

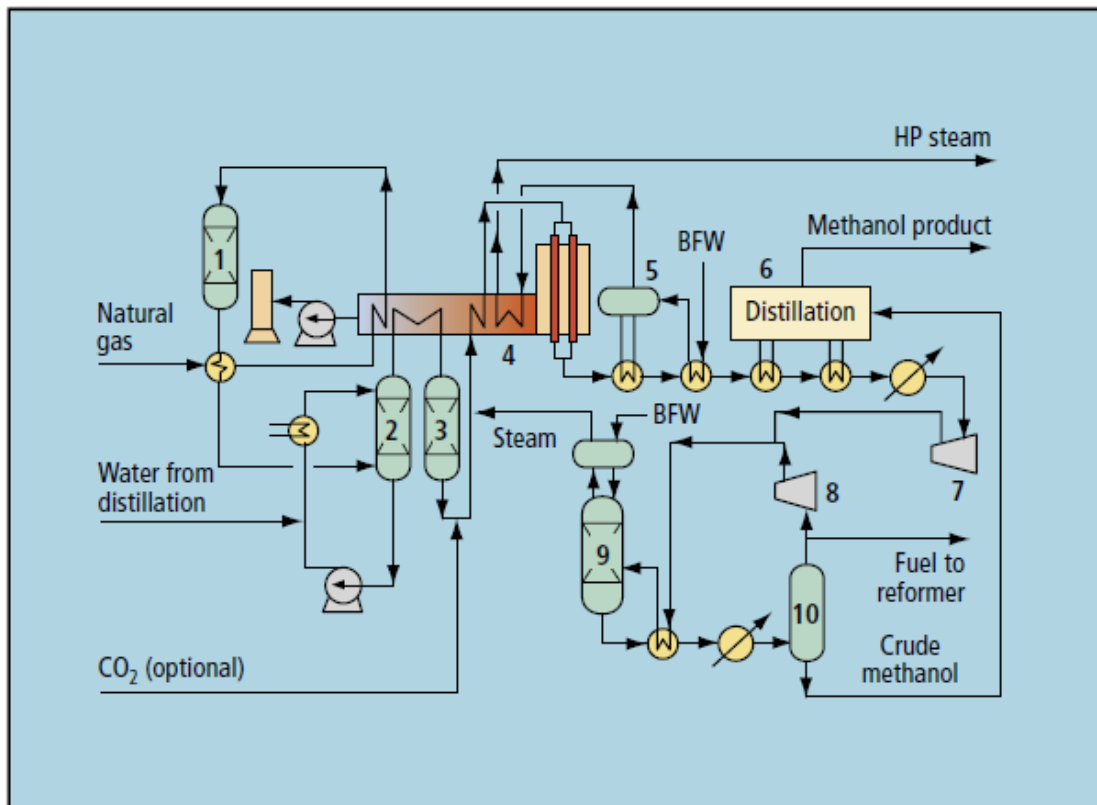
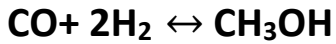
CHEMICAL PROCESS INDUSTRIE
UNIVERSITY OF DIYALA CHEMICAL
ENGINEERING DEPARTMENT

LECTURE(3)

INTERMEDIATES AND DERIVATIVES:

Methanol CH₃OH

Feed: NG or associated gas



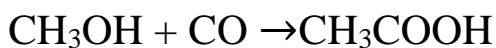
Description: (1) Gas feedstock is compressed (if required), desulfurized (2) the optional saturator, where some process steam is generated. The saturator is used where maximum water recovery is important. Further process steam is added, and the mixture is preheated and sent to the pre-reformer (3), using the Catalytic-Rich-Gas process. Steam raised in the methanol converter is added, along with available CO₂, 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.

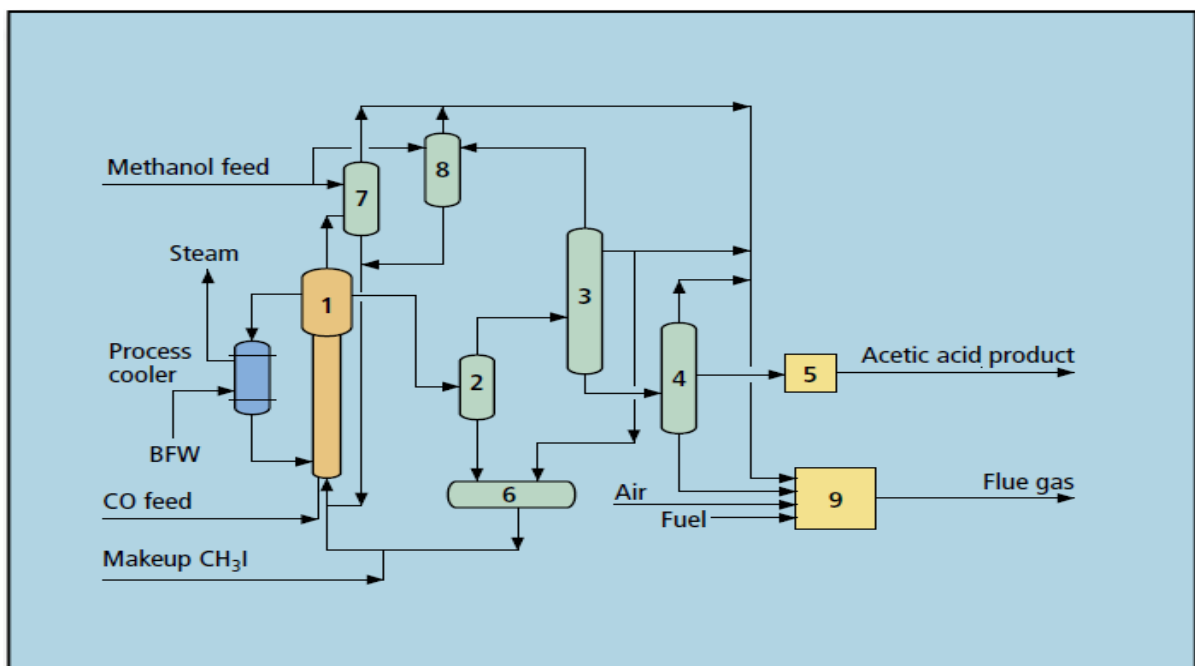
The synthesis loop comprises a circulator (8) and the converter operates around 200°C to 270°C, depending on the converter type. Reaction heat from the loop is recovered as steam, and is used directly as process steam for the reformer.

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 non condensable gases. The second column removes water, higher alcohols and similar organic heavy ends.

Acetic acid CH₃COOH



Feed: Methanol and carbon monoxide (CO) are reacted with the carbonylation reaction using a heterogeneous Rh **catalyst**.



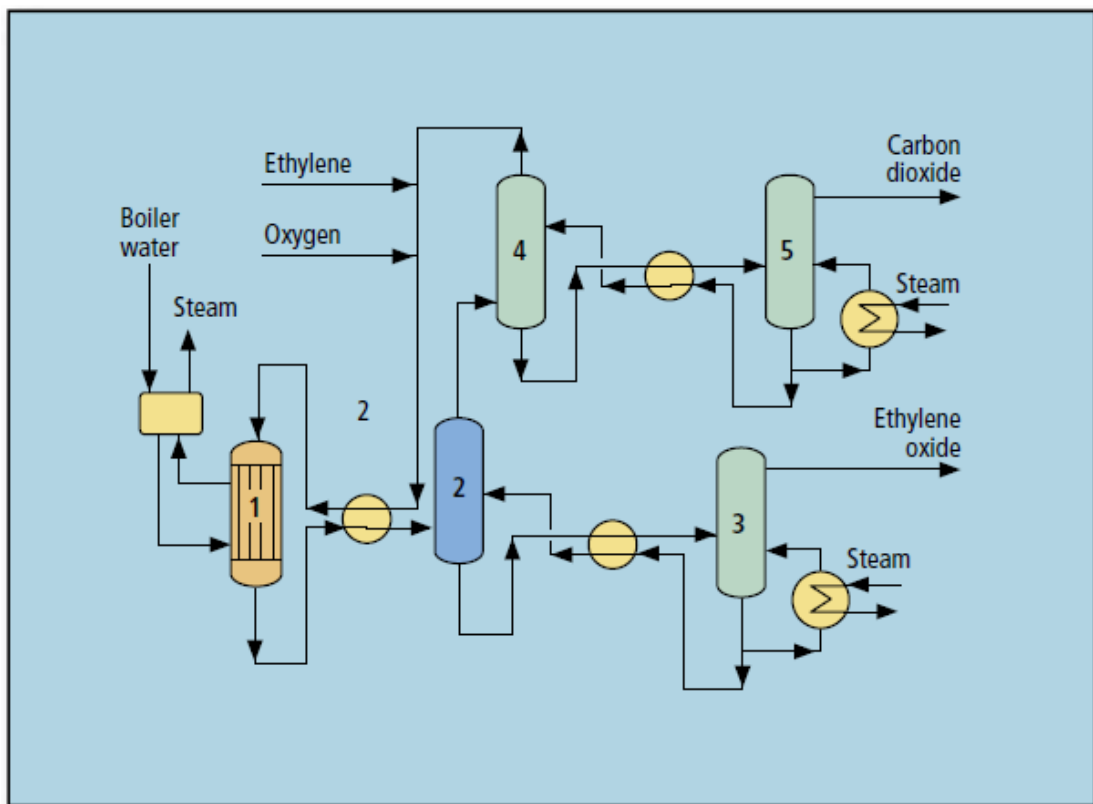
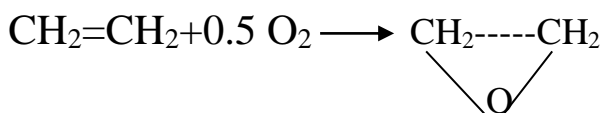
Description: Fresh methanol from absorber(7) & (8)., mixed with the recycle liquid from the recycle surge drum (6). This stream is charged to a unique bubble column reactor (1).

Carbon monoxide is compressed and sparged into the reactor riser. **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).

Ethylene Derivatives:

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

1- is a simpler 2- safer process for the production of EO 3- having lower capital investment requirements and 4- lower operating costs. Meteor Process

A- ethylene and oxygen are mixed and passed through a single-train, multi tubular catalytic reactor (1) to selectively process is a simpler, safer technology with lower facility investment costs. **B-** 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 EO reactor, is removed via activated, hot The cycle gas exiting the absorber is fed to the CO₂ removal section (4,5) where CO₂, which is co-produced in potassium carbonate treatment. The CO₂ lean cycle gas is recycled by compression back to the EO reactor.

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 CO₂ removal 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.

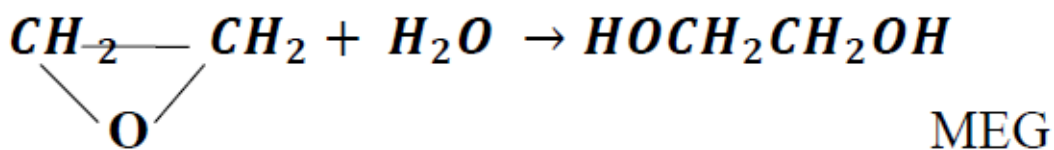
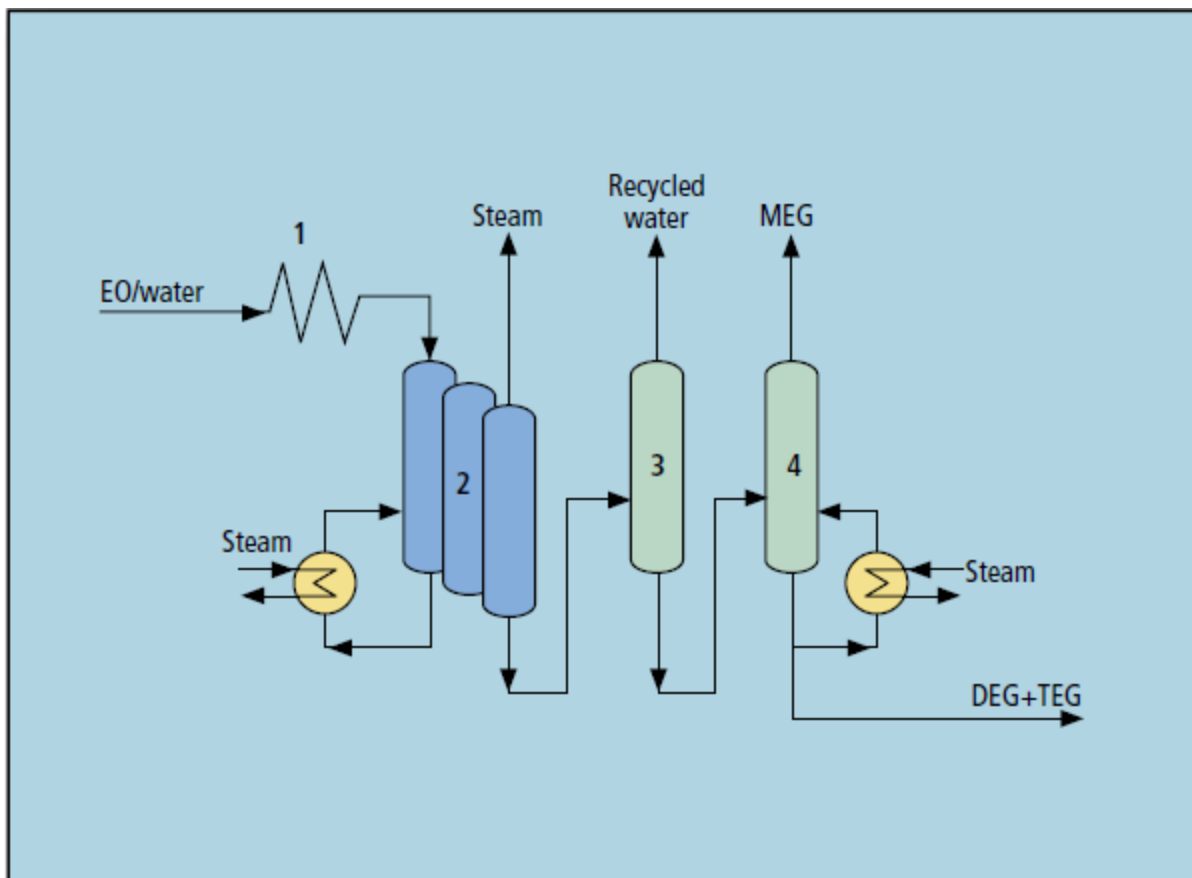
Other old method utilized air for oxidation:

Two reactors and two absorber to complete oxidation of E to produce EO.

T=260-290°C, P=10-13 atm.

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

Ethylene glycol :



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).

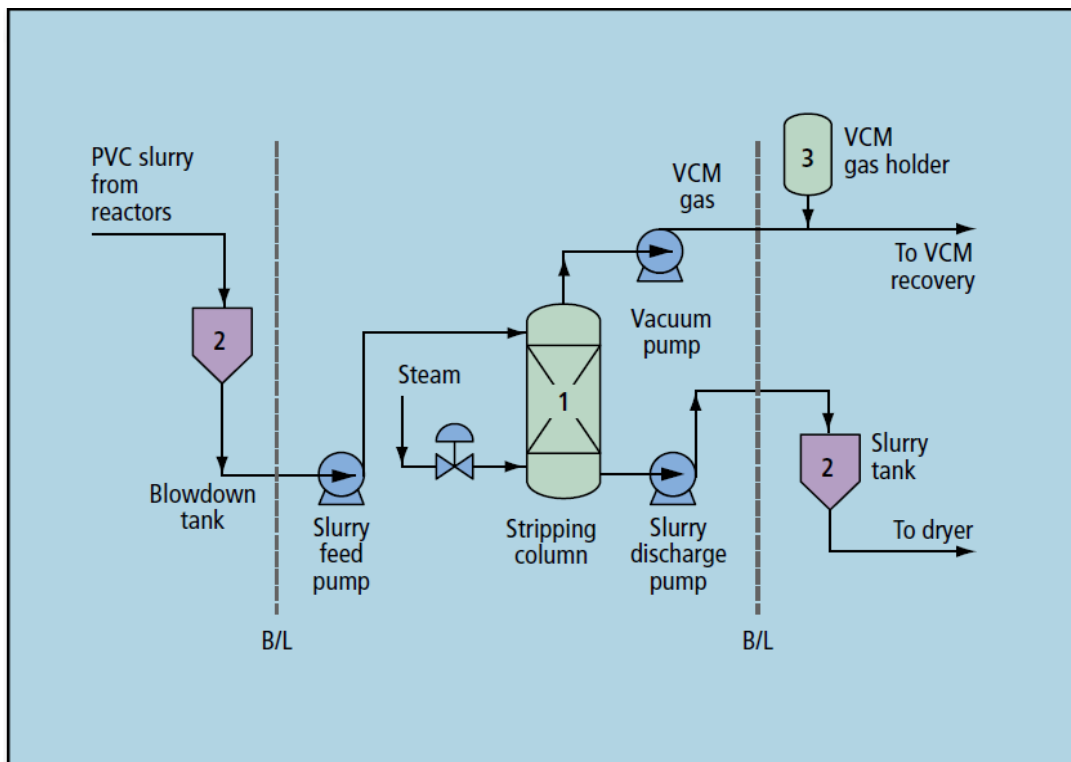
Diethylene (DEG) and triethylene (TEG) glycols are produced as co products. In a catalyzed mode, higher selectivities to MEG can be obtained, thereby reducing DEG production to one-half that produced in the uncatalyzed mode. Excess water from the reactor effluent is efficiently removed in a multi effect evaporation system (2). 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.

Uses:

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

Vinyl chloride:

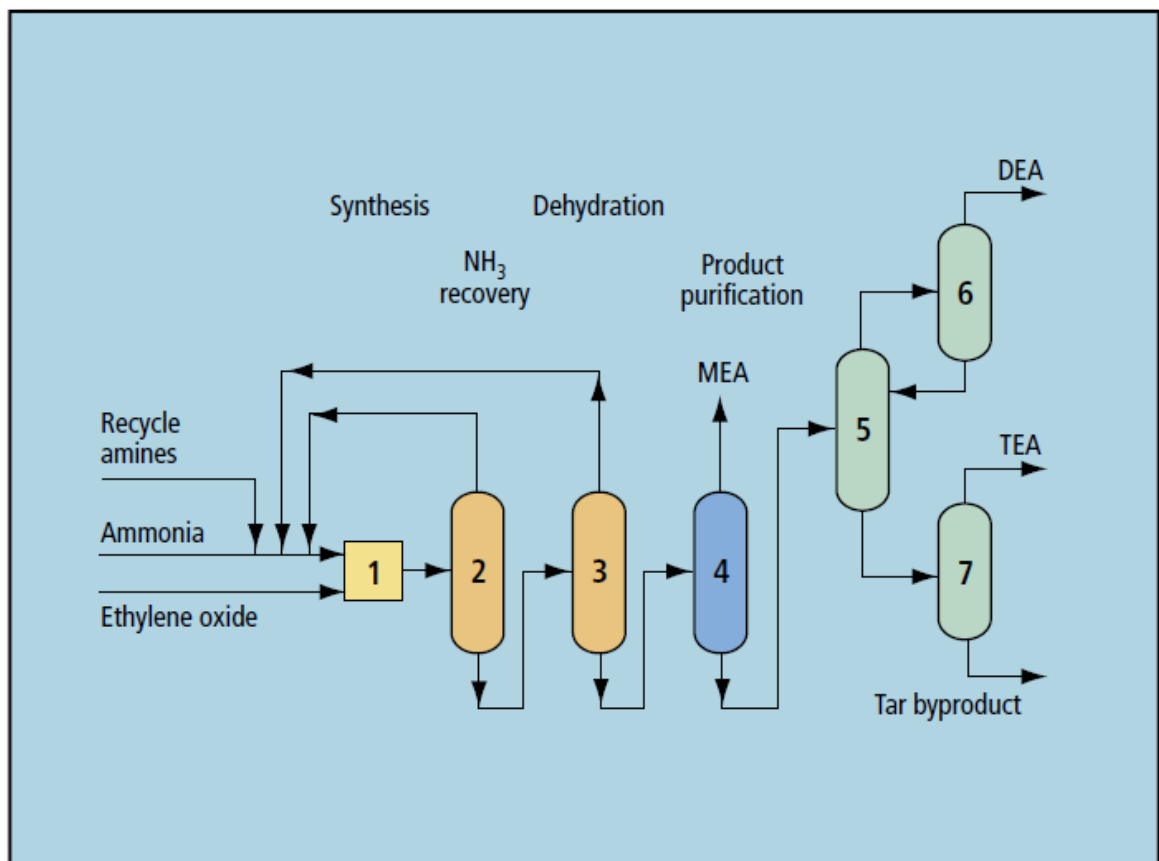
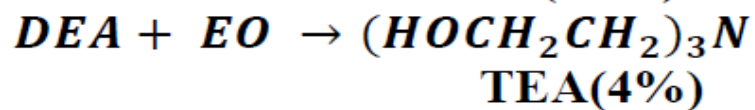
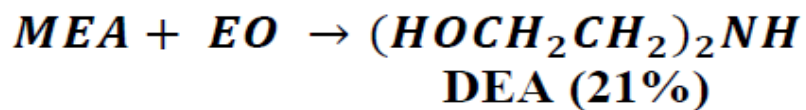
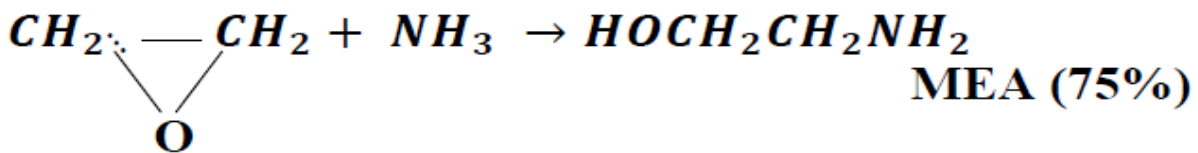
Vinylchloride monomer VCM $\text{CH}(\text{Cl})=\text{CH}_2$:



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.

-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. All process operations, including grade change, are automatically done in a completely closed system.

Ethanolamines, MEA,DEA &TEA:



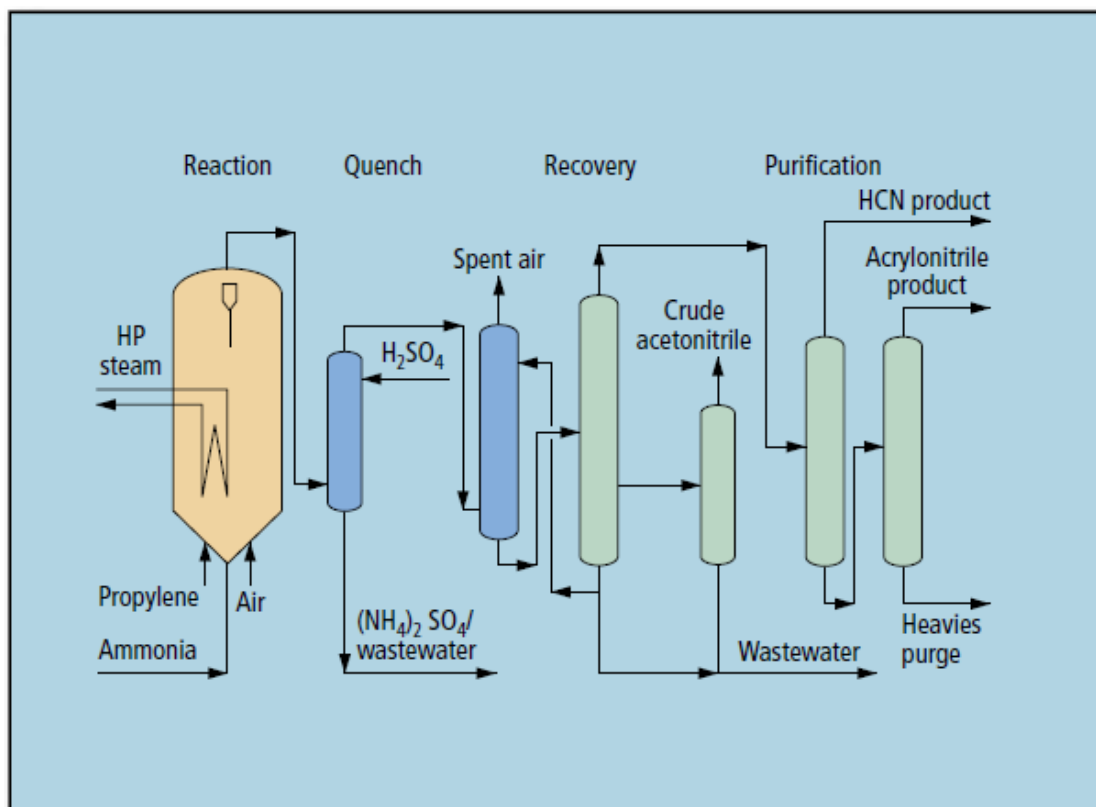
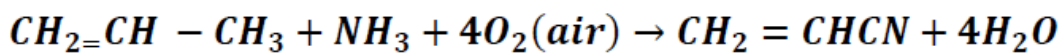
Description: Ammonia (2) and water are separated and recycled to the reaction system. Vacuum distillation (4,5,6,7) is used to produce pure MEA, DEA and TEA. A saleable heavies tar byproduct is also produced. solution, recycled amines and ethylene oxide are fed continuously to a reaction system (1) that operates under mild conditions and simultaneously produces MEA, DEA and TEA. The reactor products are sent to a separation system where ammonia Technical grade TEA (85wt%) can also be produced if required.

Uses:

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

Propylene derivatives:

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.

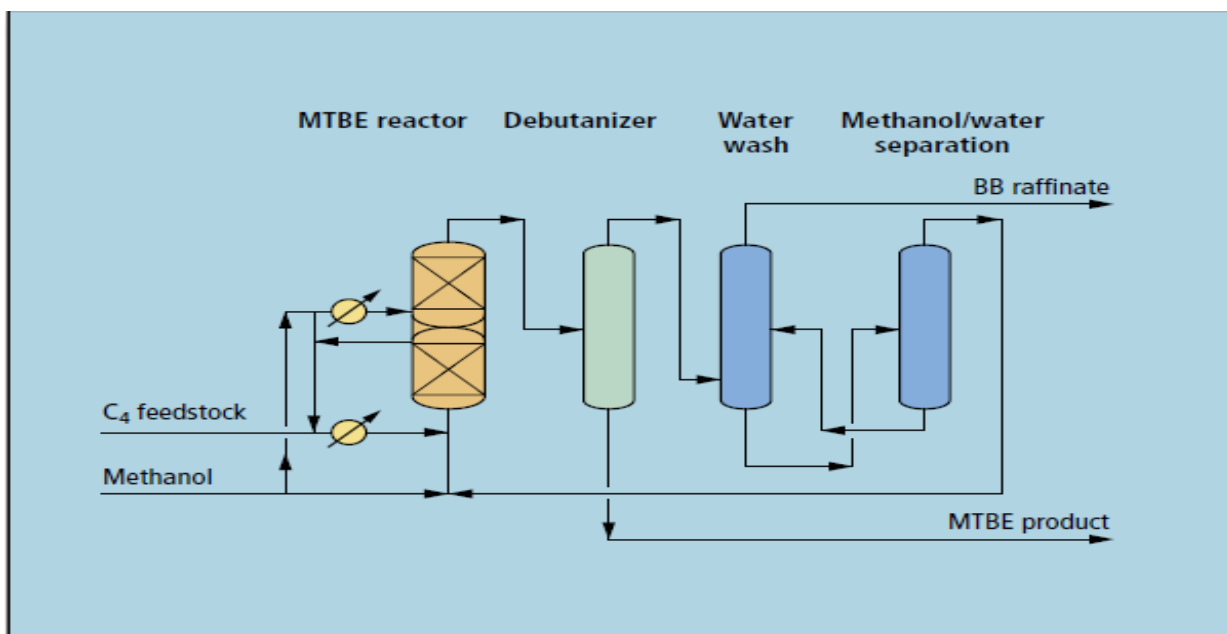
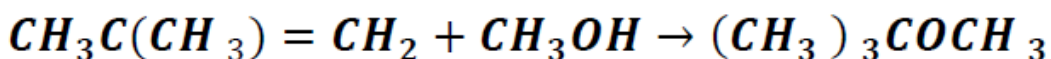
Description: Propylene, ammonia, and air are fed to a fluidized bed reactor to produce acrylonitrile (ACRN) using DuPont's proprietary catalyst system. Other useful products from the reaction are hydrogen cyanide (HCN) and acetonitrile (ACE). The reaction is highly exothermic and heat is recovered from 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.

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

Derivatives of C4 hydrocarbons:

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



Feed: 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%.

Uses: 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%.

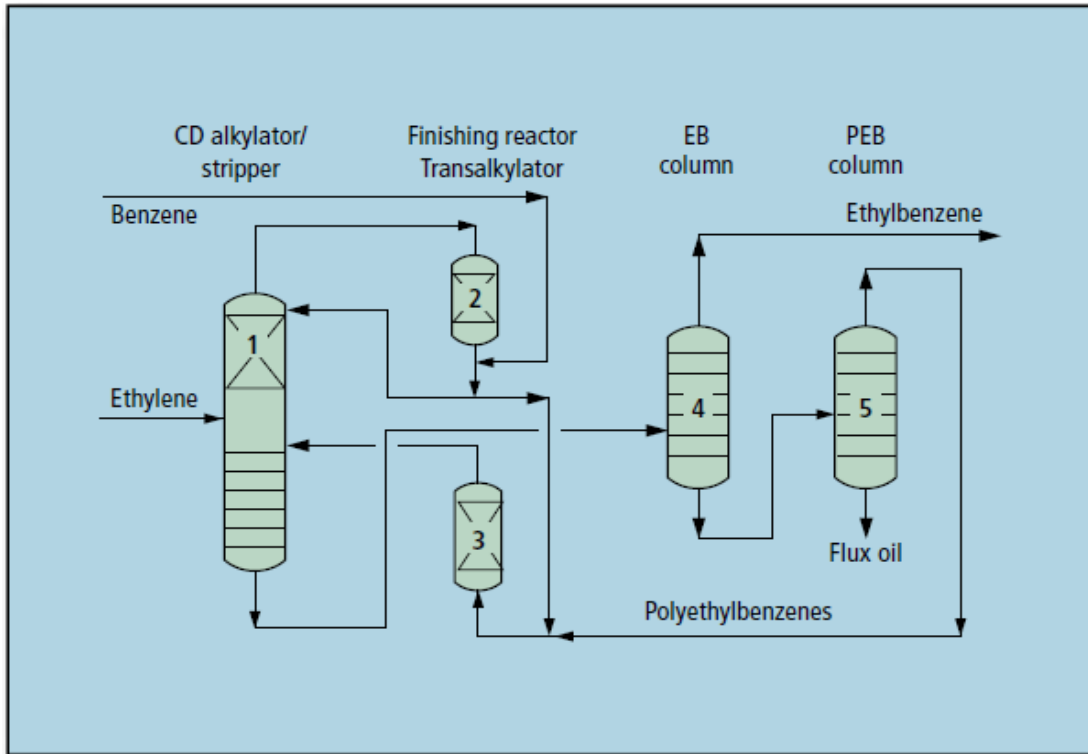
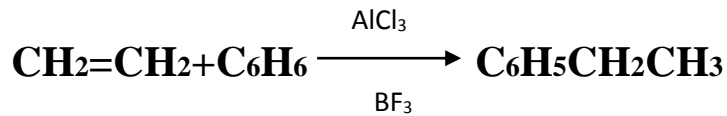
MTBE is recovered as the bottoms product of the distillation unit. The methanol-rich C4 distillate is sent to the methanol-recovery section. Water is used to extract excess methanol and recycle it back to process. The isobutene-depleted C4 stream may be sent to a raffinate stripper or to a molsieve-based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

Uses: Octane booster.

Benzene derivative:

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.

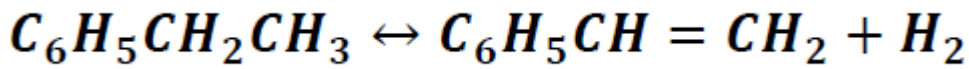
Description: The CD alkylator stripper (1) operates as a distillation column.

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.

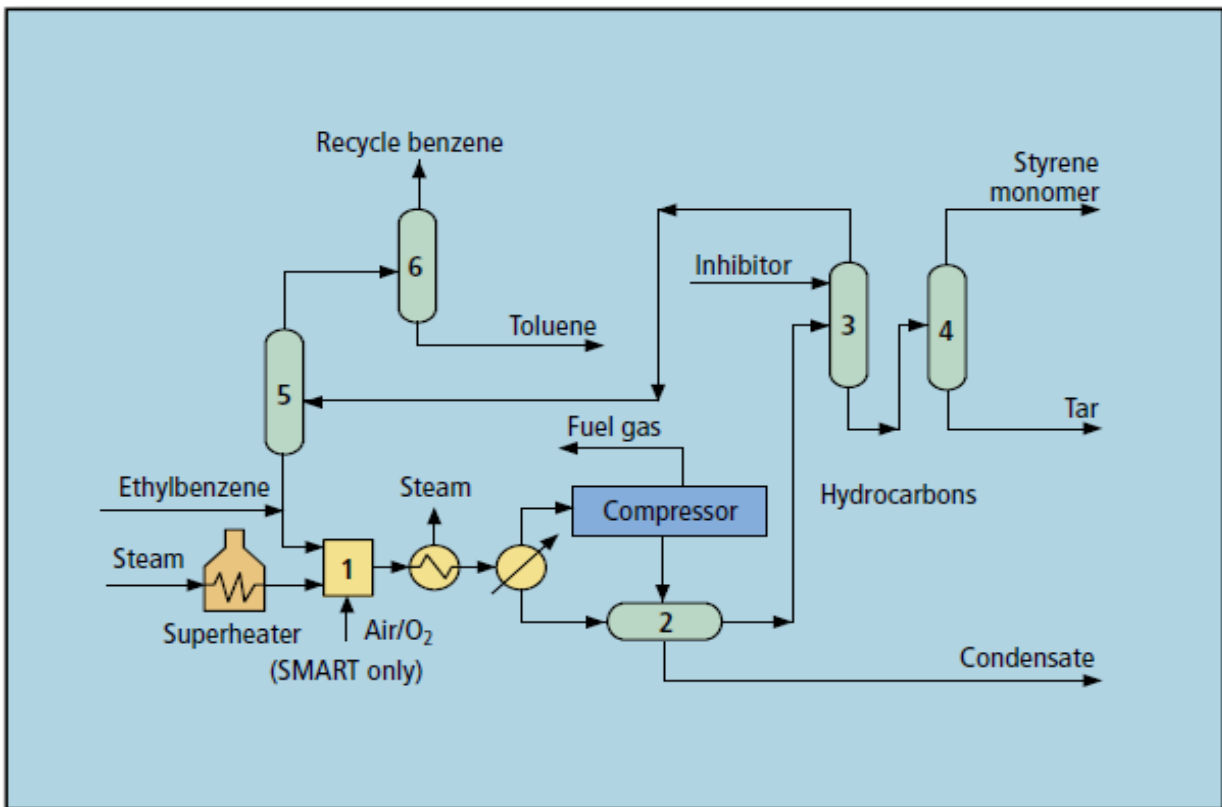
Uses: 0.5 consumption of B:in EB production: which is used in production of styrene.

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.

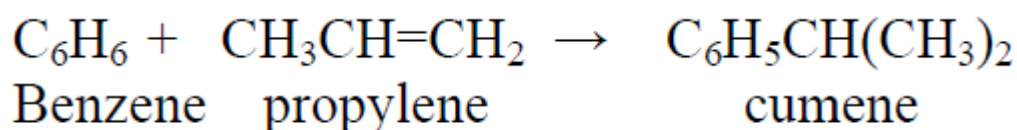
Description: In the Classic SM process, EB is catalytically dehydrogenated to styrene in the presence of steam. The vapor phase reaction is carried out at high temperature under vacuum. The EB (fresh and recycle) is combined with superheated steam, and the mixture is dehydrogenated in a multistage reactor 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.

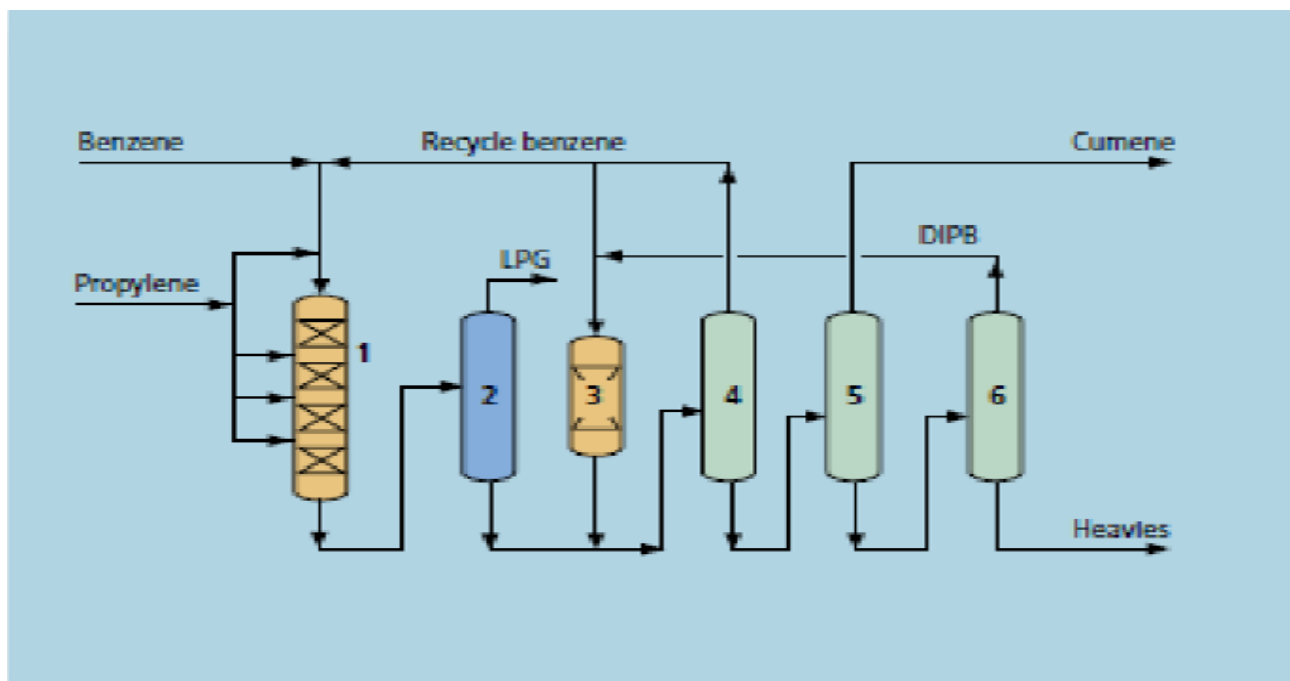
A fractionation train (3,4) separates high-purity styrene product, unconverted EB, which is recycled, and the relatively minor byproduct tar, which is used as fuel. Toluene is produced (5,6) as a minor byproduct and benzene (6) is normally recycled to the upstream EB process.

Typical SM product purity ranges 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.

Cumene:



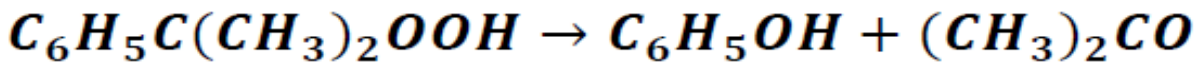
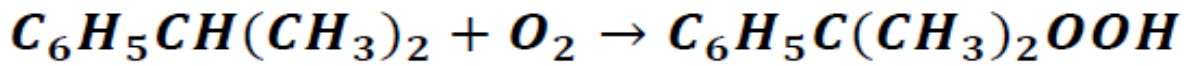
Application: To produce high-quality cumene (isopropylbenzene) by alkylating benzene with propylene (typically refinery or chemical grade) using liquid-phase Q-Max process based on zeolitic catalyst technology.



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). Diisopropylbenzene (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, on-steel construction is possible. Catalyst cycle lengths are two years and longer. The catalyst is

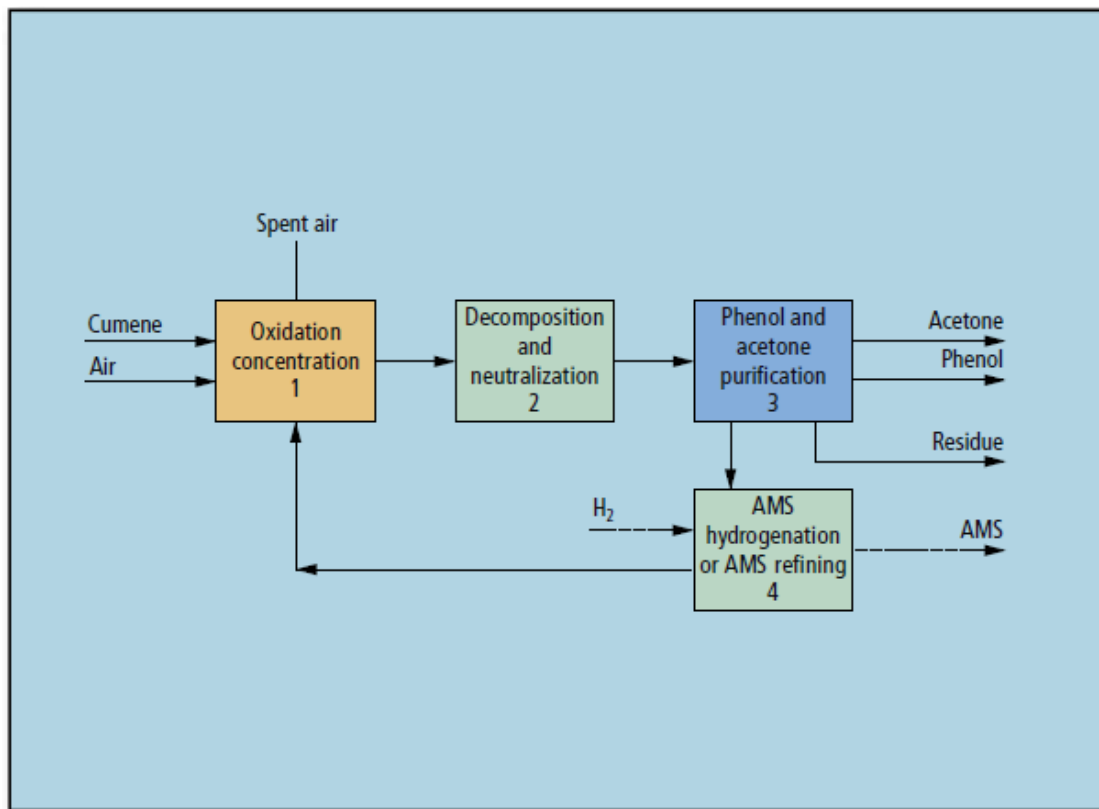
fully regenerable for an ultimate catalyst life of six years and longer. Existing plants that use SPA or AlCl_3 catalyst can be revamped to gain the advantages of Q-Max cumene technology while increasing plant capacity.

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) 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. This unique design achieves a very high selectivity to phenol, acetone. The high total yields from oxidation and decomposition combine to achieve 1.31wt cumene/wt phenol without tar cracking.

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.

Uses: Raw materials or intermediate for production of:

1- Phenol-formaldehyde resins 2- Bisphenol (for production of epoxy)

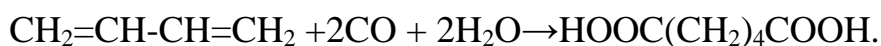
3- Caprolactum (for production of Nylon 6 monomer) 4- Adipic acid (for production of Nylon 66 monomer) 5- Salicylic acid (Aspirin production)

6- Phenol alkyl (Rubber chemical) or (production of Detergent).

Adipic acid :



Raw materials: Butadiene, CO & H₂O.



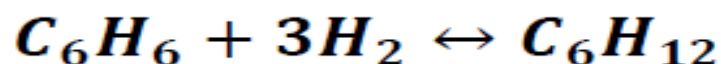
Butadiene

Adipic acid

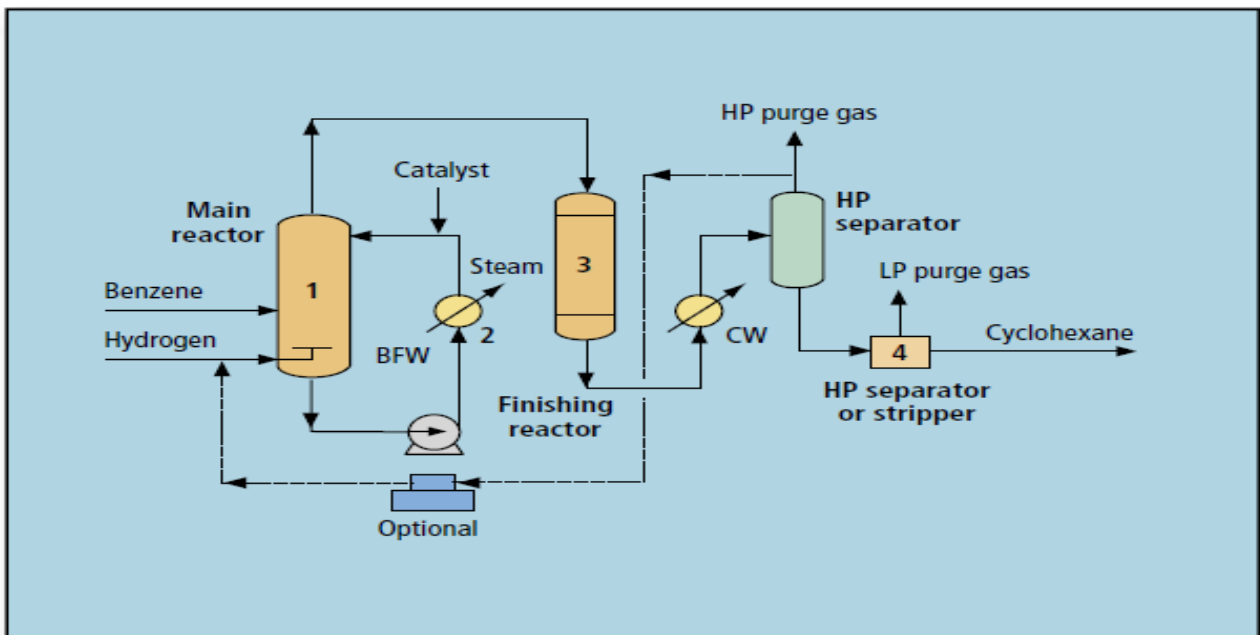
T=220°C P=75 atm. Cata: $\text{RdCl}_2/\text{CH}_3\text{I}$ Yield" 49%

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

Cyclohexane:



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



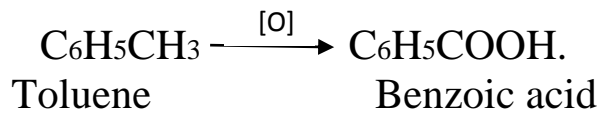
Description: The main reactor (1) converts essentially all the feed isothermally in the liquid phase at a thermodynamically-favorable low temperature using a continuously-injected soluble catalyst. The catalyst's high activity allows use of low hydrogen partial pressure, which results in fewer side reactions, e.g., isomerization or hydrocracking. The heat of reaction vaporizes cyclohexane product and, using pump around 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.

advantage of the liquid-phase process 1- lower cost compared to vapor phase processes 2- 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.

Toluene derivatives:

Benzoic acid C₆H₅COOH:

Raw materials: Toluene ,oxygen



Oxidation of toluene in liquid phase

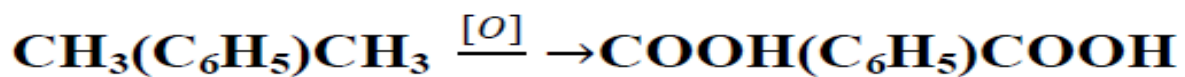
Cata.: Cobalt salt at T=165°C. or

Cobalt bromide at T=140-165 °C

P=27 atm

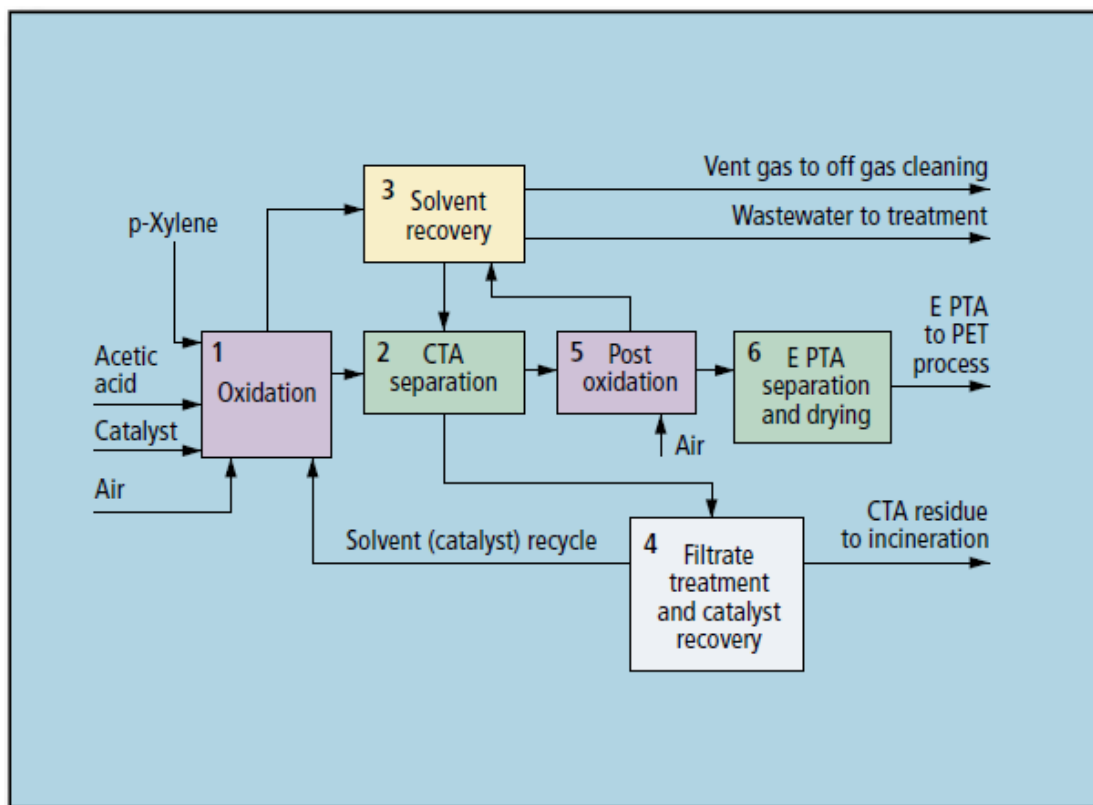
Xylene derivatives:

Terephthalic acid (EPTA) COOH(C₆H₅)COOH



P-xylene

TPA



Uses; 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: 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.

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.