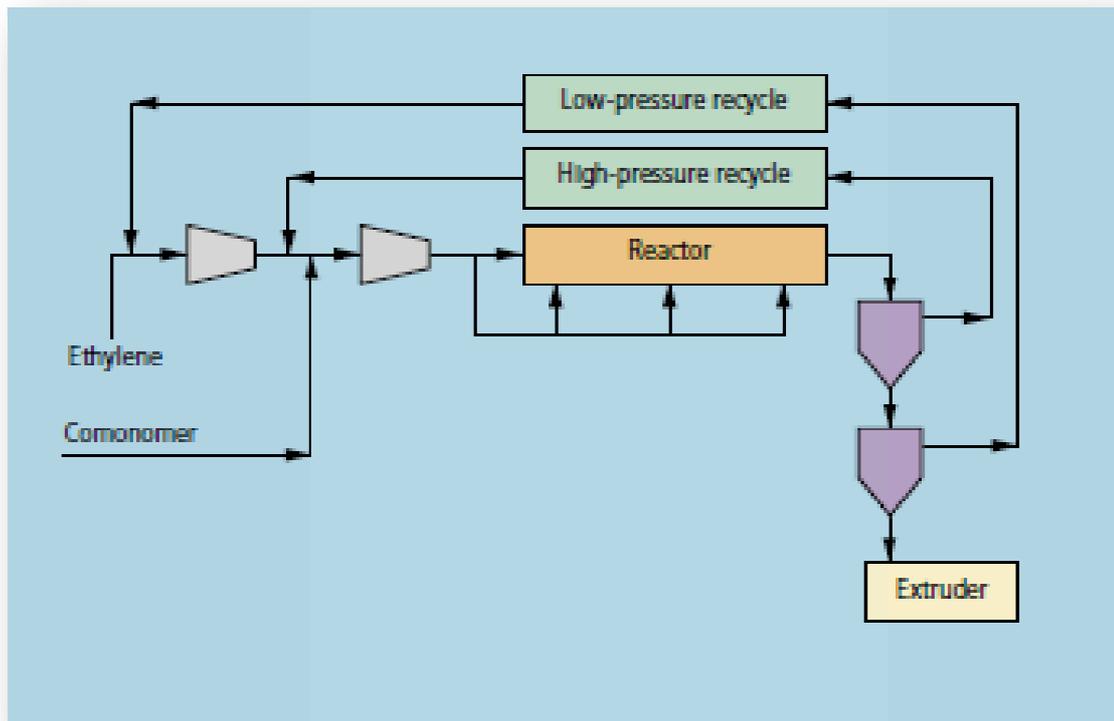
Application: To produce linear low-density polyethylene (LLDPE) to high density polyethylene (HDPE) using the low-pressure, gas-phase UNIPOL PE process.

Description: A wide range of polyethylenes is made in a gas-phase, fluidized-bed reactor using proprietary solid and slurry catalysts. The product is in a dry, free-flowing granular form substantially free of fines as it leaves the reactor and is converted to pellet form for sale. Melt index and molecular weight distribution are controlled by selecting the proper catalyst type and adjusting operating conditions. Polymer density is controlled by adjusting comonomer content of the product. High productivity of conventional and metallocene catalysts eliminates the need for catalyst removal. The simple and direct nature of this process results in low investment and operating costs, low levels of environmental pollution, minimal potential fire and explosion hazards, and easy operation and maintenance. Gaseous ethylene, comonomer and catalyst are fed to a reactor (1) containing a fluidized bed of growing polymer particles and operating near 25 kg / cm² and approximately 100 °C. A conventional, single-stage, centrifugal compressor (2) circulates reaction gas, which fluidizes the reaction bed, provides raw material for the polymerization reaction, and removes the heat of reaction from the bed. Circulating gas is cooled in a conventional heat exchanger (3).

The granular product flows intermittently into product discharge tanks (4) where unreacted gas is separated from the product and returned to the reactor. Hydrocarbons remaining with the product are removed by purging with nitrogen. The granular product is subsequently pelletized in a low-energy system (5) with the appropriate additives for each application.

Products: Polymer density is easily controlled from 0.915 to 0.970 g/cm. Depending on catalyst type, molecular weight distribution is either narrow or broad. Melt index may be varied from less than 0.1 to greater than 200. Grades suitable for film, blow-molding, pipe, roto-molding and extrusion applications are produced.

Commercial plants: Ninety-six reaction lines are in operation, under construction or in the design phase worldwide with single-line capacities ranging from 40,000 tpy to more than 450,000 tpy



Application: The high-pressure *Lupotech* TS or TM tubular reactor process is used to produce low-density polyethylene (LDPE) homopolymers and EVA copolymers. Single-train capacity of up to 400,000 tpy can be provided.

Description: Ethylene, initiator and, if applicable, comonomers are fed to the process and compressed to pressures up to 3,100 bar before entering the tubular reactor. In the TS mode, the complete feed enters the reactor at the inlet after the preheater; in the TM mode, part of the gas is cooled and quenches the reactor contents at various points of injection. The polymer properties (MI, \bar{M}_w , MWD) are controlled by the initiator, pressure, temperature profile and comonomer content. After the reactor, excess ethylene is recovered and recycled to the reactor feed stream. The polymer melt is mixed with additives in an extruder to yield the final product. A range of products can be obtained using the *Lupotech* T process, ranging from standard LDPE grades to EVA copolymers or N-butyl-acrylate modified copolymer. The products can be applied in (shrink) film extrusion, injection molding, extrusion blow molding, pipe extrusion, pipe coating, tapes and monofilaments. There is no limit to the number of reactor grades that can be produced. The

product mix can be adjusted to match market demand and economical product ranges. Advantages for the tubular reactor design with low residence time are easy and quick transitions, startup and shutdown. Reactor grades from MI 0.15 to \square 50 and from density 0.917 to 0.934 g/cm³, with comonomer content up to 30% can be prepared.

Economics: Consumption, per metric ton of PE:

Ethylene, t 1.010

Electricity, kWh 700–1,000

Steam, t –1.2 (export credit)

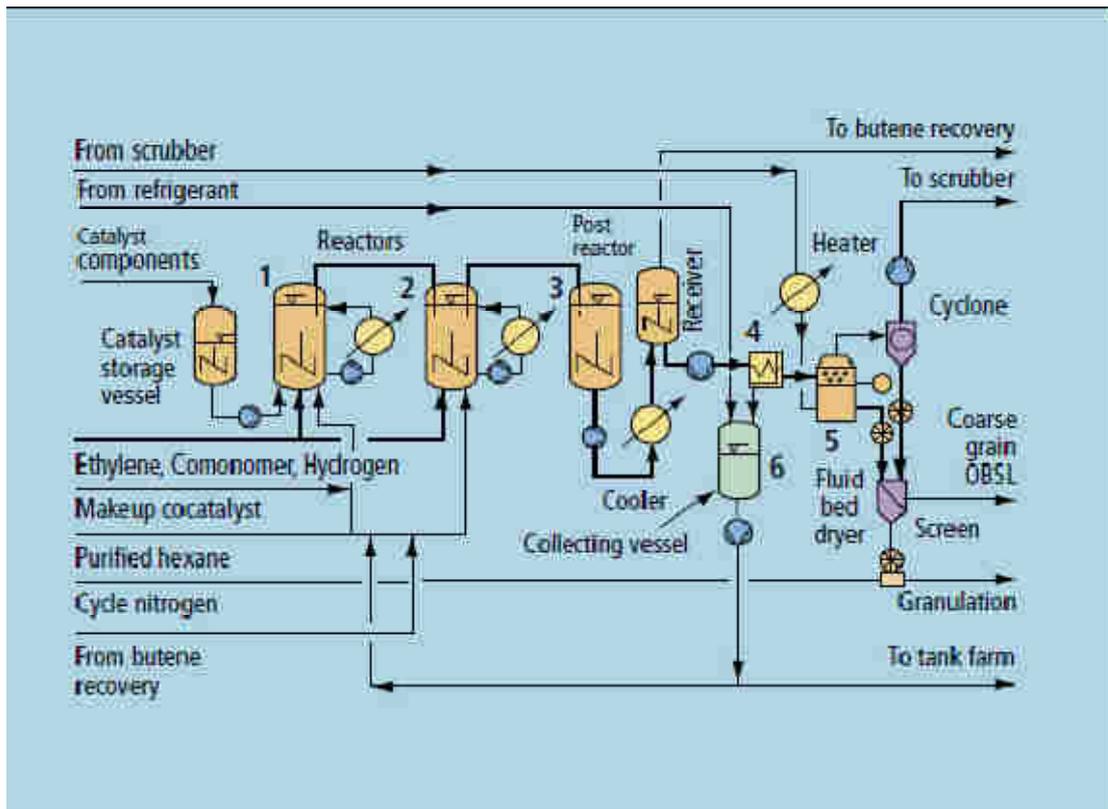
Nitrogen, Nm³ 4

Commercial plants: Many *Lupotech* T plants have been installed after the first plant in 1955, with a total licensed capacity of 4.4 million tons.

Basell operates LDPE plants in Europe with a total capacity of close to 1 million tpy. The newest state-of-the-art *Lupotech* TS unit at Basell's site in Aubette, France, was commissioned in 2000; with a capacity of 320 thousand tons, it is the largest single-line LDPE plant.

Note: When tubular reactor is used LDPE produced is used for production of films while when Autoclaves reactor used LDPE produced is used for forcoatings

3-Polyethylene, HDPE



Application: To produce high-density polyethylene (HDPE) using the stirred-tank, heavy-diluent *Hostalen* process.

Description: The *Hostalen* process is a slurry polymerization method with two reactors parallel or in series. Switching from a single reaction to a reaction

in cascade enables producing top quality unimodal and bimodal polyethylene (PE) from narrow to broad molecular weight distribution (MWD) with the same catalyst. Polymerization occurs in a dispersing medium, such as n-hexane, using a very high-activity Ziegler catalyst. No deactivation and catalyst removal is necessary because a very low level of catalyst residue remains in the polymer. For unimodal-grade production the catalyst, the dispersing medium, monomer and hydrogen are fed to the reactor (1, 2) where polymerization occurs. In the case of bimodal grade production, the catalyst is only fed to the first reactor (1); the second step polymerization occurs under different reaction conditions with respect to the first reactor. Also ethylene, butene and further dispersing medium are fed to the second reactor (2). Reactor conditions are controlled continuously, thus a very high-quality PE is manufactured.

Finally, the HDPE slurry from the second reactor is sent to the postreactor (3) to reduce dissolved monomer, and no monomer recycling is needed. In the decanter (4), the polymer is separated from the dispersing medium. The polymer containing the remaining hexane is dried in a fluidized bed dryer (5) and then pelletized in the extrusion section. The separated and collected dispersing medium of the fluid separation step(6) with the dissolved co-catalyst and comonomer is recycled to the polymerization reactors. A small part of the dispersing medium is distilled to maintain the composition of the diluent.

Products: The cascade technology enables the manufacturing of tailor-made products with a definite MWD from narrow to broad MWD. The melt flow index may vary from 0.2 (bimodal product) to over 50(unimodal product). Homopolymers and copolymers are used in various applications such as blow-molding (large containers, small bottles), extrusion molding (film, pipes, tapes and monofilaments, functional packaging) and injection molding (crates, waste bins, transport containers).

Economics: Consumption, per metric ton of PE (based on given product mix):

Ethylene and comonomer, t 1.015

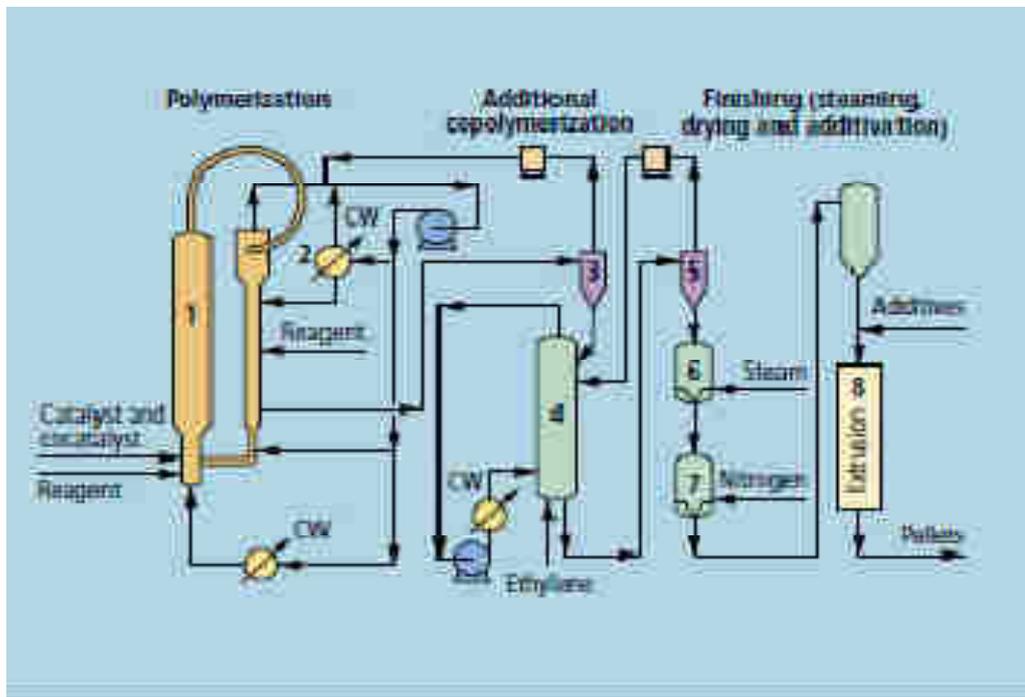
Electricity, kWh 500

Steam, kg 450

Water, cooling water, $\Delta T = 10^{\circ}\text{C}$, mt 175

Commercial plants: There are 33 *Hostalen* plants in operation or under construction

5-Polypropylene:



Application: *Spheripol* process technology produces propylene-based polymers including homopolymer PP and many families of random and heterophasic impact and specialty impact copolymers.

Description: In the *Spheripol* process, homopolymer and random copolymer polymerization takes place in liquid propylene within a tubular loop reactor (1). Heterophasic impact copolymerization can be achieved by adding a gas-phase reactor (3) in series. Removal of catalyst residue and amorphous polymer is not required. Unreacted monomer is flashed in a two-stage pressure system (2, 4) and recycled back to the reactors. This improves yield and minimizes energy consumption. Dissolved monomer is removed from the polymer by a steam sparge (5). The process can use lower-assay chemical-grade propylene (94%) or the typical polymerization-grade (99.5%).

Yields: Polymer yields of 40,000 – 60,000 kg / kg of supported catalyst are obtained. The polymer has a controlled particle size distribution and an isotactic index of 90 – 99%.

Economics: The *Spheripol* process offers a broad range of products with excellent quality and low-capital and operating costs.

Consumption, per metric ton of PP:

Propylene and comonomer, t 1.002–1.005

Catalyst, kg 0.016–0.025

Electricity, kWh 80*

Steam, kg 280

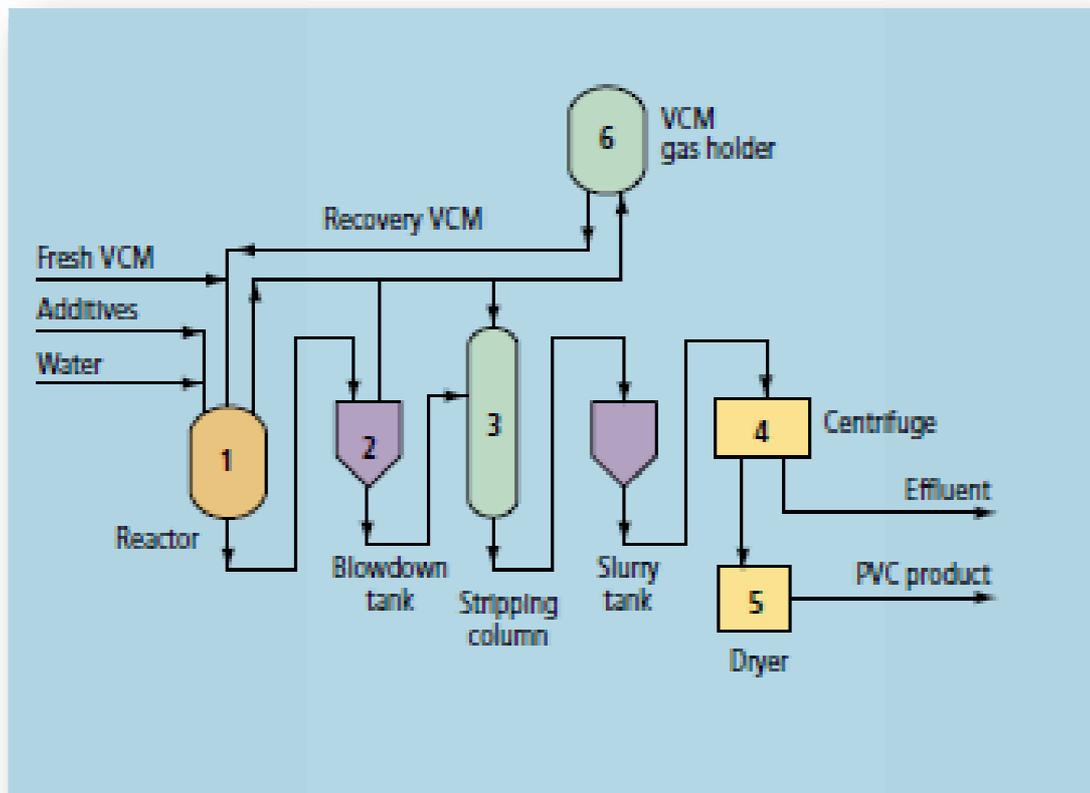
Water, cooling, mt 90

* In case of copolymer production, an additional 20 kWh is required.

Products: The process can produce a broad range of propylene-based polymers, including homopolymer PP, various families of random copolymers and terpolymers, hetero phasic impact and speciality impact copolymers (up to 25% bonded ethylene), as well as high-stiffness, high clarity copolymers.

Commercial plants: *Spheripol* technology is used for about 50% of the total global PP capacity. There are 94 *Spheripol* process plants operating World wide with total capacity of about 17 million tpy. Single-line design capacity is available in a range from 40,000 to 550,000 tpy.

6-PVC (suspension)



Application: A process to produce polyvinyl chloride (PVC) from vinylchloride monomer (VCM) using suspension polymerization. Many types of PVC grades are produced including: commodity, high K-value, low K-value, matted type and co-polymer PVC. The PVC possesses excellent product qualities such as easy processability and good heat stability.

Description: PVC is produced by batch polymerization of VCM dispersed in water. Standard reactor sizes are 60, 80, 100 or 130 m³. The stirred reactor (1) is charged with water, additives and VCM. During polymerization reaction, the temperature is controlled at a defined temperature depending on the grade by cooling water or chilled water. At the end of the reaction, the contents are discharged into a blow down tank (2) where most of the un reacted VCM is flashed off. The reactor is rinsed and sprayed with an anti-fouling agent, and is ready for the following batch. The PVC slurry containing VCM is continuously fed to the stripping column(3). The column has a proprietary design and effectively recovers VCM from the PVC slurry without any deterioration of PVC quality. After stripping, the slurry is de-watered (4), and dried

effectively by the proprietary dryer (5). It is then passed to storage silos for tanker loading or bagging. Recovered VCM is held in a gas holder (6), then compressed, cooled and condensed to be reused for the following polymerization batch.

Economics:

Raw materials and utilities, per ton of PVC:

VCM, t 1.003

Electricity, kWh 160

Steam, t 0.7

Additives, for pipe grade, \$US 12

Commercial plants: The process has been successfully licensed 15 times worldwide. Total capacity of the Chisso process in the world is more than 1.5 million tpy. In addition, Chisso VCM removal technology has been licensed to many PVC producers worldwide.

Synthetic fibers

Fibers":Length/diameter>100: (1)Textiles are main use.

1-Must have high tensile strength.

2-Usually highly crystalline and highly polar.

(2)Formed by spinning:ex.extrude polymer through a spinneret:

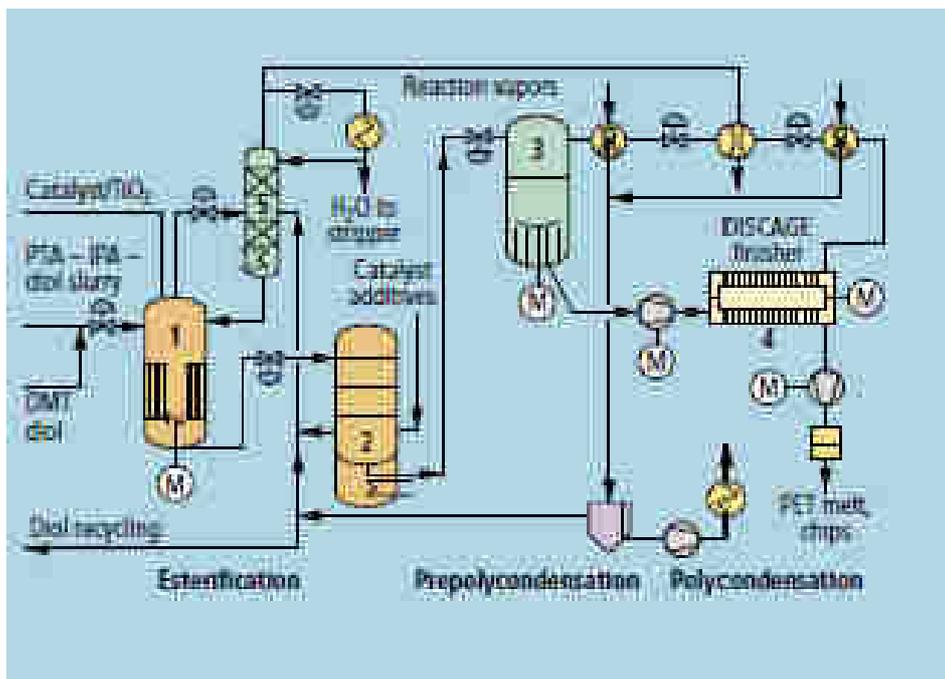
Pt plate with 1000"s of holes for nylon. Melt spinning

Ex. Rayon-dissolved in solvent then pumped through die head to make fibers. Solution spinning

(3) The fibers are drawn .

(4)Lead to a highly aligned chains-febrile structure.

1-Polyesters (polyethylene terephthalate)



Application: To produce polyesters for resin and textile applications from terephthalic acid (PTA) or dimethyl terephthalate (DMT) and diols [ethylene glycol (EG) or others], using the UIF-proprietary four-reactor(4R)- process including DISCAGE-finisher

Description: A slurry composed of PTA and EG, or molten DMT and EG is fed to the first esterification/ester-interchange reactor (1) in which main reaction occurs at elevated pressure and temperatures (200°C–270°C). Reaction vapors—water or methanol—are sent to a low/high

boiler separation column. High boilers are reused as feedstock. The oligomer is sent to a second cascaded, stirred reactor (2) operating at a lower pressure and a higher temperature. The reaction conversion continues to more than 97%. Catalyst and additives may be added. Reaction vapors are sent to the process column (5). The oligomer is then prepolymerized by a third cascaded reactor (3) under subatmospheric pressure and increased temperature to obtain a degree of polycondensation >20. Final polycondensation up to intrinsic viscosities of $i. V. = 0.9$ is done in the DISCAGE-finisher (4). Pelletizing or direct melt conversion usage is optional. EG is recovered by condensing process vapors at vacuum conditions. Vacuum generation may be done either by water vapor as a motive stream or by the diol (EG). The average product yield exceeds 99%.

Economics: Typical utility requirements per metric ton of PET are:

Electricity, kWh 55.0

Fuel oil, kg 61.0

Nitrogen, Nm³ 0.8

Air, Nm³ 9.0

Commerical plants:

Thirteen lines with processing capacities ranging

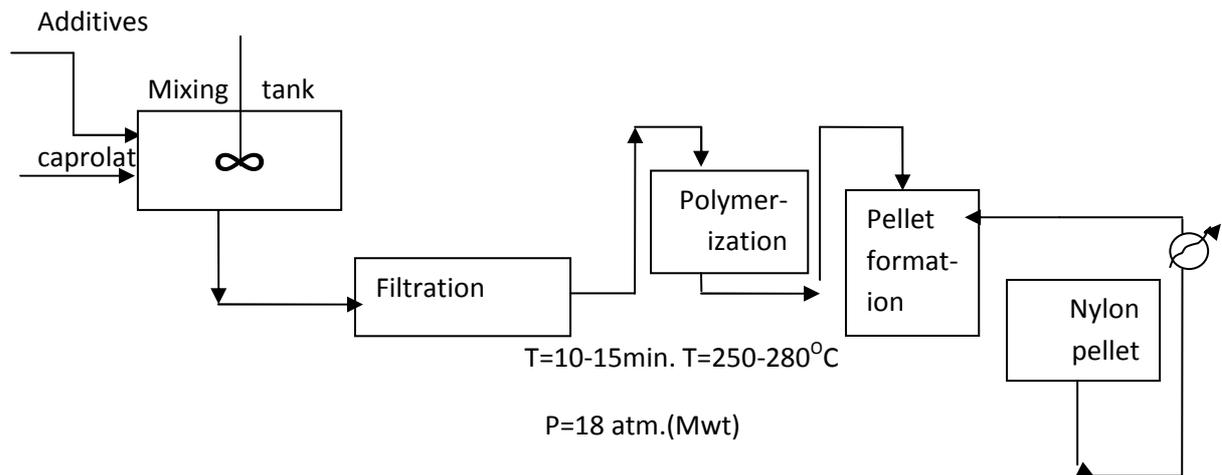
from 100 to 700 mtpd are operating; more than 50 polyester CP plants have been built worldwide. Presently, 700 mtpd lines are in operation as

single-train lines, including a single finisher.

2-Nylon 6

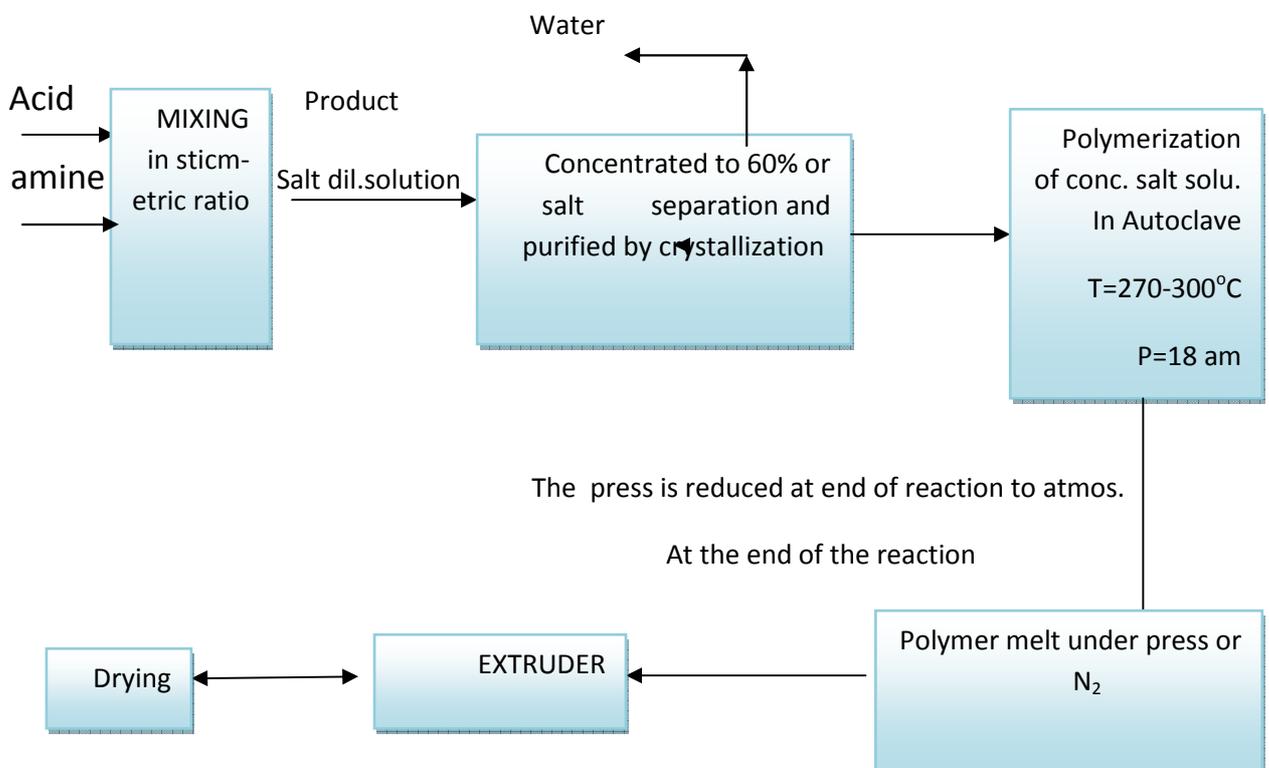
Is a polyamide contain -CONH-

Raw material:Caprolactum.



3-Nylon 66:

Polymer is produced from hexamethylene adipamide which produced from condensation polymerization of adipic acid and hexamethylenediamine.



4-Acrylic :

Uses: Wool replacement.

Production: Copolymerization of acrylonitrile with comonomer in presence of reaction initiators either free radicals or anionic at low temperature.

Polymerization on industrial scale:

1-Suspnsion polymerization: in presence of water

2-Solution polymerization: in presence of suitable solvent :DMF or DMSO.

