Synthetic Organic Chemical Industries

Petrochemicals

Chemicals form C_1, C_2, C_3, C_4 Compounds

Chemicals from Aromatics

PETROCHEMICALS

- Petrochemicals refers to all those compounds that can be derived from the petroleum refinery products .

- Petrochemicals play an important role on our food, clothing, shelter and leisure. Because of low cost and easy availability, oil and natural gas are considered to be the main sources of raw materials for most petrochemicals.

Principal Raw Materials

Typical feedstocks to petrochemical processes include

- Natural Gas (largely methane, ~ 4% ethane)
- Liquefied Petroleum Gas (Propane, Butane)
- Refinery Off-Gases (Hydrogen, H_2S)
- Hydroforming (Benzene, Toluene, Xylene)
- Naphtha and Fuel Oil
- Petroleum Coke

Classification

- Petrochemicals can be broadly classified into three categories-

  a) **Light Petrochemicals:** These are mainly used as bottled fuel and raw materials for other organic chemicals. The lightest of these -- methane, ethane and ethylene -- are gaseous at room temperature. The next lightest fractions comprise petroleum ether and light naphtha with boiling points between 30 and 160˚C.

  b) **Medium Petrochemicals:** Hydrocarbons with 6 – 12 carbon atoms are called "gasoline", which are mainly used as automobile fuels. Octane, with eight carbons, is a particularly good automobile fuel, and is considered to be of high quality. Kerosene contains 12 to 15 carbons and is used in aviation fuels, and also as solvents for heating and lighting.

  c) **Heavy Petrochemicals:** These can be generally categorized as diesel oil, heating oil and lubricating oil for engines and machinery. They contain around 15 and 18 carbon atoms with boiling points between 300 and 400˚C. The heaviest fractions of all are called "bitumens" and are used to surface roads or for waterproofing.

Chemicals from C_1 Compounds

Methanol

Formaldehyde

**Chloro-methanes**

14 April 2012

Methanol

- Methanol or methyl alcohol is colorless liquid with B.P. 65 ^{0}C.
- <u>Uses :</u> Production of acetic acid, formaldehyde, di-methyl ether, olefins etc.
- Methods of production
  - <u>Catalytic hydrogenation of carbon monoxide</u>
  - Oxidation of LPG to give oxygenated hydrocarbons
- Chemical Reactions Involved
  - $CO + 2H_2 \rightleftharpoons CH_3OH$ $\qquad \Delta H = -26.4$ kcal
- Side reactions
  - $CO + 3H_2 \rightarrow CH_4 + H_2O$ $\qquad \Delta H = -50$ Kcal
  - $2CO + 2H_2 \rightarrow CH_4 + CO_2$ $\qquad \Delta H = -60.3$ Kcal
  - $xCO + yH_2 \rightarrow$ Higher mol wt. alcohols and hydrocarbons

Manufacture of Methanol from Synthesis Gas

- Synthesis gas is mixture of $H_2 + CO$ in various ratios.
- When synthesis gas is subjected to high pressure and moderate temperature conditions, it converts to methanol.
- Followed by this, the methanol is separated using a series of phase separators and distillation columns.
- Synthesis gas preparation (Steam reforming)
  - $H_2 : CO = 2.25$
- Methanol Production
  - Catalyst : $Cu/ZnO/Cr_2O_3/Al_2O_3$
  - $T = 300\text{-}375\ ^0C$
- Methanol Purification
  - Permanganate
  - Stripping
  - Fractionation

Methanol Production Technology
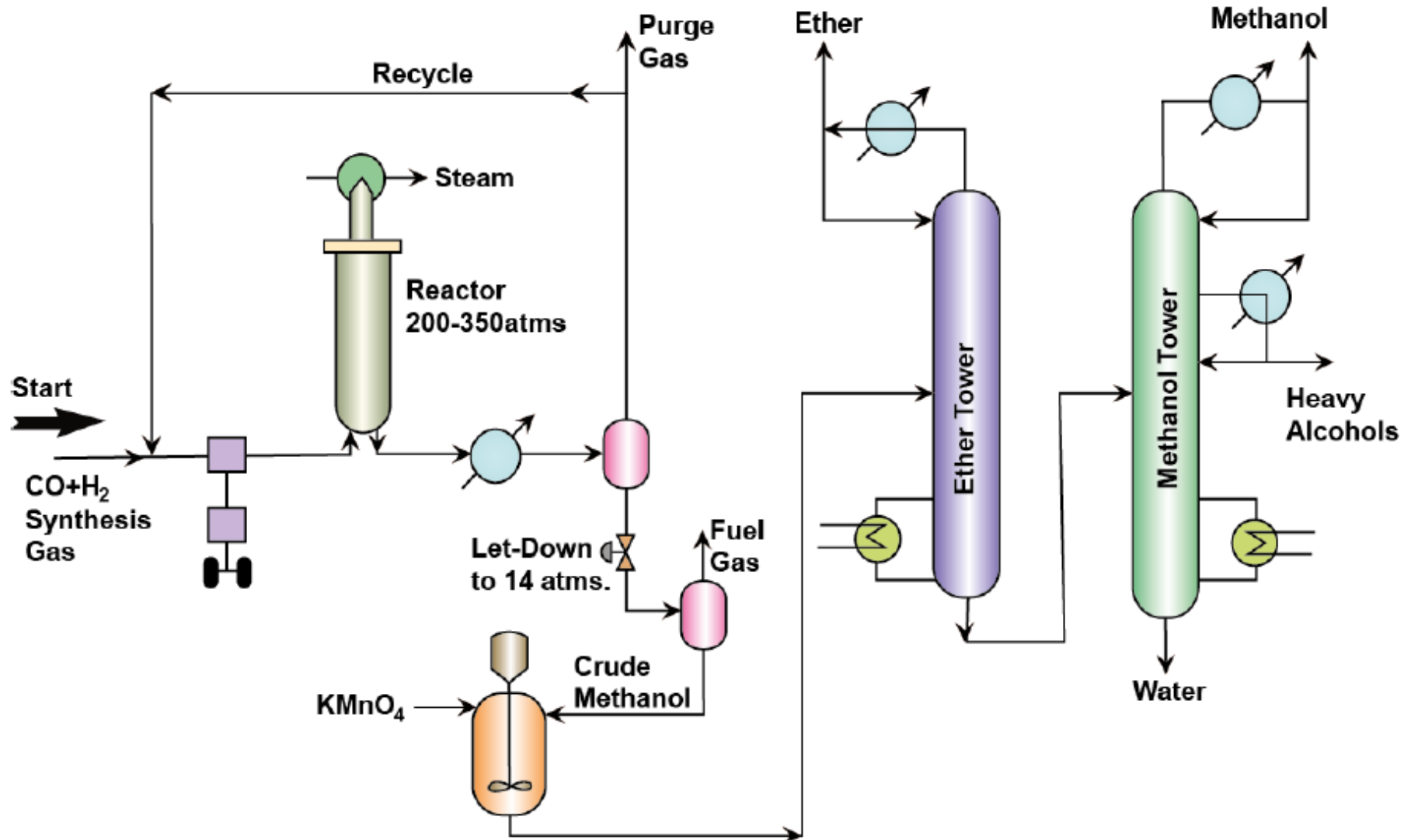
Process Description

- H_2 and CO adjusted to molar ratio of 2.25

- The mixture is compressed to $200 - 350$ atms.

- Recycle gas (Unreacted feed) is also mixed and sent to the compressor

- Then eventually the mixture is fed to a reactor. Steam is circulated in the heating tubes to maintain a temperature of $300 - 375$ ˚C

- After reaction, the exit gases are cooled

- After cooling, phase separation is allowed. In this phase separation operation methanol and other high molecular weight compounds enter the liquid phase and unreacted feed is produced as the gas phase.

- The gas phase stream is purged to remove inert components and most of the gas stream is sent as a recycle to the reactor.

- The liquid stream is further depressurized to about 14 atms to enter a second phase separator that produces fuel gas as the gaseous product and the liquid stream bereft of the fuel gas components is rich of the methanol component.

- The liquid stream then enters a mixer fed with $KMNO_4$ so as to remove traces of impurities such as ketones, aldehydes etc.

- Eventually, the liquid stream enters a distillation column that separates dimethyl ether as a top product.

- The bottom product from the first distillation column enters a fractionator that produces methanol, other high molecular weight alcohols and water as three different products.

Major engineering problems

- Thermodynamic and kinetic considerations of synthesis gas
  - Temp. < 260 ^{0}C is not economic
  - Pressure : balance between pressurized reactor & recycle cost
  - Optimum condition : 50% conversion per pass at 240 atm and 300 ^{0}C
- Reactor design
  - Thick walled Pr vessel (steel) lined with Cu
  - Heat exchange to control highly exothermic reaction
    - Use of compressed gas, flow in shell. Catalyst zones bleed of cold gas
  - Circulating high Pr water and waste heat boiler
- Catalyst fouling
  - Excess H_2 to avoid higher mol. wt. material
- Inert gas accumulation
  - During high recycle loads, inert gas accumulation can avoid by side stream purge on the recycle gas.
- Modern Process are low pressure processes (50 bar).

Formaldehyde (HCHO)

- Properties :   B.P. = -19C
  - Solubility : Soluble in water, alcohol and polar solvent, slightly soluble in HC's

- Methods of production
  - Catalytic oxidation -dehydrogenation of methanol
  - Oxidation of methane or LPG to give oxygenated hydrocarbon

- Chemical Reactions
  - $CH_3OH + \frac{1}{2} O_2 \rightleftharpoons HCHO + H_2O$ $\Delta H = -37$ Kcal
  - $CH_3OH \rightarrow HCHO + H_2$ $\Delta H = +19.8$ Kcal
  - Side reaction- complete combustion
  - $CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -162$ Kcal

- The reactions are carried out in vapor phase.
- Catalyst: Silver or zinc oxide(Ag/ Cu) gauze catalysts on wire gauge are used.
- Operating conditions: Near about atmospheric pressure and temperature 500 – 600 ˚C

Process description
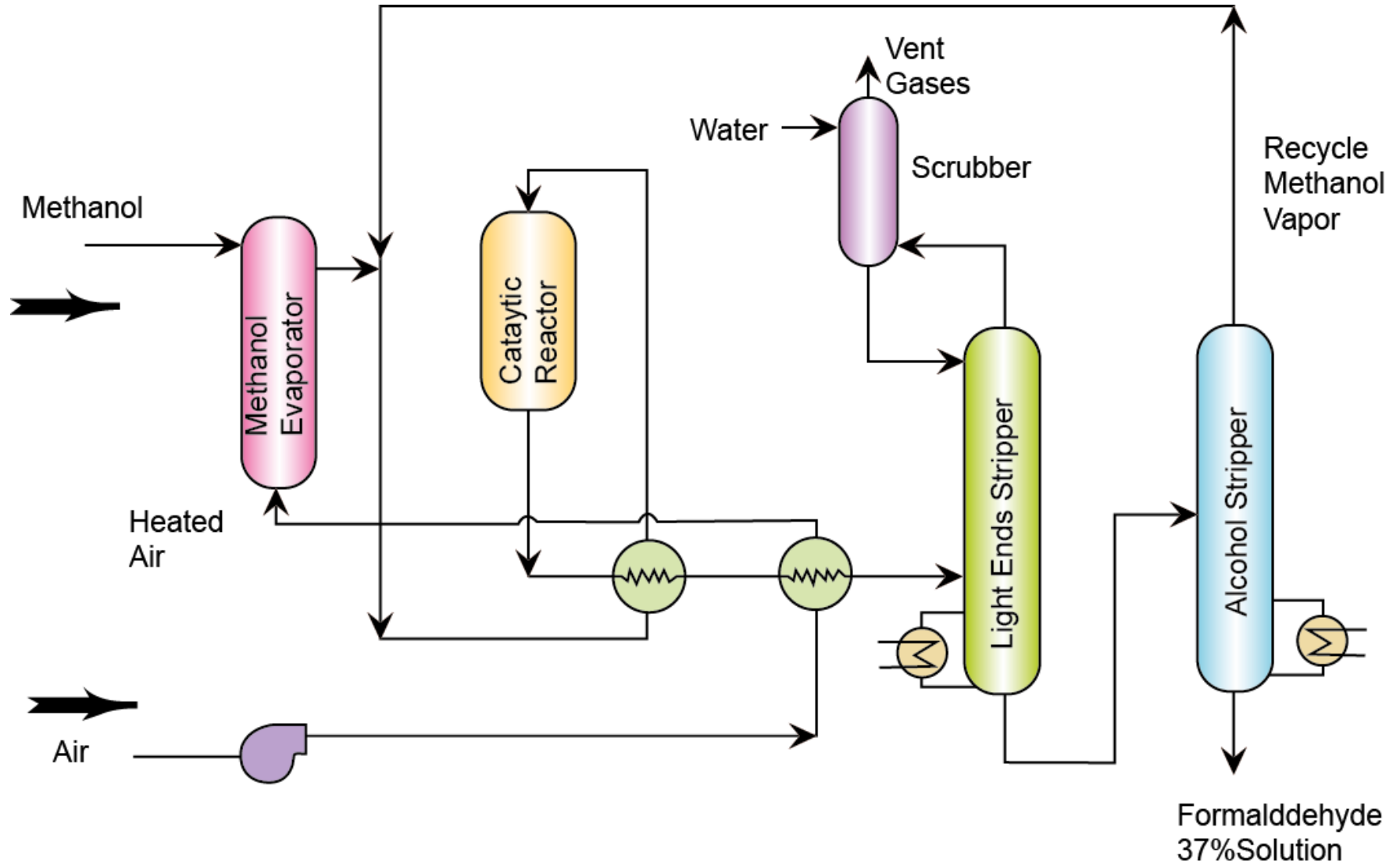
Process Description

- Air is sent for pre-heating using reactor outlet product and heat integration concept.
- Eventually heated air and methanol are fed to a methanol evaporator unit which enables the evaporation of methanol as well as mixing with air. The reactor inlet temperature is 54 ˚C.
- The feed ratio is about $30 - 50 \%$ for CH_3OH: O_2
- After reaction, the product is a vapor mixture with temperature $450 - 900$ ˚ C
- After reaction, the product gas is cooled with the heat integration concept and then eventually fed to the absorption tower.
- The absorbent in the absorption tower is water as well as formaldehyde rich water.
- Since formaldehyde rich water is produced in the absorption, a portion of the rich water absorbent solution from the absorber is partially recycled at a specific section of the absorber.
- From the absorber, HCHO + methanol rich water stream is obtained as the bottom product.
- The stream is sent to a light end stripper eventually to remove any light end compounds that got absorbed in the stream. The vapors from the light end unit consisting of light end compounds can be fed at the absorption unit at specific location that matches with the composition of the vapors in the absorption column.
- Eventually, the light end stripper bottom product is fed to a distillation tower that produces methanol vapor as the top product and the bottom formaldehyde + water product (37 % formaldehyde concentration).
- Pure formaldehyde is not stable and tends to produce a trimer or polymer. Formaldehyde is stable in only water and therefore, 37% formaldehyde solution with $3 - 15 \%$ methanol (stabilizer) is produced as formalin and sold.

Major engineering problems

- Methanol conversion
  - Catalyst provides a heat balance via two reactions, which require some methanol recycle.
  - Process modification with mixed oxide catalyst Mo, V and/or Fe has given > 90% yield with no methanol recycle.

- Choice of space velocity
  - Low space velocity results in high combustion to $CO+CO_2$
  - High velocity results in low methanol conversion
  - The compromise finds 4-5% $CO+CO_2$ in the reactor tail gas

Chloromethanes

- The direct chlorination of methane (without any catalyst) leads to a series of chloromethanes

	Density (g/cc)	B.P. ($^\circ$C)
Methyl chloride CH_3Cl	0.92	-24.1
Methylene chloride CH_2Cl_2	1.33	40.1
Chloroform $CHCl_3$	1.49	61.2
Carbon tetrachloride CCl_4	1.59	76.8

- Uses
  - Solvents
  - Intermediated products
  - CCl_4 and $CHCl_3$ for synthesis of hydrocarbons containing F and Cl

- **Methods of production**
  - Direct thermal methane chlorination
  - CH_3Cl by reaction of CH_3OH + HCl
  - CCl_4 by reaction of CS_2 + Cl_2 – older process

- **Methane Chlorination**
  - Chemical reactions

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

  - Highly exothermic reactions ($-\Delta H$= 24 Kcal/mole)
  - The feed molar ratio affects the product distribution. When CH_4/Cl_2 is about 1.8, then more CH_3Cl is produced. On the other hand, when CH_4 is chosen as a limiting reactant, more of CCl_4 is produced. Therefore, depending upon the product demand, the feed ratio is adjusted.

Flow Sheet : Chloromethane Production
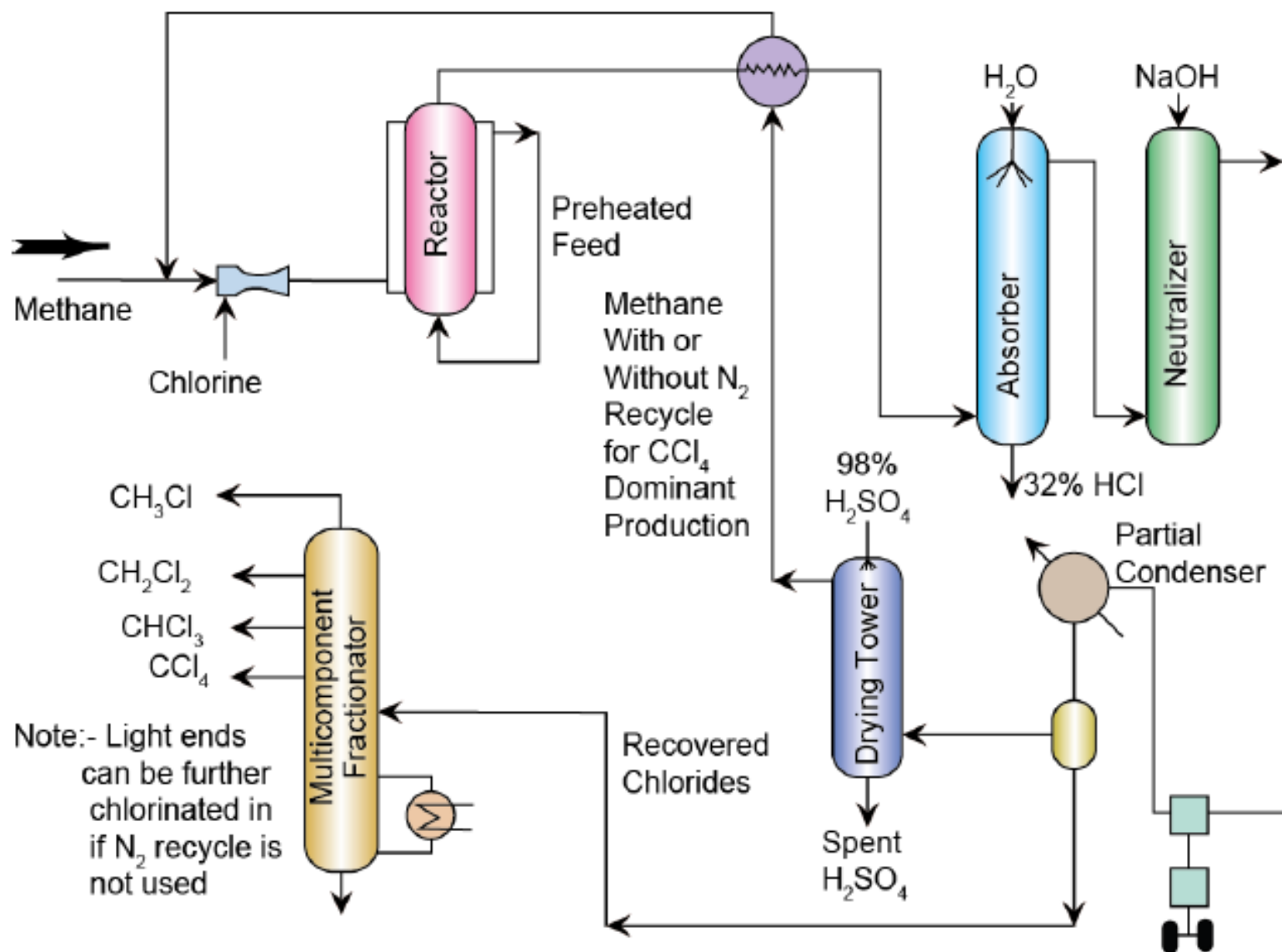
Process Description

- Methane and Cl_2 are mixed and sent to a furnace
- The furnace has a jacket or shell and tube system to accommodate feed pre-heating to desired furnace inlet temperature (about $280 - 300$ °C).
- To control temperature, N_2 is used as a diluent.
- Depending on the product distribution desired, the CH_4/Cl_2 ratio is chosen.
- The product gases enter an integrated heat exchanger that receives separated CH_4 (or a mixture of $CH_4 + N2$) and gets cooled from the furnace exit temperature (about 400°C).
- Eventually, the mixture enters an absorber where water is used as an absorbent and water absorbs the HCl to produce 32 % HCl.
- The trace amounts of HCl in the vapor phase are removed in a neutralizer fed with NaOH
- The gas eventually is compressed and sent to a partial condenser followed with a phase separator. The phase separator produces two streams namely a liquid stream consisting of the chlorides and the unreacted CH_4/N_2.
- The gaseous product enters a dryer to remove H_2O from the vapor stream using 98% H_2SO_4 as the absorbent for water from the vapor.
- The chloromethanes enter a distillation sequence. The distillation sequence consists of columns that sequentially separate CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4.

Major engineering problems

- ## Reaction control
  - Highly exothermic reaction : can be explosive

I	II	III	II

0	2	4	6	8	10	12	14	16	18

  Reaction rate conditions as Cl_2 / CH_4 mole ratio
    - I process operating conditions
    - II burning or uncontrolled heat liberation
    - III detonation condition
  - Methane recycle, use diluent gas N_2, use liquid co solvent , add Cl_2 stage wise along the reactor

- ## Product ratio control
  - CH_3Cl produces largely but demand is for $CHCl_3$ & CCl_4
    - CH_4 / Cl_2 ratio 0.5 to 0.8 with N_2 diluent and operation with recycle
  - Strip out light chlorinated product and add excess chlorine

- ## Utilization of HCl to produce more CH$_3$Cl
  - Methanol root to produce methyl chloride
    - Vapor phase reaction- Alumina catalyst
    - Liquid phase reaction- Zn or aluminum chloride
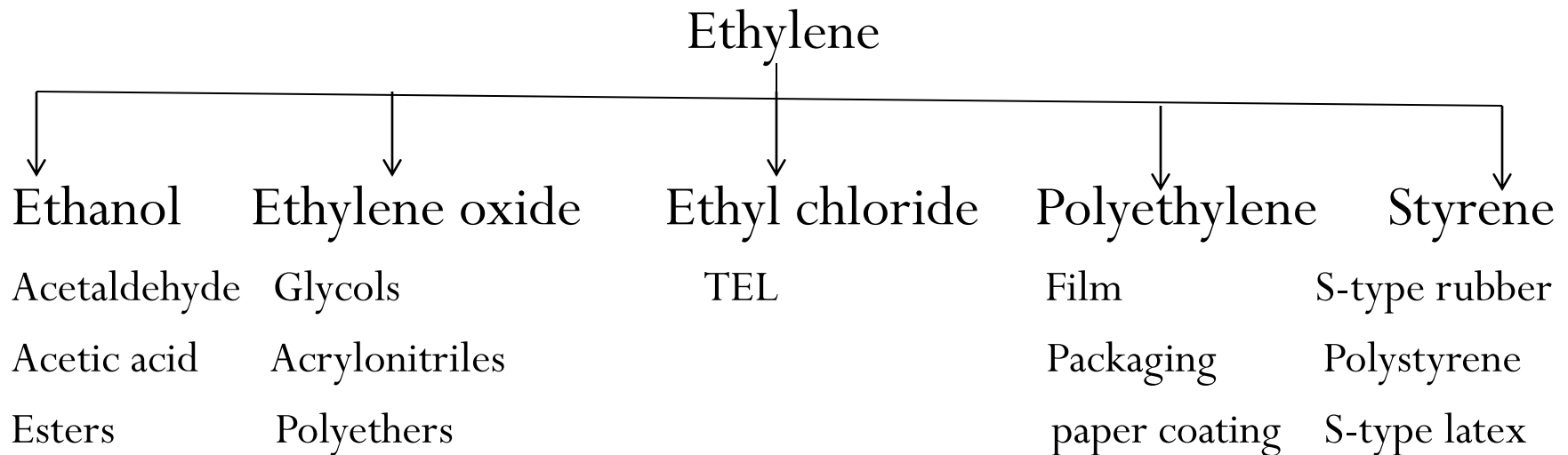
Chemicals From C_2 Compounds

Ethylene and Acetylene

Ethylene Dichloride

Vinyl Chloride Monomer
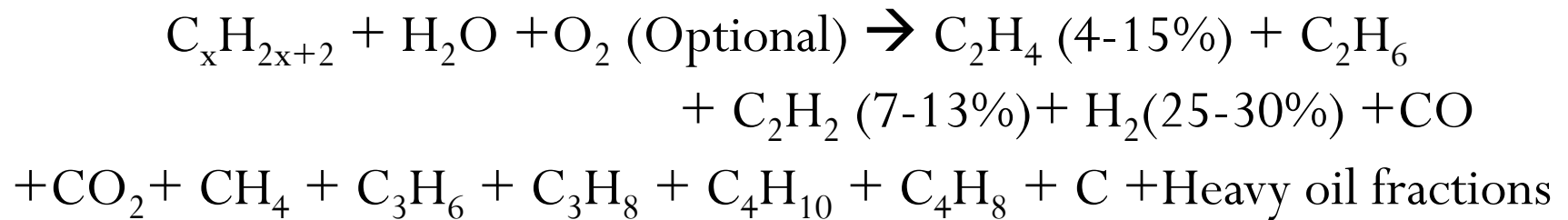
Ethylene and Acetylene
(Via steam cracking of hydrocarbon)

- The steam cracking process produces ethylene/acetylene in ratio of 0.3 to 2.0 depending on operating conditions.

- Consumption Pattern

Ethylene

Ethanol	Ethylene oxide	Ethyl chloride	Polyethylene	Styrene
Acetaldehyde	Glycols	TEL	Film	S-type rubber
Acetic acid	Acrylonitriles		Packaging	Polystyrene
Esters	Polyethers		paper coating	S-type latex

# Various methods of production

- Steam pyrolysis (cracking) of petroleum from LPG and naphtha feedstocks

- Thermal pyrolysis of ethane/propane

- Separation from refinery gases – Limited amount

- Dehydration of ethanol- not competitive for large-scale requirements

Steam Cracking of Petroleum Hydrocarbons

$$C_xH_{2x+2} + H_2O + O_2 \text{ (Optional)} \rightarrow C_2H_4 \text{ (4-15\%)} + C_2H_6$$
$$+ C_2H_2 \text{ (7-13\%)} + H_2 \text{(25-30\%)} + CO$$

$+ CO_2 + CH_4 + C_3H_6 + C_3H_8 + C_4H_{10} + C_4H_8 + C + \text{Heavy oil fractions}$

- The reaction is pretty complex as we produce about 10 to 12 compounds in one go.

- The flowsheet will be reaction-separation-recycle system only in its topology. But the separation system will be pretty complex.

- Important separation tasks: Elimination of CO and CO_2, Purification of all products such as ethylene, acetylene etc.

- Typical feed stocks are Ethane, LPG & Naphtha

- Reaction temperature is about $700 - 800$ $^\circ$C (Vapor phase reaction).

Process flow chart
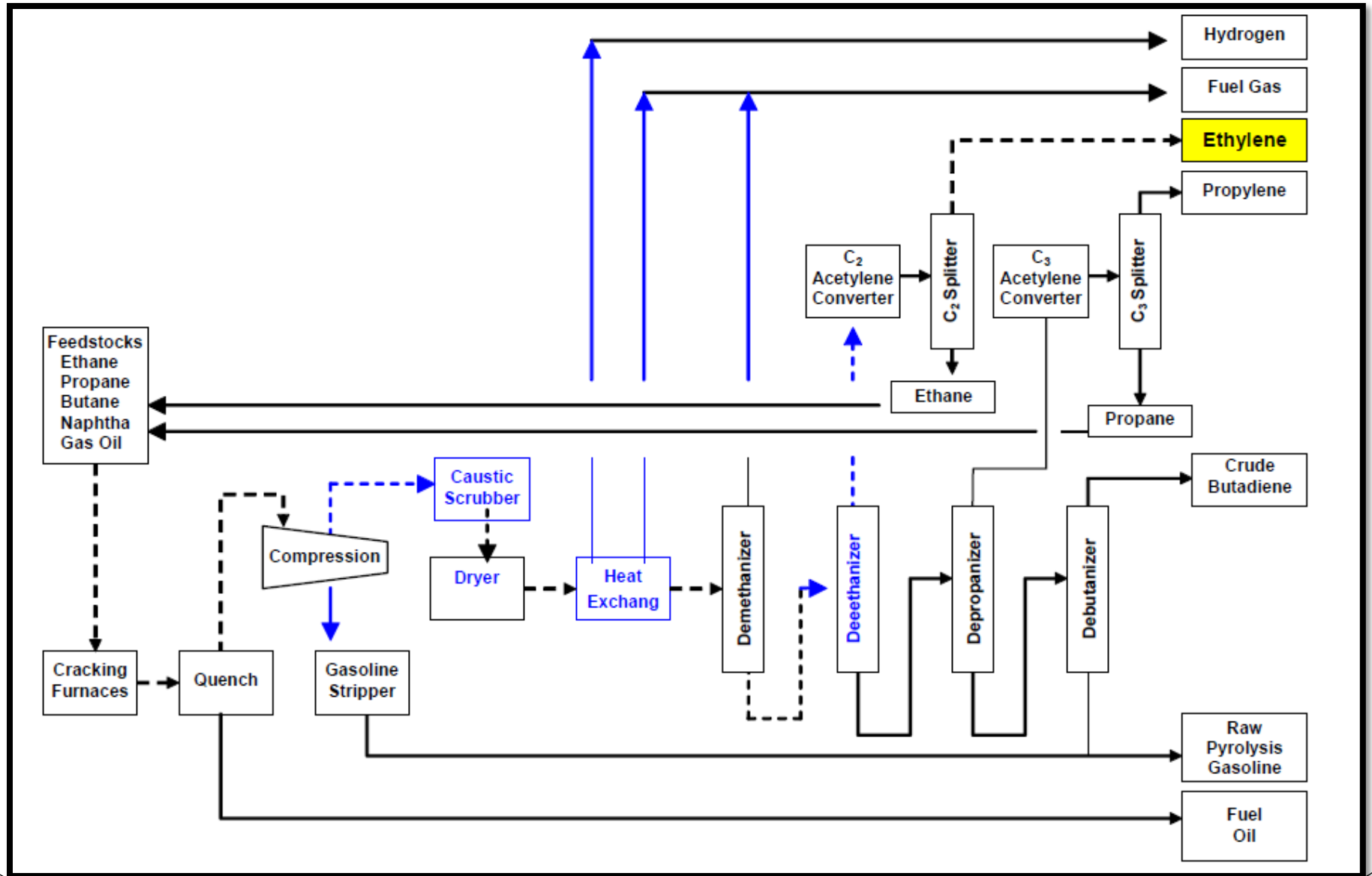
Process flow diagram
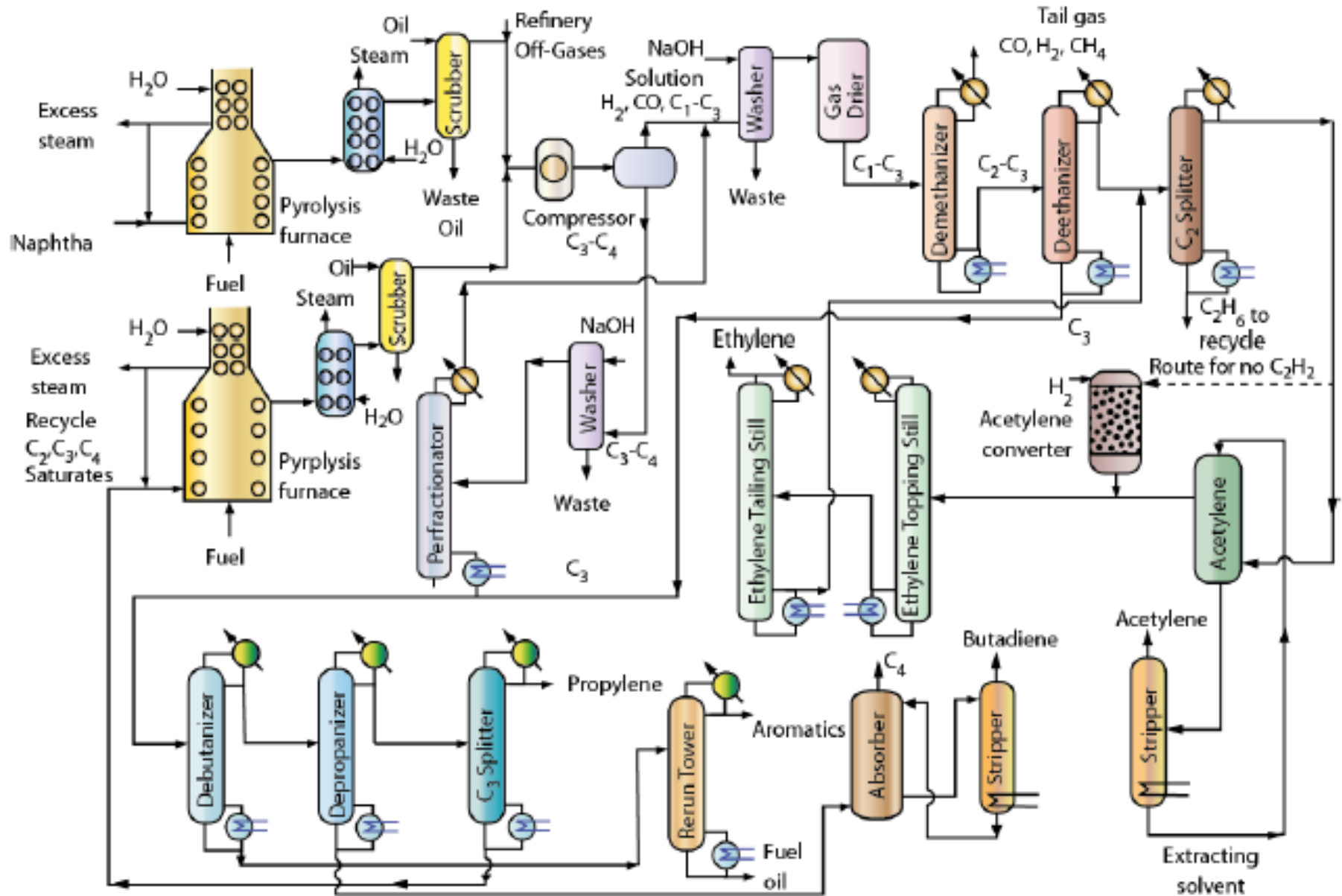
Major Engineering Issues

- Choice of process
  a) Feed type
     - CH_4 or natural gas-gives mainly CO, H_2 , C_2H_2
     - C_2, C_3 - gives CO, H_2 , C_2H_2, C_2H_4
     - C_4 and higher- spectrum of products

  b) Choice of pyrolysis agent
     - Heat only, non catalytic-original process (no longer attractive)
     - Heat + catalyst –used in dehydrogenation of butylene to butadiene
     - Heat + steam, non-catalytic – thermal reforming/ steam cracking
     - Heat + steam, catalytic – catalytic reforming (Synthesis gas preparation)
     - Oxygen, non-catalytic – partial combustion process (syn gas, acetylene)
     - Oxygen, steam, non-catalytic – modified partial combustion, more C_2

c.) Choice of pyrolysis equipment

Tubular, indirect fired – used for catalytic reaction

Coiled pipe furnace- used for non-catalytic reaction without oxygen

Combustion type burner- used for reaction where oxygen is introduced

Temperature, contact time, quench time for optimum cracking to the correct product ratio and yield with carbon formation
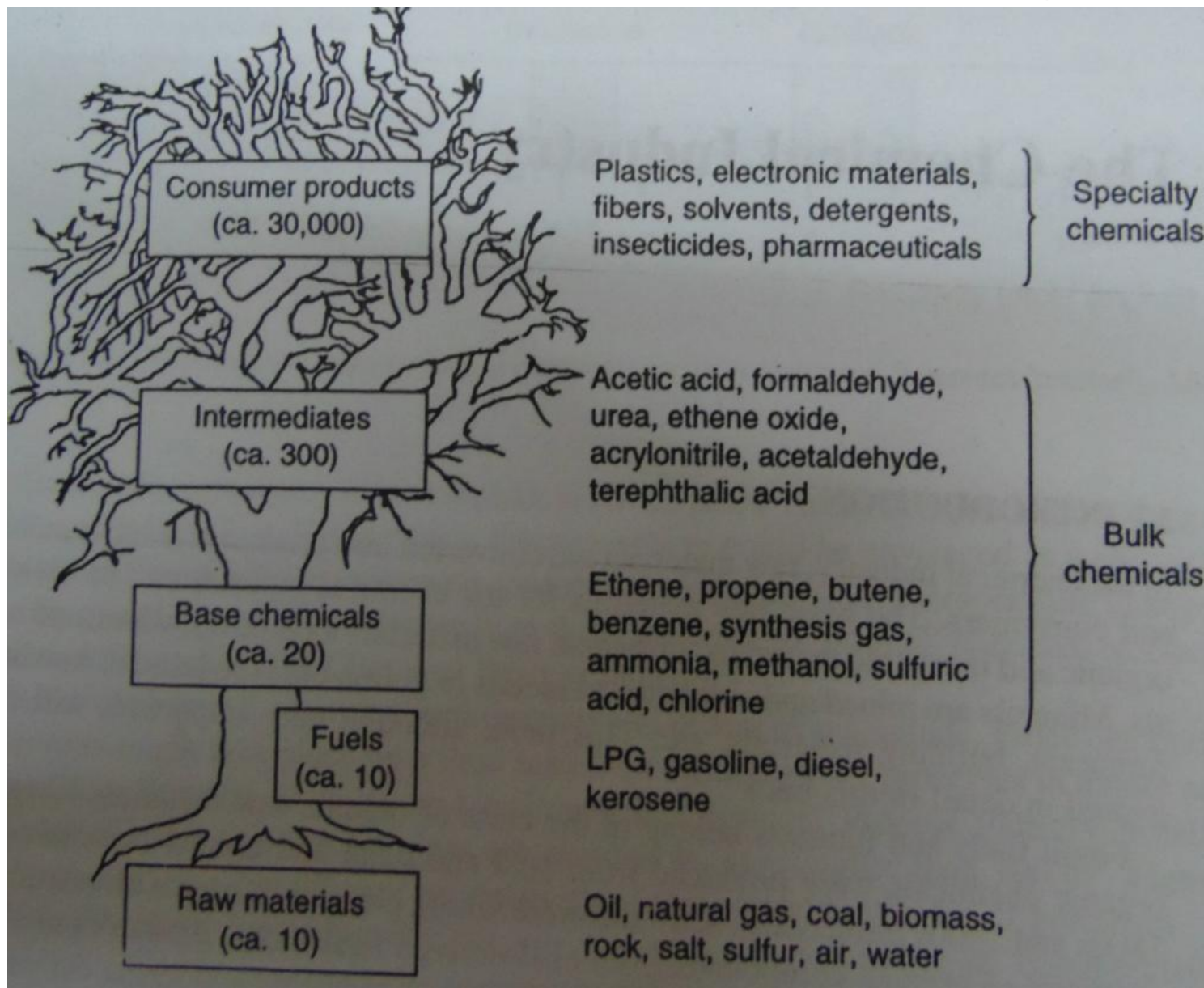
- Steam economy
  - Heat added in pyrolysis section can be recovered by incorporating stack and quench boiled heat transfer surface
  - Resulting high pressure steam makes the plant self –sufficient

- Product ratio control
  - The product effluent composition is controlled by steam-hydrocarbon mole ratio and residence time.
  - If no acetylene is desired, the light ends gas is split at the C_2 level and acetylene is mildly hydrogenated to ethylene.

Structure of chemical industry

Consumer products (ca. 30,000) — Plastics, electronic materials, fibers, solvents, detergents, insecticides, pharmaceuticals — Specialty chemicals

Intermediates (ca. 300) — Acetic acid, formaldehyde, urea, ethene oxide, acrylonitrile, acetaldehyde, terephthalic acid — Bulk chemicals

Base chemicals (ca. 20) — Ethene, propene, butene, benzene, synthesis gas, ammonia, methanol, sulfuric acid, chlorine — Bulk chemicals

Fuels (ca. 10) — LPG, gasoline, diesel, kerosene

Raw materials (ca. 10) — Oil, natural gas, coal, biomass, rock, salt, sulfur, air, water

Vinyl Chloride Monomer

Use : Precursor/ Raw material for Poly vinyl chloride (PVC)

Made from : Ethylene dichloride (EDC) or 1,2 – Dichloroethane

EDC & VCM process in conjunction

Vinyl Chloride Monomer (VCM)

- **Properties**
  - Molecular weight : 62.5
  - Boiling point : -13.9°C
  - Hence has a high vapor pressure at ambient temperature. It is therefore manufactured under strict quality and safety control.
- **Use :** Mainly as precursor (monomer/ raw material) for poly vinyl chloride (PVC) polymer.
- **Raw material**
  - Ethylene and chlorine produces ethylene dichloride (EDC) as intermediate product.
  - Further conversion of EDC to VCM

- Methods of production from ethylene (obtained from thermal cracking)
  - **Acetylene-HCl reaction**
    - High energy input
    - environmental impact as the use of the mercury-based catalyst involved
  - **Balanced Process (Pyrolysis)**
    - Direct chlorination $CH_2CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$ (EDC)
    - Oxychlorination $CH_2CH_2 + 2\ HCl + \frac{1}{2}\ O_2 \rightarrow$ EDC$+ H_2O$
    - EDC pyrolysis $2\ EDC \rightarrow 2\ CH_2CHCl$ (VCM) $+ 2\ HCl$
    - **Overall reaction**

      $$\textbf{2 CH}_2\textbf{CH}_2 + \textbf{Cl}_2 + \textbf{½ O}_2 \rightarrow \textbf{2 CH}_2\textbf{CHCl} + \textbf{H}_2\textbf{O}$$

    - No generation of HCl
   - 95% of the world's VCM is produced utilizing the balanced process

Balanced Process for VCM
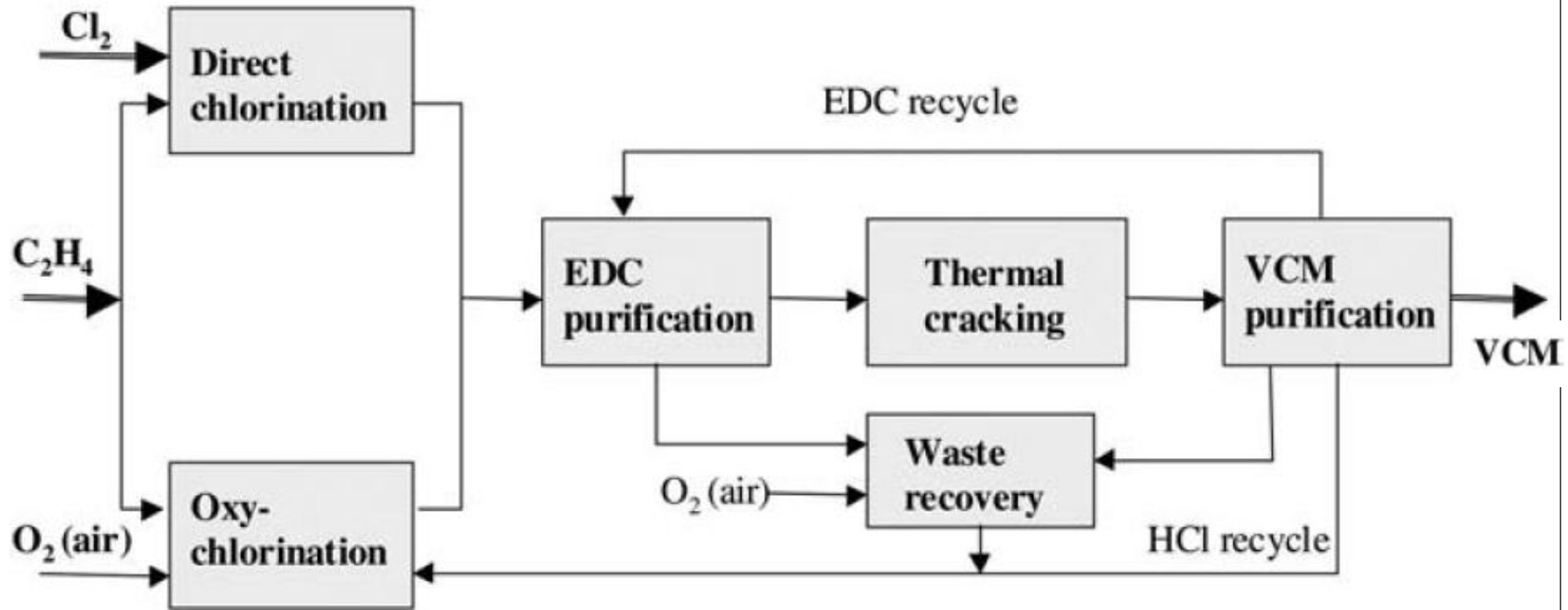
PROCESS DESCRIPTION

- Under the direct chlorination method, ethylene and chlorine (obtained from electrolysis of salt) react within a catalyst ($FeCl_3$),-containing reactor to form the intermediate material EDC.
  - T = 50-90 °C
- EDC is then thermally cracked to yield VCM.
- When the hydrogen chloride obtained as by-product from the above method reacts with ethylene in the presence of catalyst and air (or oxygen), EDC is obtained again. This is called the oxychlorination process.
  - Catalyst : copper chloride impregnated on alumina.
- T = 200°C and pressures of $1.5 - 5$ bar, in fixed - bed or fluid - bed reactors.
- When EDC from the oxychlorination process is dehydrated and then thermally cracked (together with the EDC from the direct chlorination process), VCM is obtained.
  - The endothermic reaction takes place at temperatures between 480- 550°C and pressures from 3 to 30 bar. The reaction device consists of a long tubular coil placed in a furnace.

- After pyrolysis, the mixture is submitted to rapid cooling by quench. This operation prevents further decomposition of VCM, but also removes the coke and other high - molecular impurities.

- **Liquid - Separation System** The mixture is shared approximately in equal parts between HCl, VCM and EDC.
  - Split 1: top HCl ($+C_2H_2$)/bottoms (VCM + EDC)
  - Split 2: top crude VCM/bottoms crude EDC
  - Split 3: top Lights (C_4H_5 Cl)/bottoms crude EDC
  - Split 4: top pure EDC/bottoms TCE and heavies
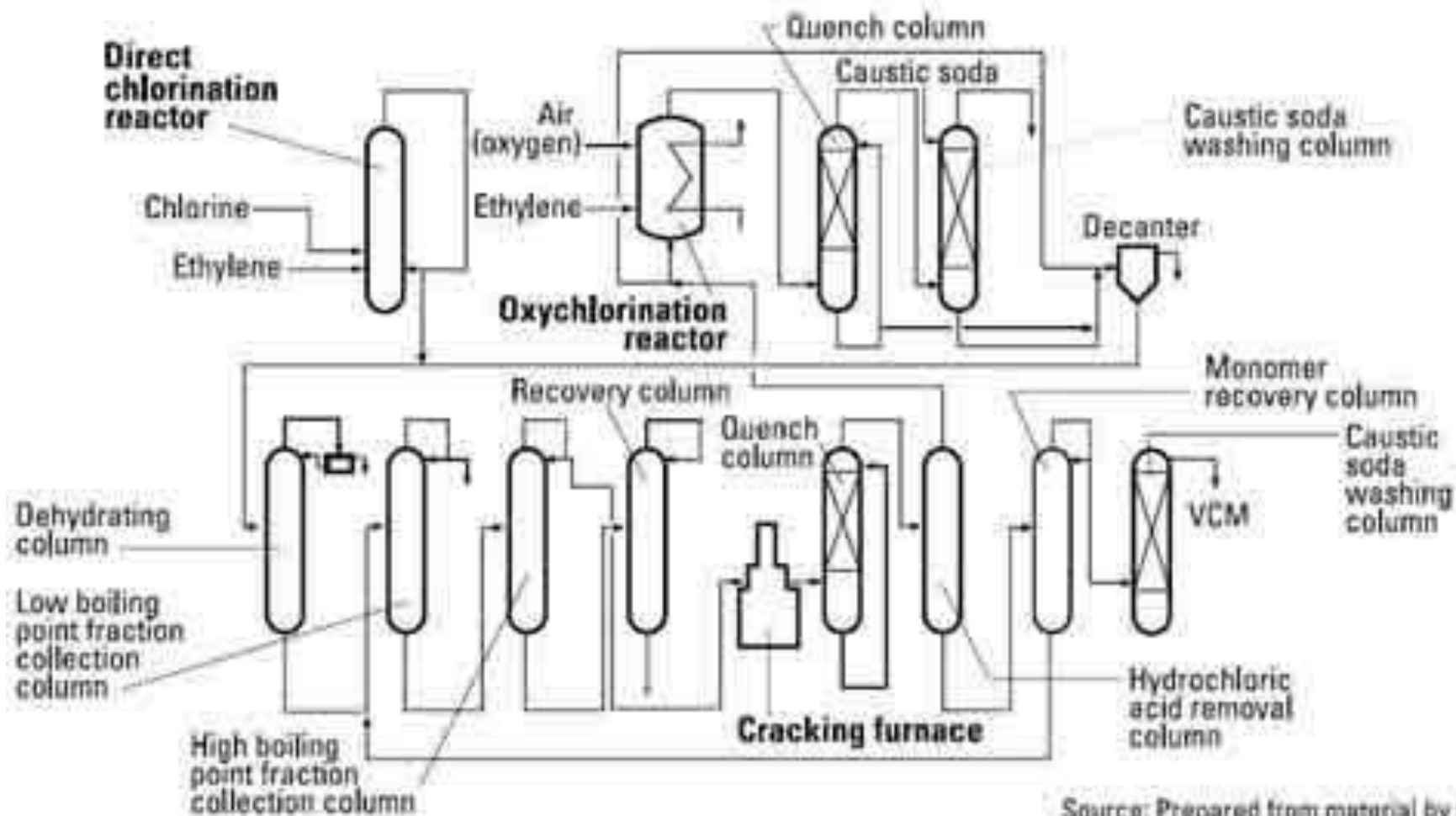
Source: Prepared from material by the JPI
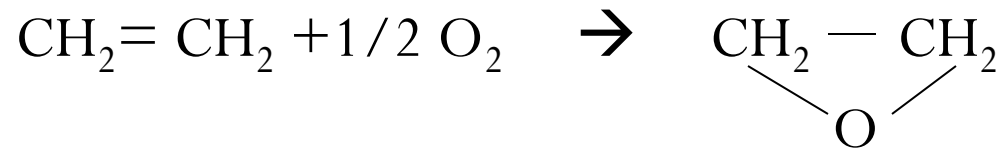
Major engineering problems

- **Carbon formation**
  - Occurs steadily until reactor has too high a pressure drop
  - Causing shut-down and periodic cleaning
  - Increasing conversion beyond 50% by longer residence time or higher temperature increase carbon formation and polymerization
  - Reactor conditions need to be worked out to optimize recycle loading versus reactor down time and loss of yield.
- **Excessive corrosion** : Can be avoid by keep the system free of water vapors
- Development of proper cracking catalyst that prevent polymerization during reaction.
- Stabilization of vinyl chloride monomer
  - Use antioxidants to avoid interference in polymerization process.
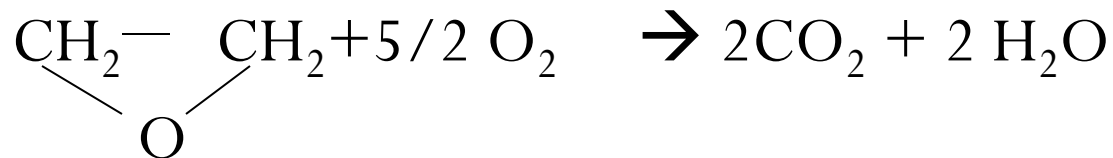
Ethylene Oxide

- Properties :

  - Mol wt : 44.05   B.P. = 10.7 ˚C

- Highly reactive chemical; an important raw material for production of ethylene glycol, ethanolamines, surfactant.

- Reaction is a good example of selective oxidation.

- Silver is the only metal known to catalyze this reaction with sufficient selectivity.

- <u>Methods of production</u>

  - Direct oxidation of ethylene (Air or oxygen)

  - Chlorohydrination of ethylene (Inefficient, cause major pollution problems)

Reactions & Kinetics

- Basic reaction

$$CH_2 = CH_2 + 1/2\ O_2 \rightarrow CH_2 - CH_2$$
$$\diagdown\ O\ \diagup$$

- Side reaction

$$CH_2 = CH_2 + 3\ O_2 \rightarrow 2CO_2 + 2\ H_2O$$

$$CH_2 - CH_2 + 5/2\ O_2 \rightarrow 2CO_2 + 2\ H_2O$$
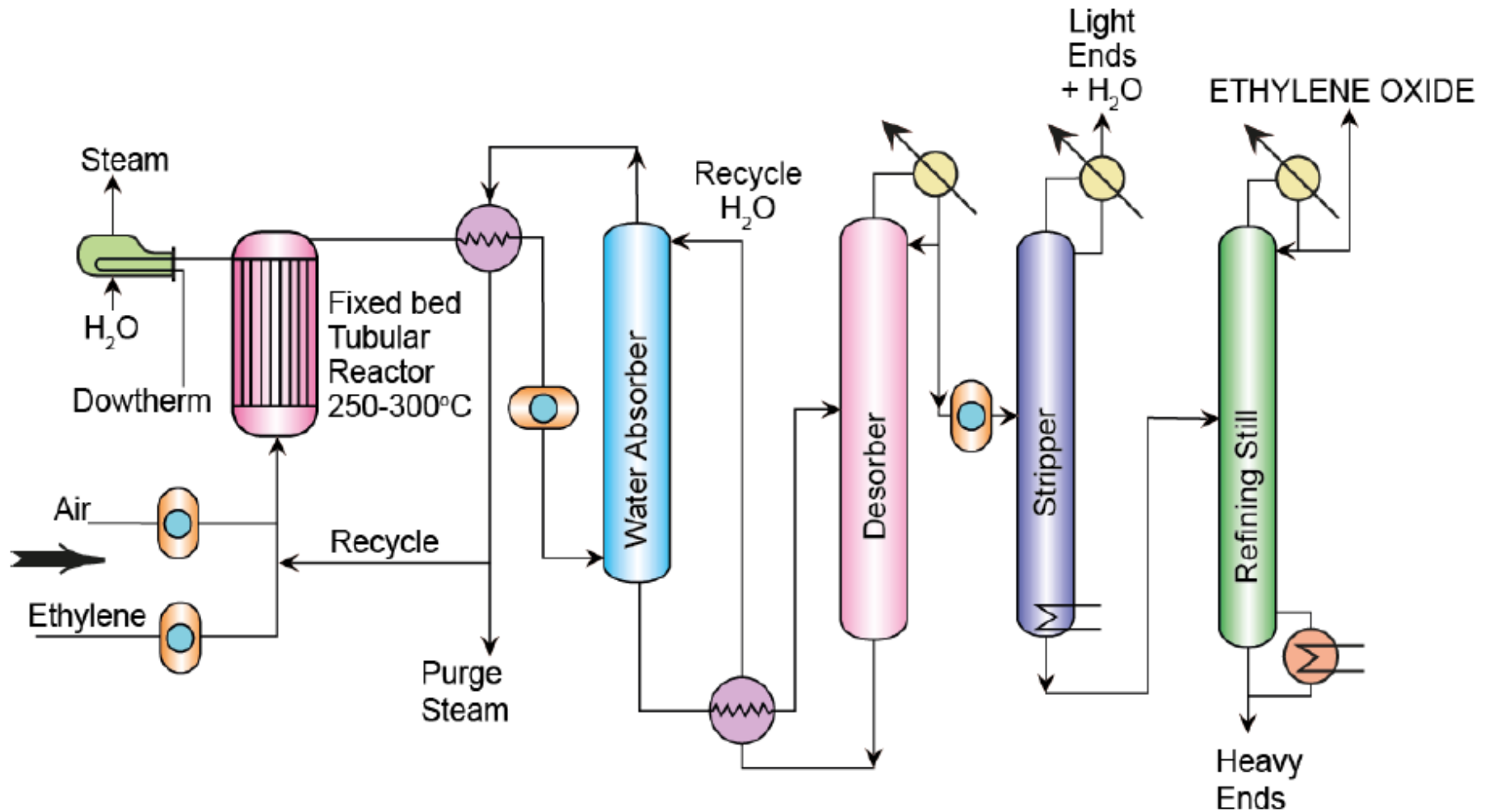$$\diagdown\ O\ \diagup$$

All 3 reactions are highly exothermic

Activation energy of undesired reactions > desired reaction

Temperature sensitive process, demands good T control.

Process Flow sheet

Process description

- Ethylene (95-98% purity) and oxygen (air with 95 mole % of oxygen) are mixed in a ratio of 1:10 by weight and passed over a catalyst consisting of silver oxide deposited on an inert carrier. Generally an anti catalyst such as ethylene dichloride (about 2% based on the weight of ethylene) is added to the ethylene feed to suppress the formation of carbon dioxide. At a pressure of 4-5 atmosphere and temperature of 250-300°C, when a contact time of 1 sec is used, about 50 % of ethylene is converted. 25% of the ethylene is converted to ethylene oxide.

- Commercial processes operate under recycle conditions in a packed bed multitubular reactor. The reactor is of shell and tube type comprised of several thousand mild steel or stainless steel tubes.

- The effluent gases from the reactor are washed with water under pressure in an absorber. The ethylene is absorbed and sent to a desorber to desorb the water, which is used for the absorption. This water is recycled.

- The overhead product from the desorber is sent to a steam stripper to remove the dissolved gases. The water- ethylene oxide mixture with small amount of ethylene and other impurities are fed to a fractionating column to purify the ethylene oxide to 99 mole%.

- **Ethylene oxide purification:** The main impurities in ethylene oxide are water, traces of carbon dioxide, acetaldehyde and formaldehyde. The water and heavy ends are removed in the distillation column, which works under atmospheric pressure.

- **Catalyst:** There are four basic components in commercial ethylene oxide catalyst: the active catalyst metal (silver); the bulk support (alumina, silicon carbide); catalyst promoters (alkaline earth metals) that increase selectivity and/or activity and improve catalyst life; and inhibitors or anticatalysts (organic halides) that suppress the formation of carbon dioxide and water without appreciably reducing the rate of formation of ethylene oxide.

- **Operating pressure:** Operating pressure has a marginal effect on the economics of the ethylene oxide process. High-pressure increases production due to higher gas density, increases heat transfer, increases ethylene oxide and carbon dioxide recovery in the absorber, and lower the compression costs. Also, since the total number of moles decreases in the formation of ethylene oxide from ethylene and oxygen, high pressure is consistent with high conversion. However high pressures reduce the flammable limit of the process gas as well as increase equipment costs. Typical pressures are 4-5 atmospheres.

Major Engineering Problems

- **Volume ratio of air-ethylene**
  - Low ethylene concentrations of 3-5% in air : explosion limit
  - Done by recycle inerts from absorber after side stream purge to remove some $CO_2 + H_2O$
  - Explosion hazards can be minimized by use of explosion-proof standards and careful operating procedures.
- **Use of series reactors**
  - Two reactor in series are used to convert more of ethylene
  - Economic balance between cost of ethylene and fixed charge on additional reactor

- **Air versus oxygen**
  - With oxygen, space time yield increased by 3-4 times
  - The absorber can be smaller since product concentrations are 6 times greater than with the air system
- **Fluidized bed versus fixed bed**
  - Fluid bed : ideal for heat control
  - Limitation : wide spread RTD due to mixing, catalyst sintering, transfer of AgO to vessel wall.
- **Hydration of ethylene oxide to glycol**
  - Hydration reaction is thermodynamically possible (T=150 ^{0}C)
  - Water is used in absorbing-desorbing train to maintain temperature 20-30 ^{0}C.
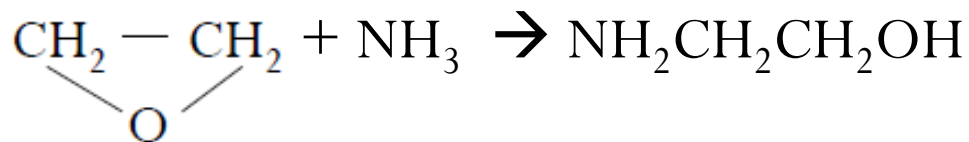
Ethanolamines

- In the industry received as a result of synthesis of ethylene oxides and ammonia. In the course of the further rectification Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA) are separated out.

- Properties

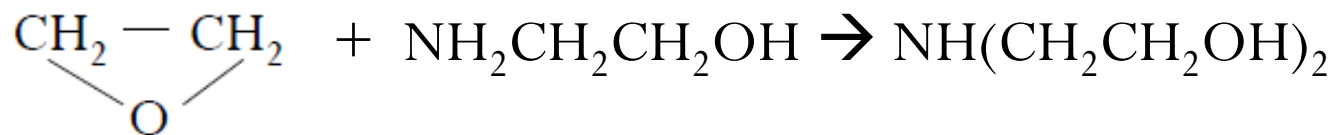|	MEA	DEA	TEA
B.P. (°C)	170.5	270 (decomp.)	360(decomp.)
Purity	80-98%, containing higher amines and water	94-95 %, containing MEA, TEA	80% technical grade with 2% MEA and 15% DEA, 98% high purity grade

- Ethanolamines are the base materials and are a part of compoundings of ready products in many sectors : from petro- and gas-processing, detergent in cement and metallurgical, to cosmetic, pharmaceutical and agricultural.

- At the moment the world demand for Ethanolamine exceeds 1,5 million tons per year, increasing by 5-7 % annually.
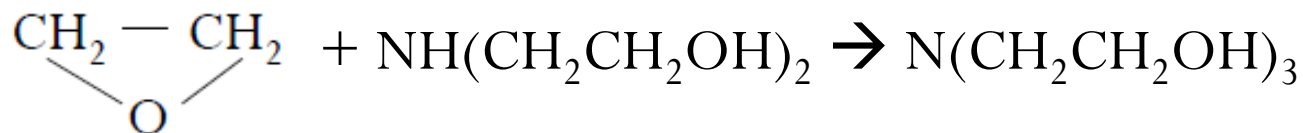
- **Chemical Reactions**
  - Reaction of ethylene oxide with ammonia

$$CH_2 - CH_2 \backslash O / + NH_3 \rightarrow NH_2CH_2CH_2OH \qquad \text{Monoethanolamine}$$

$$CH_2 - CH_2 \backslash O / + NH_2CH_2CH_2OH \rightarrow NH(CH_2CH_2OH)_2 \qquad \text{Diethanolaamine}$$

$$CH_2 - CH_2 \backslash O / + NH(CH_2CH_2OH)_2 \rightarrow N(CH_2CH_2OH)_3 \qquad \text{Triethanolamine}$$

- The above reactions are series reaction scheme.
- Reactions are exothermic.
- Ammonia is in aqueous phase and ethylene oxide is in vapor state. Therefore, the reaction will be gas-liquid reaction.

Process Description

- Manufacturing process of ethanolamine consists of the following stages:
  - Ethanolamine synthesis
  - Distilling off ammonium
  - Rectification – separation of individual ethanolamines
- Synthesis is carried out in a liquid phase from an ethylene and ammonia (25-30%) in the aqueous medium, at temperature of 40-80ºC and pressure of 20-40 atm. Reaction is autocatalytic and doesn't demand the special catalyst. Process is characterized by high output and quality of commercial ethanolamines.

Process Flow Diagram
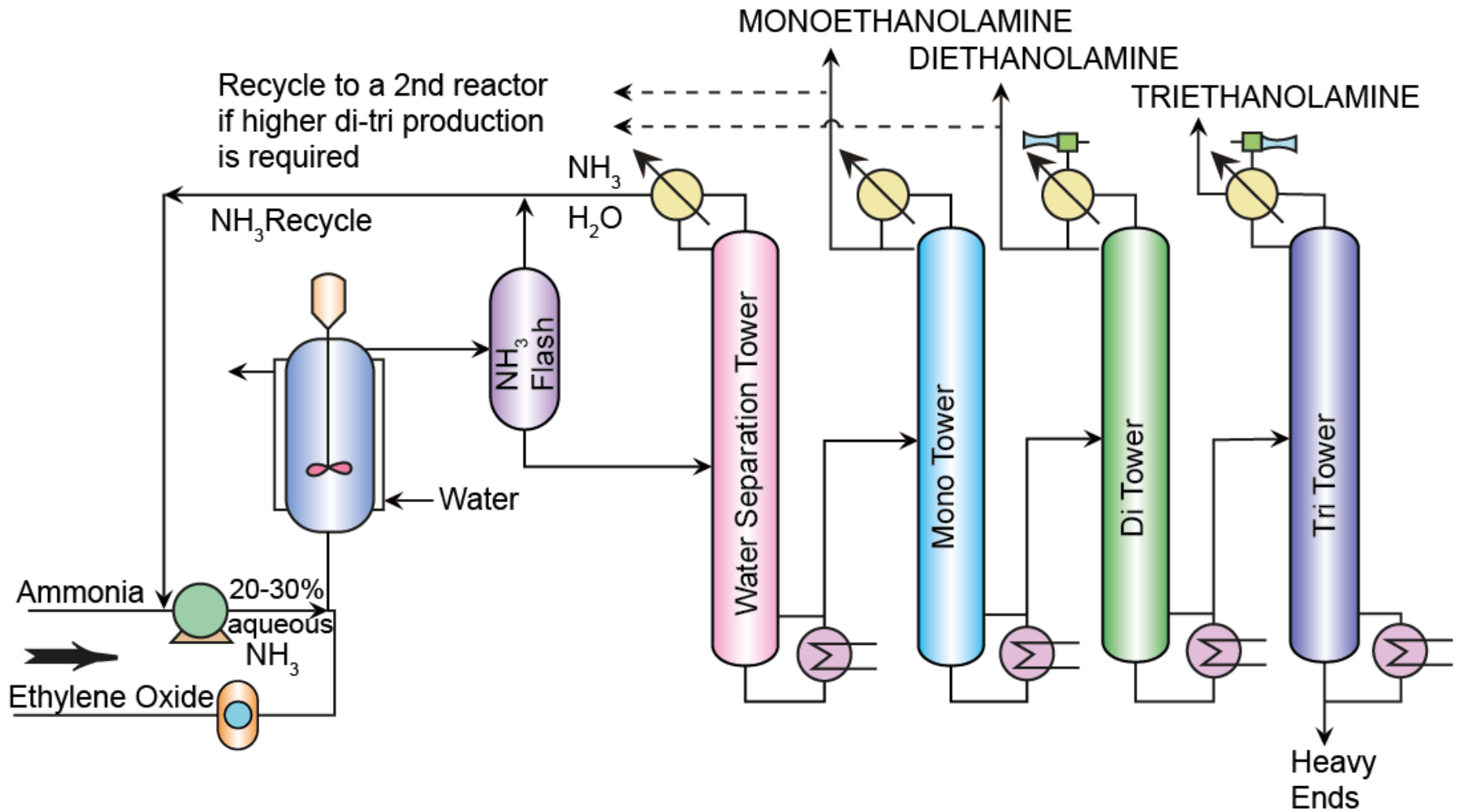
Major Engineering Issues

- **Kinetics of complex series reactions**
  - Temperature affects the specific rate constants
  - Residence time in reactor is important
- **Reactor design**
  - After determining the rate-constant data, computer optimization can be done.
  - A/E ratio= 0.5-3.0; T = 35-275 ^{0}C; Pr=1-100 atms.
- **Process alternatives**
  - When di or triethanolamine are predominant : Recycle lower amines to a separator and add ethylene oxide
  - Too low an ammonia gives rise to amino-ethers, this can be suppressed by addition of CO_2
- **Recovery and purification system**
  - High boiling point of di- and tri- compounds with decomposition and color deterioration requires the more expensive vacuum fractionation system
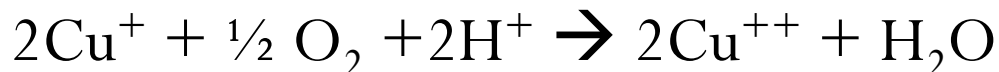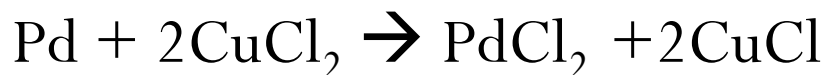
Acetaldehyde (CH_3CHO)

- One of the important petrochemical, raw material for acetic acid, acetic anhydride, acetate esters etc.

- Methods of Production

  - Hydration of acetylene (Higher cost, Obsolete).

  - WACKER OXIDATION

    - Formed by the selective catalytic oxidation of ethylene

$$CH_2 = CH_2 + \tfrac{1}{2} \, O_2 \rightarrow CH_3CHO \quad (\Delta H = -244 KJ/mol)$$

    - Series of oxidation-reduction reaction

$$CH_2 = CH_2 + PdCl_2 + H_2O \rightarrow CH_3CHO + 2HCl + Pd$$

$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$$

$$2Cu^+ + \tfrac{1}{2} \, O_2 + 2H^+ \rightarrow 2Cu^{++} + H_2O$$

Process description

- Ehene and oxygen are fed into the lower part of reactor in which the circulation occurs by the upward movement of the gas bubbles.
- Catalyst is in aqueous solution phase is also fed from bottom.
- The reactor operates at the boiling point of the reaction mixture, so the heat can be removed by evaporation of water and acetaldehyde.
- The gas stream leaving the top of the reactor is cooled and sent to a gas-liquid separator, where the catalyst solution is separated for recycle and regeneration.
- The gas phase, rich in unconverted ethene, is cooled and scrubbed with water to recover acetaldehyde which is completely miscible with water.
- The dilute acetaldehyde is purified and concentrated in two stages.
  - In first stage, light by product (chloromethane, chloroethane) are removed by extractive distillation.
  - In second stage, heavy product (acetic acid and other organic compounds) and water are removed. A small amount of make-up HCl solution is added to the reactor to compensate for the chloride losses.
- ** Ethene is chosen to be in such excess that the mixture should outside the higher explosion limit.

Process Flow Diagram
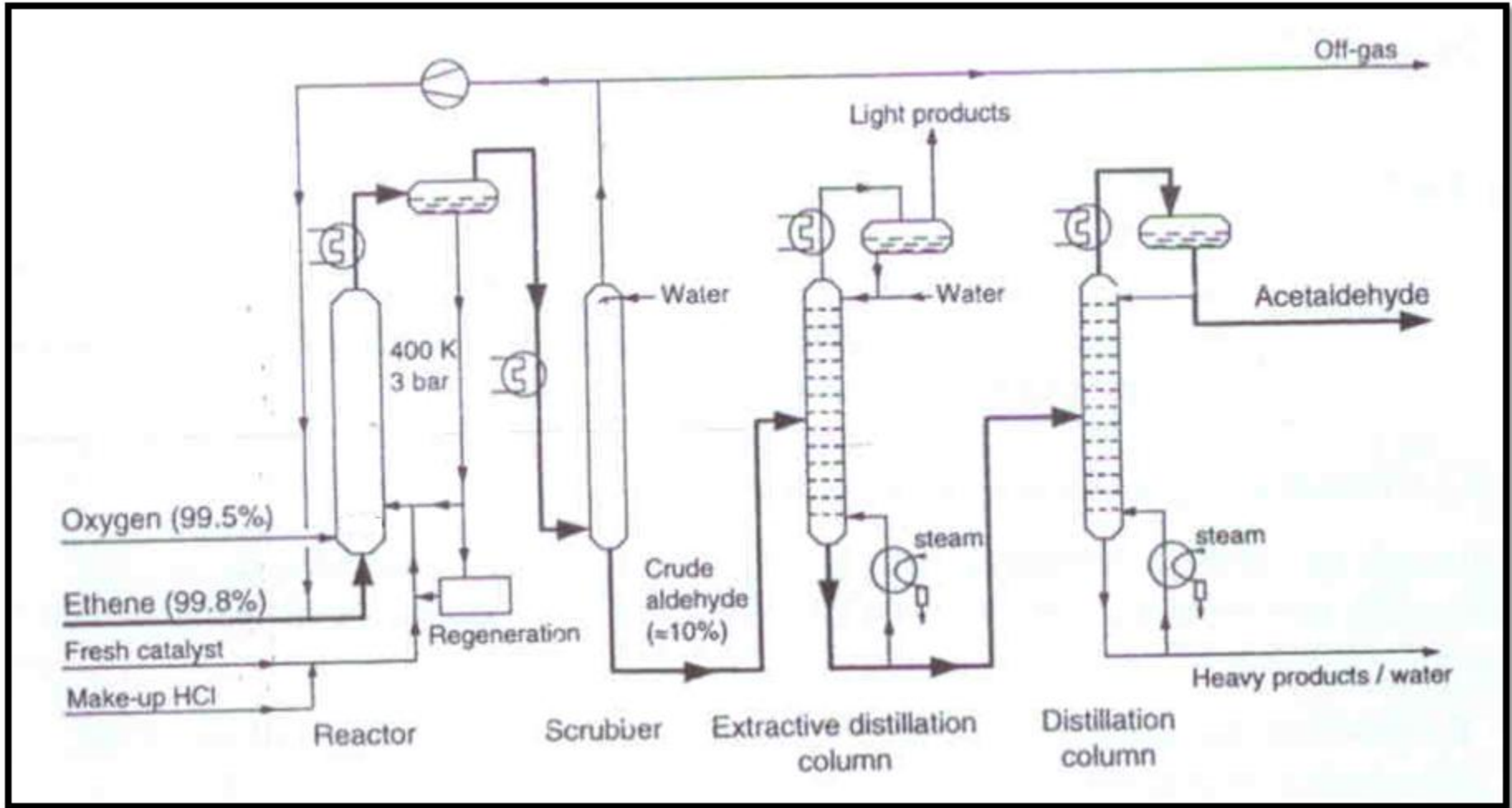
Engineering Issue

- Two stage process : Employ two separate reactors; the reaction of ethene with $PdCl_2$ and oxidation of Pd with Cu^{++} occur in the first reactor, while oxidation of Cu^+ with air (rather O_2 in single stage) takes place in the second reactor. In both the one- and two stage process the acetaldehyde yield is about 95%.

- By-products are formed. Both the single stage and the two-stage process yield chlorinated HC's, chlorinated acetaldehydes, acetic acid.

- Expensive construction materials have to be used in both processes because the acidic catalyst solution is very corrosive. Suitable material titanium, acid-proof ceramics, tantalum.

- Wastewater is a problem. It contains chlorinated hydrocarbons, which are toxic and non-degradable. Chlorine-free catalysts have been studied but have not (yet) been commercialized.
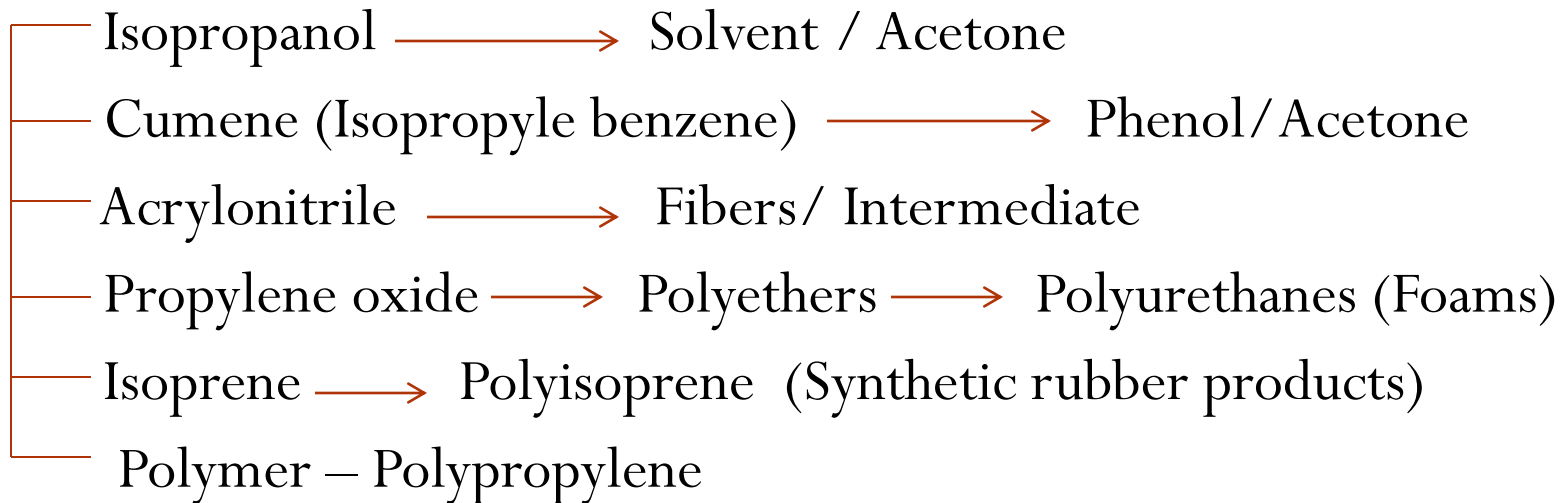
CHEMICALS FROM C$_3$ COMPOUNDS

Propylene

- Processes within refinery which gives propylene are:
  - Steam cracking of hydrocarbons
  - Direct pyrolysis of propane
  - Refinery off-gases

- Consumption pattern for Propylene

Isopropanol $\longrightarrow$ Solvent / Acetone

Cumene (Isopropyle benzene) $\longrightarrow$ Phenol/Acetone

Acrylonitrile $\longrightarrow$ Fibers/ Intermediate

Propylene oxide $\longrightarrow$ Polyethers $\longrightarrow$ Polyurethanes (Foams)

Isoprene $\longrightarrow$ Polyisoprene (Synthetic rubber products)

Polymer – Polypropylene

Isopropanol

- Properties
  - A colorless liquid .
  - Miscible with water.
  - It melts at -89°C and boils at 82.3°C.
  - Oxidation of isopropanol is now the major source of acetone.
- Methods of production:
  - Direct catalytic hydration of propylene (Using solid acid catalyst, Pure propylene is required))
  - Hydration of propylene via sulfation and hydrolysis (Indirect process)
- Uses:
  - As a coolant. As a coupling agent.
  - Production of polyvinyl fluoride.
  - IPA is used also in the production of acetone .
  - Production of other chemicals (such as isopropyl acetate and Isopropylamine.
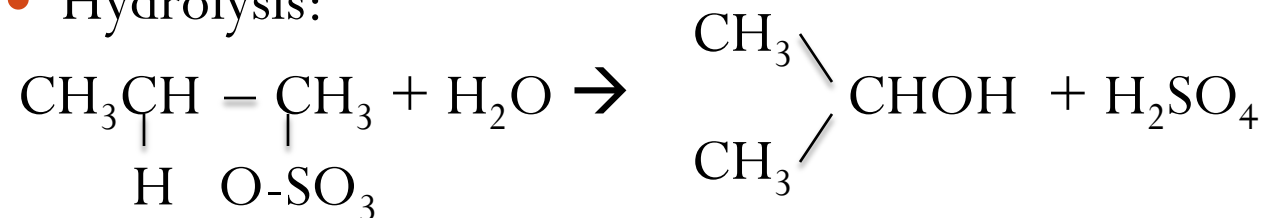
Isopropanol manufacture

## Hydration of propylene via sulfation and hydrolysis

Reaction

- Sulfation:

$$CH_3CH=CH_2 + H_2SO_4 \rightarrow (CH_3)_2CH(OSO_3H) \text{ Isopropyl acid sulphate}$$

- Hydrolysis:

$$CH_3\underset{H}{CH} - \underset{O\text{-}SO_3}{CH_3} + H_2O \rightarrow \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} CHOH + H_2SO_4$$

  - Thus sulfuric acid is regenerated in the process
  - Side reaction: Di-isopropyl ether forms
  - The primary reaction is a gas liquid reaction in which propylene is absorbed into a tray tower fed with sulfuric acid.

- Operating conditions: Room temperature but $20 - 25$ atms pressure
- Reaction is highly exothermic

Process Flow sheet
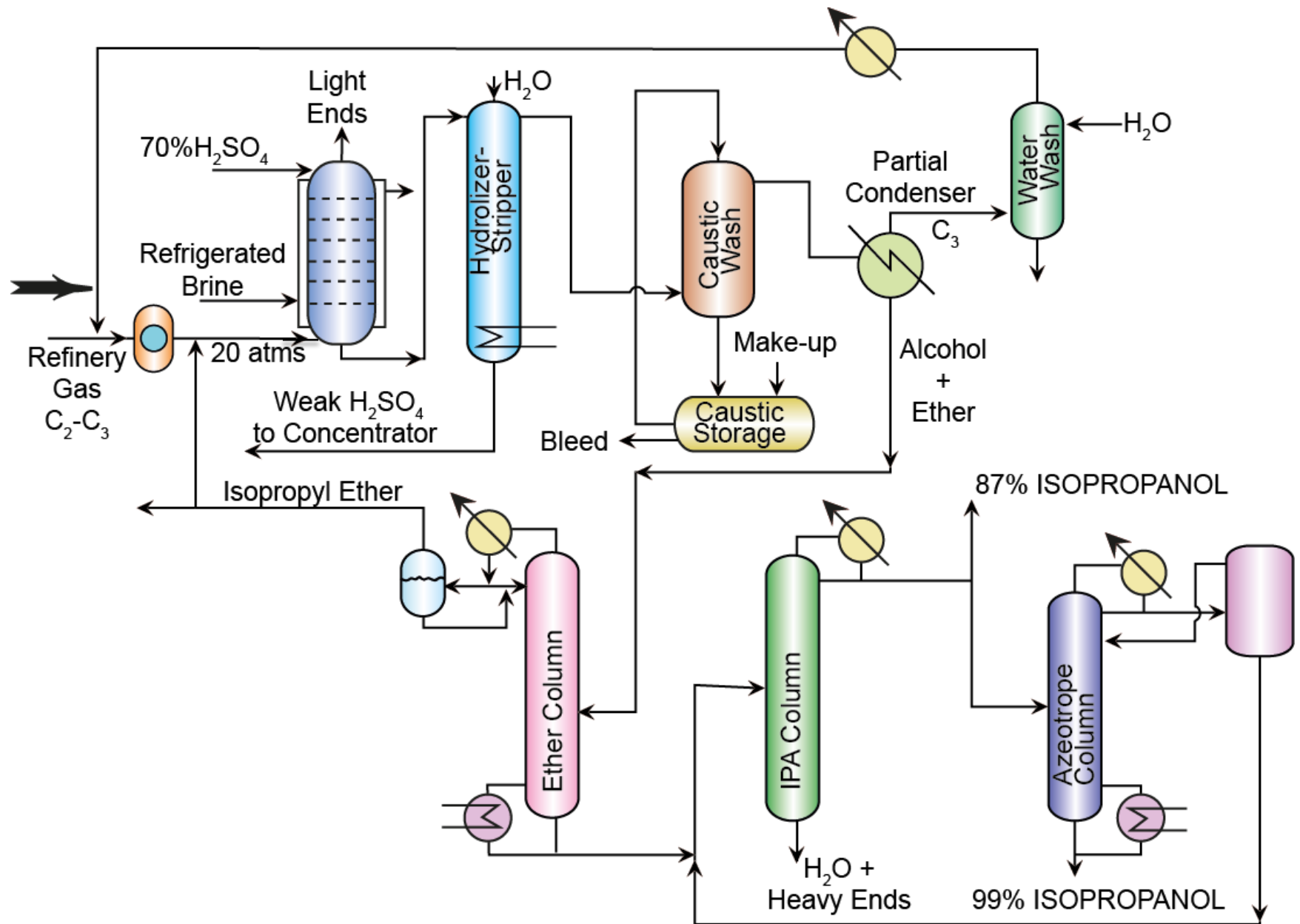
Process Description

- Either pure propylene or a mixture of Propylene and other C_2, C_3 components can be fed to a reactor.

- The hydrocarbon feed is compressed and fed to the reactor at about $20 - 25$ atms pressure.

- Sulfuric acid of about 70% acid strength is fed in a countercurrent mode to the tray column where reactive absorption takes place. Here, sulfonation reaction takes place.

- The reaction is highly exothermic and therefore, refrigerated brine is used to control the temperature in the absorber. Jacketed arrangement will be preferred for the tray absorption column to circulate the refrigerated brine in the cooling jacket.

- After reaction, the unreacted light ends such as saturated components will leave the unit as the gas stream.

- The sulfonated product rich stream is then sent to a hydrolyzer cum stripper where isopropanol is produced and is vaporized due to existing stripper temperatures.

- The hydrolyzer is fed with water to facilitate the conversion of the sulfonate product.

- The isopropanol rich vapors then enter a caustic wash unit to remove the acidic impurities.

- The isopropanol rich vapors then enter a partial condenser which separates the unreacted propylene from the alcohol + ether mixture. Here, propylene is separated as the vapor and alcohol + ether is separated as the liquid stream.

- The separated propylene gas is once again subjected to water wash to remove soluble impurities (such as ethers and alcohols). Subsequently, pure propylene is sent to mix with the fresh feed stream. Before sending to the unit, the propylene is cooled to room temperature so as to have identification conditions as the fresh feed stock.

- The alcohol and ether enter an ether column that separates isopropyl ether which is returned to the reactor.

- The bottom product consisting of isopropyl alcohol and water is sent to a isopropyl alcohol column that produces water + heavy ends as the bottom product and 87 % isoprpanol-water azeotrope mixture as the top product.

- The azeotrope is sent to an azeotropic distillation column that uses isopropyl ether as a azeotropic agent to obtain 99 % isopropanol as the bottom product. The top product is a mixture of isopropyl ether and water. The top product is a low boiling azeotrope. This stream upon gravity settling will produce the isopropyl ether as the top product which is sent as a reflux stream to the azeotropic column. The bottom product is a mixture of isopropanol and water is recycled back to the isopropyl alcohol column along with the bottom product generated from the ether separating column.
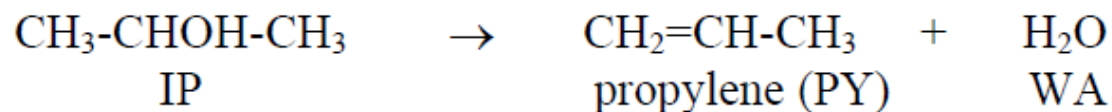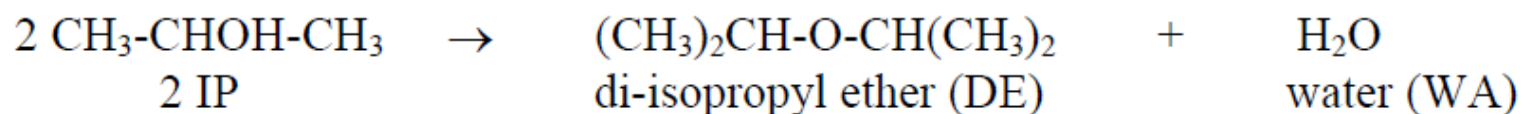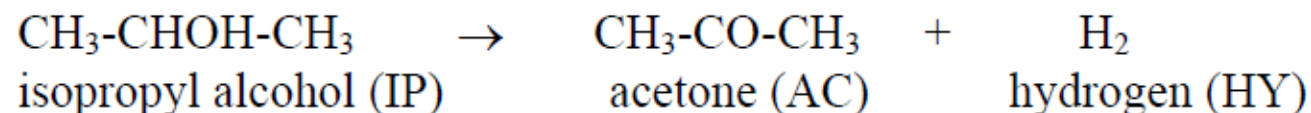
ACETONE

- B.P. = 56.5 °C
- Acetone is one of the most widely used industrial solvents and is increasingly used as a chemical intermediate.
- Acetone is extremely flammable with a high vapor pressure; use only with good ventilation and avoid all ignition sources.
- It readily mixes with most organic solvents and mixes completely with water.

Methods of production:

- Acetone is typically produced in commercial quantities as a by-product during the formation of phenol. However, acetone manufactured thus generally contains small amounts of the reactant benzene and the desired product phenol.
- Catalytic dehydrogenation of isopropanol : alternative processes (which do not involve benzene) more attractive.

Catalytic dehydrogenation of Isopropanol

Main Reaction

$$CH_3\text{-}CHOH\text{-}CH_3 \rightarrow CH_3\text{-}CO\text{-}CH_3 + H_2$$

isopropyl alcohol (IP)   acetone (AC)   hydrogen (HY)

$$2\ CH_3\text{-}CHOH\text{-}CH_3 \rightarrow (CH_3)_2CH\text{-}O\text{-}CH(CH_3)_2 + H_2O$$

2 IP   di-isopropyl ether (DE)   water (WA)

$$CH_3\text{-}CHOH\text{-}CH_3 \rightarrow CH_2\text{=}CH\text{-}CH_3 + H_2O$$

IP   propylene (PY)   WA

- Reaction pressure: $3 - 4$ atms
- Reaction temperature: $400 - 500$ ºC
- Copper catalyst on porous carrier is used
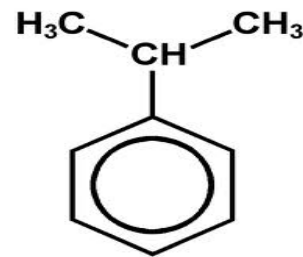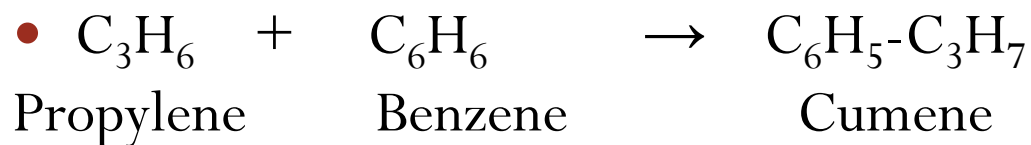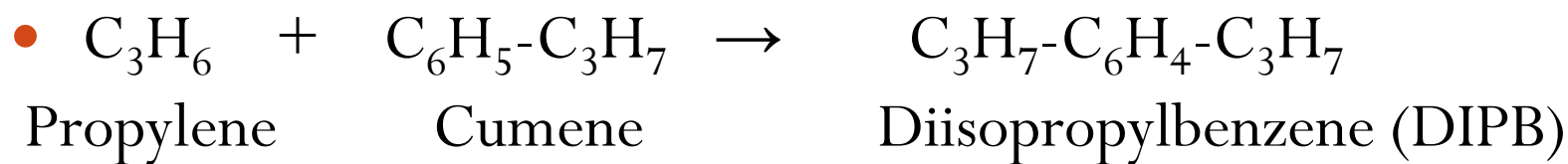- Vapor phase reaction

Process Flow sheet
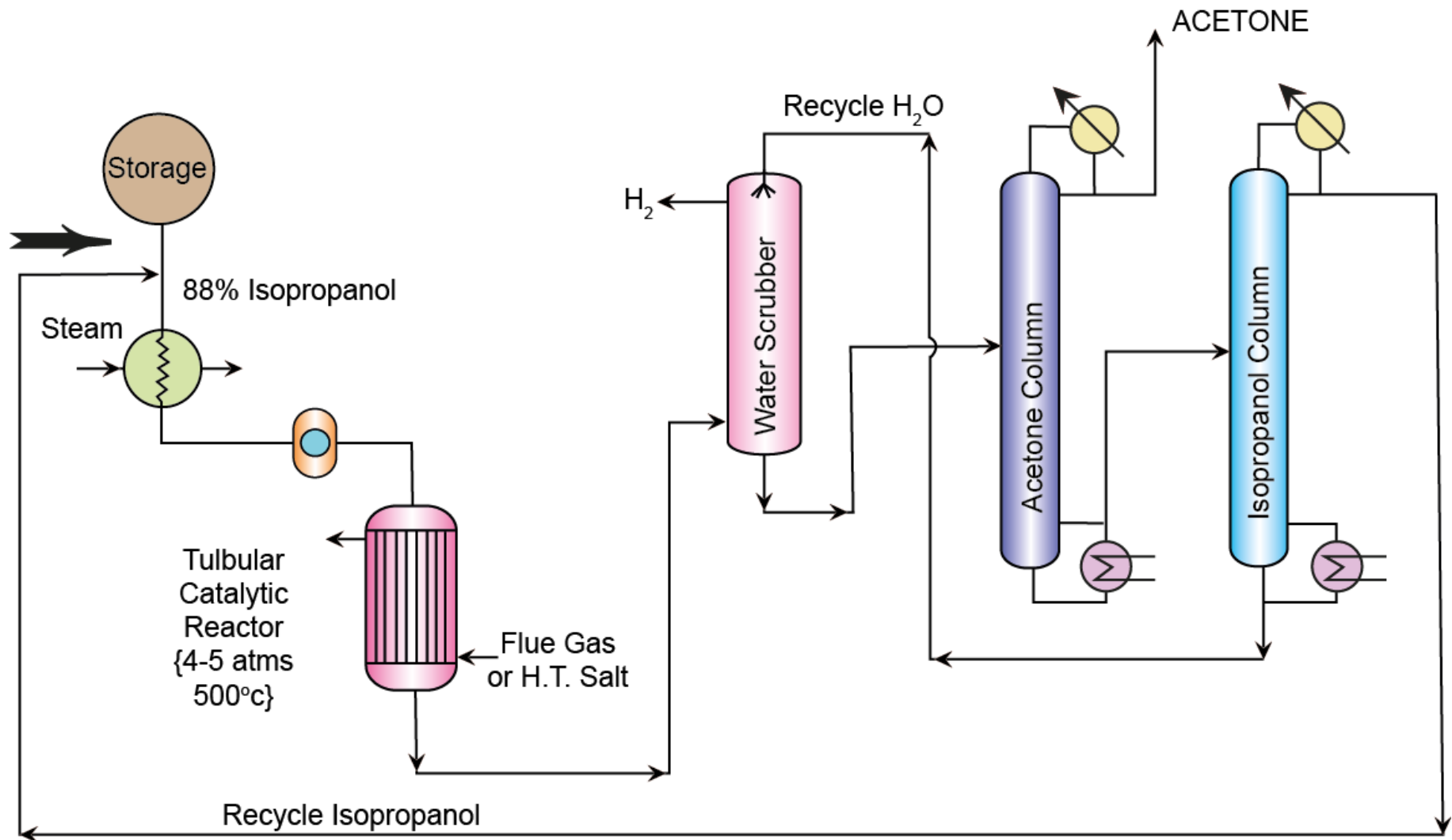
Cumene (Isopropyl Benzene)

- Cumene is produced in large scale plants as intermediate for the phenol manufacturing; it is used as raw material for obtaining phenol and acetone. Cumene is produced by reacting benzene and propylene.

- The reactions for cumene production from benzene and propylene are as follows:

Main Reaction

- C_3H_6 + C_6H_6 → C_6H_5-C_3H_7

  Propylene   Benzene   Cumene

Side Reaction

- C_3H_6 + C_6H_5-C_3H_7 → C_3H_7-C_6H_4-C_3H_7

  Propylene   Cumene   Diisopropylbenzene (DIPB)

Phenol

- Phenol is one of the most important petrochemicals. Ranging from solvents to polymers, phenol is required for several petrochemical processes as an important raw material.

- Phenol can be produced from many sources such as
  - Peroxidation of Cumene followed by hydrolysis of the peroxide (Most common route, Produces 'Acetone' as by product)
  - Two stage oxidation of Toluene
  - Chlorination of Benzene and hydrolysis of chloro-benzene
  - Direct oxidation of Benzene

CHEMICALS FROM C$_4$ COMPOUNDS

BUTANE AND BUTENES

BUTADIENE

Properties

- *Description : Colorless gas*

- *Molecular formula* C_4H_6 $(CH_2=CH.CH=CH_2)$

- *Boiling point* $-4.4\ ^oC$

- *Solubility Very slightly soluble in water (735 mg/L);* soluble in ethanol, ether, acetone, benzene and organic solvents.

- It is a hazardous chemical due to its flammability, reactivity, and toxicity.

Uses

- Used primarily as a chemical intermediate

- As a monomer in the manufacture of polymers such as synthetic rubbers or elastomers : styrene-butadiene rubber (SBR), polybutadiene rubber (PBR), polychloroprene (Neoprene) and nitrile rubber (NR).

- Major use of butadiene is in the production of tires.

- Manufacture of polymers, latexes, and plastics.

Production Methods : Butadiene is produced commercially by three processes:

- Steam Cracking of Paraffinic Hydrocarbons: In this process, butadiene is a co-product in the manufacture of ethylene (the ethylene co-product process).

- Catalytic Dehydrogenation of n-Butane and n-Butene (the Houdry process).

- Oxidative Dehydrogenation of n-Butene (the Oxo-D or O-X-D process).

Each of these processes produces a stream commonly referred to as crude butadiene that is rich in 1,3-butadiene.

Steam Cracking of Paraffinic Hydrocarbons

Flow path for C₄ Components including butadiene
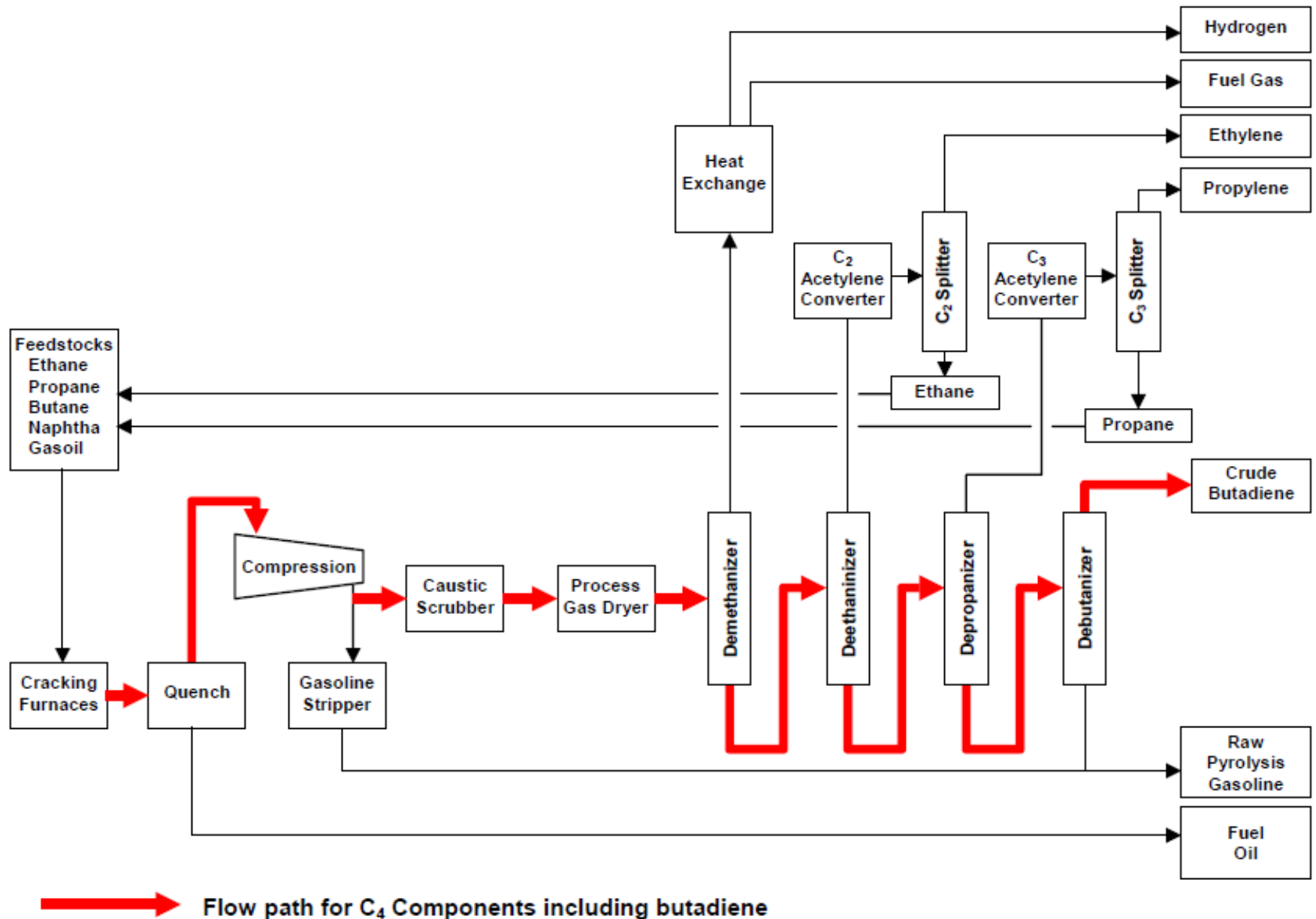
Quality of a crude C$_4$ stream via steam cracking process
(Vary from source to source)

Table 1.1: Example of a Crude Butadiene Analysis

Component	Crude Butadiene Vol %	Example Range
C3 & Lighter	0.40	0.01-1.00
i-Butane	1.00	0.50-18.00
n-Butane	5.00	3.00-33.00
Butene-2 (Cis)	4.05	2.50-10.00
Butene-2 (Trans)	5.45	3.50-12.00
Butene-1	14.88	7.00-17.00
i-Butylene	22.50	12.00-27.00
1,2-Butadiene	0.16	0.10-2.00
1,3-Butadiene	44.00	10.00-75.00
C4 Acetylenes	1.41	0.05-3.50
M-Acetylene	0.06	0.01-0.50
E-Acetylene	0.20	0.01-1.00
V-Acetylene	1.15	0.01-2.50
C5+	0.90	0.10-4.00
Other	0.25	
	100.0	

# Catalytic Dehydrogenation of n-Butane and n-Butene (the Houdry process).

- The catalytic dehydrogenation of n-butane is a two-step process; initially going from n-butane to n-butenes and then to butadiene. Both steps are endothermic.
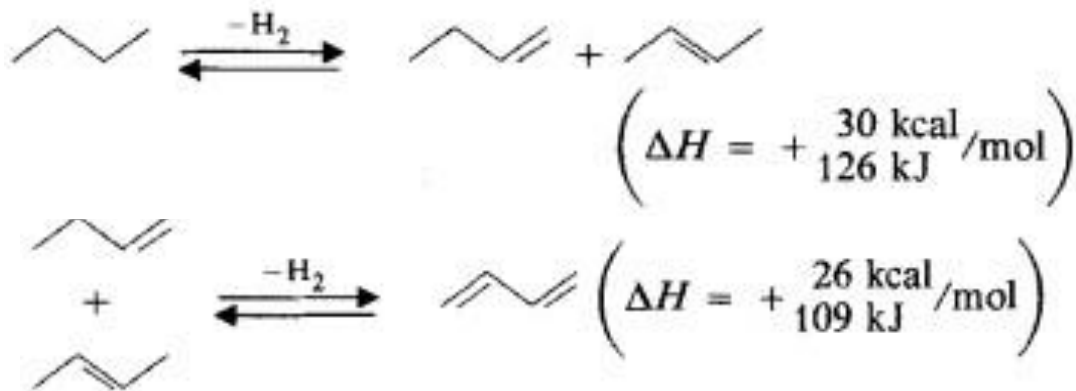
- Relatively high temperatures (600-700 °C) are necessary to achieve economical conversions. At these temperatures, side reactions such as cracking and secondary reactions involving the unsaturated compounds become important. Therefore, a short residence time and a selective catalyst must be used.

- In the Houdry process, n-butane is dehydrogenated over chromium-alumina oxide catalysts.

Process Flow Sheet

Figure 1.2: Catadiene Process*
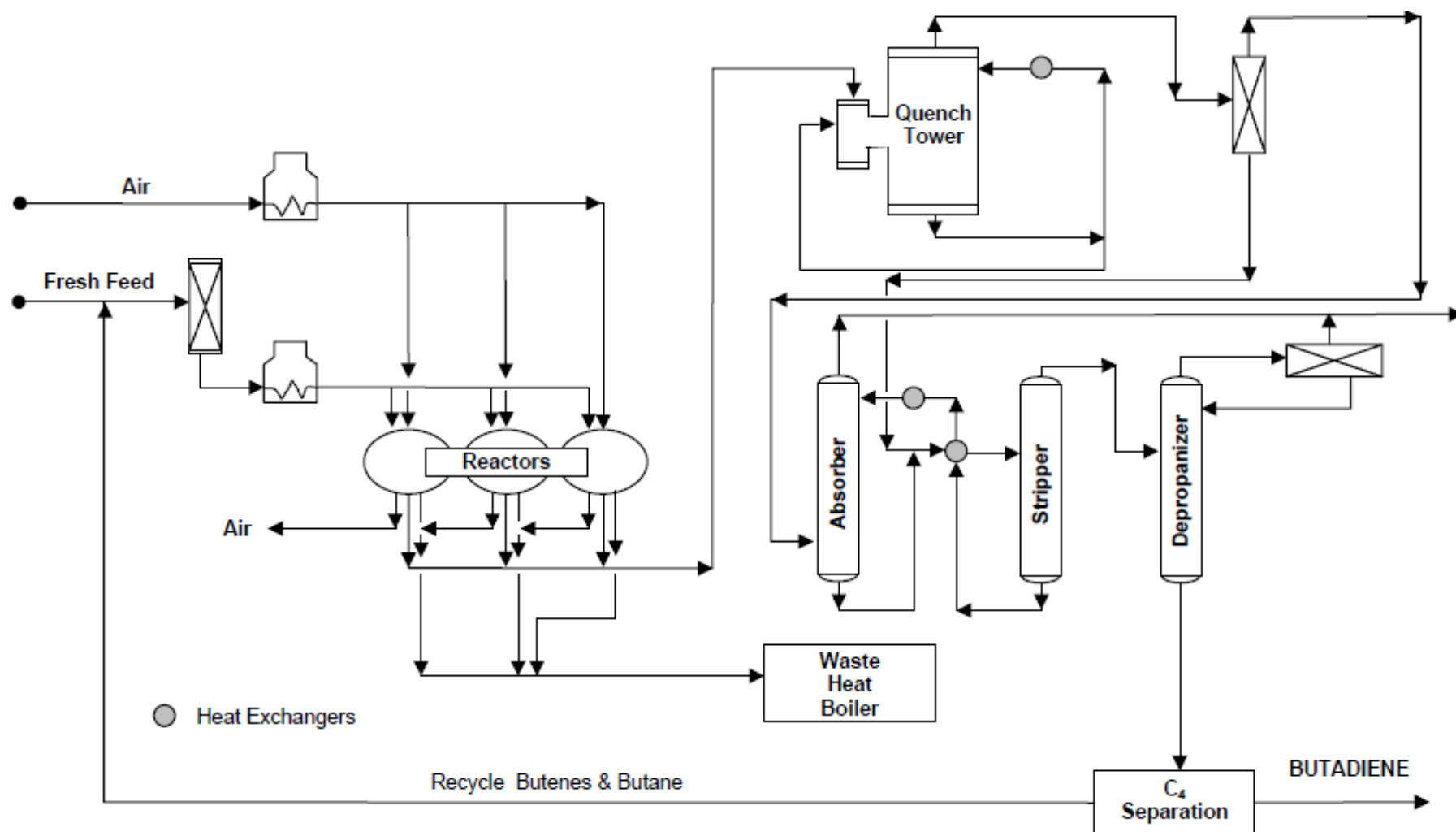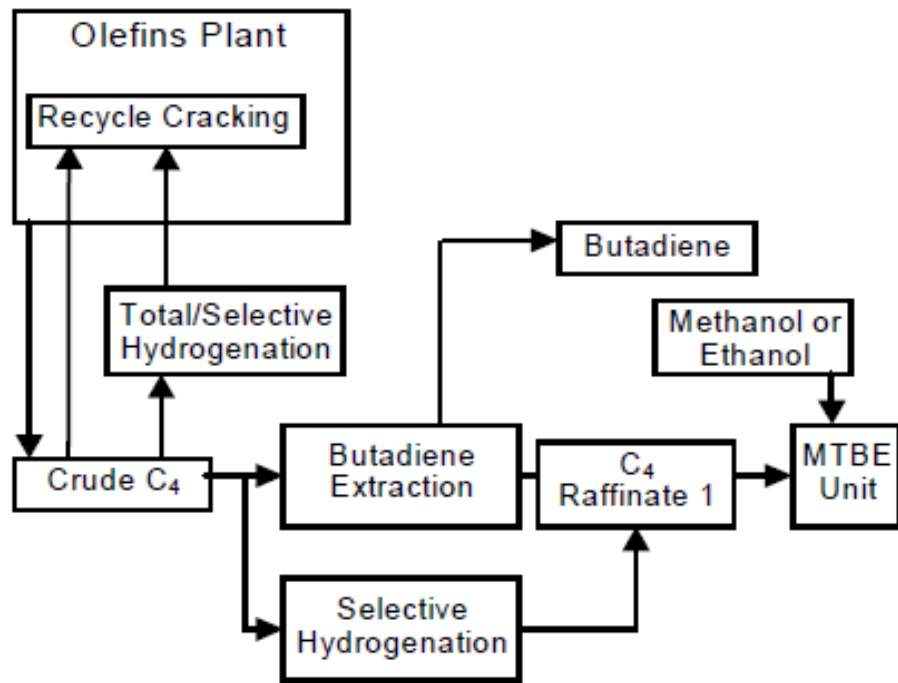
Process Description

- The reactors normally operate at 0.2-0.4 bar absolute pressure and approximately 600-680 °C. Three or more reactors can be used to simulate continuous operation: while the first reactor is on-line, the second is being regenerated, and the third is being purged prior to regeneration.

- Residence time for feed in the reactor is approximately 5-15 minutes. As the endothermic reaction proceeds, the temperature of the catalyst bed decreases and a small amount of coke is deposited.

- In the regeneration cycle, this coke is burned with preheated air, which can supply essentially all of the heat required to bring the reactor up to the desired reaction temperature.

- The reactor effluent goes directly to a quench tower, where it is cooled. This stream is compressed before feeding an absorber/stripper system, where a C_4 concentrate is produced to be fed to a butadiene extraction system for the recovery of high purity butadiene.

Butadiene Production via Oxidative Dehydrogenation of n-Butenes (the Oxo-D or O-X-D process)
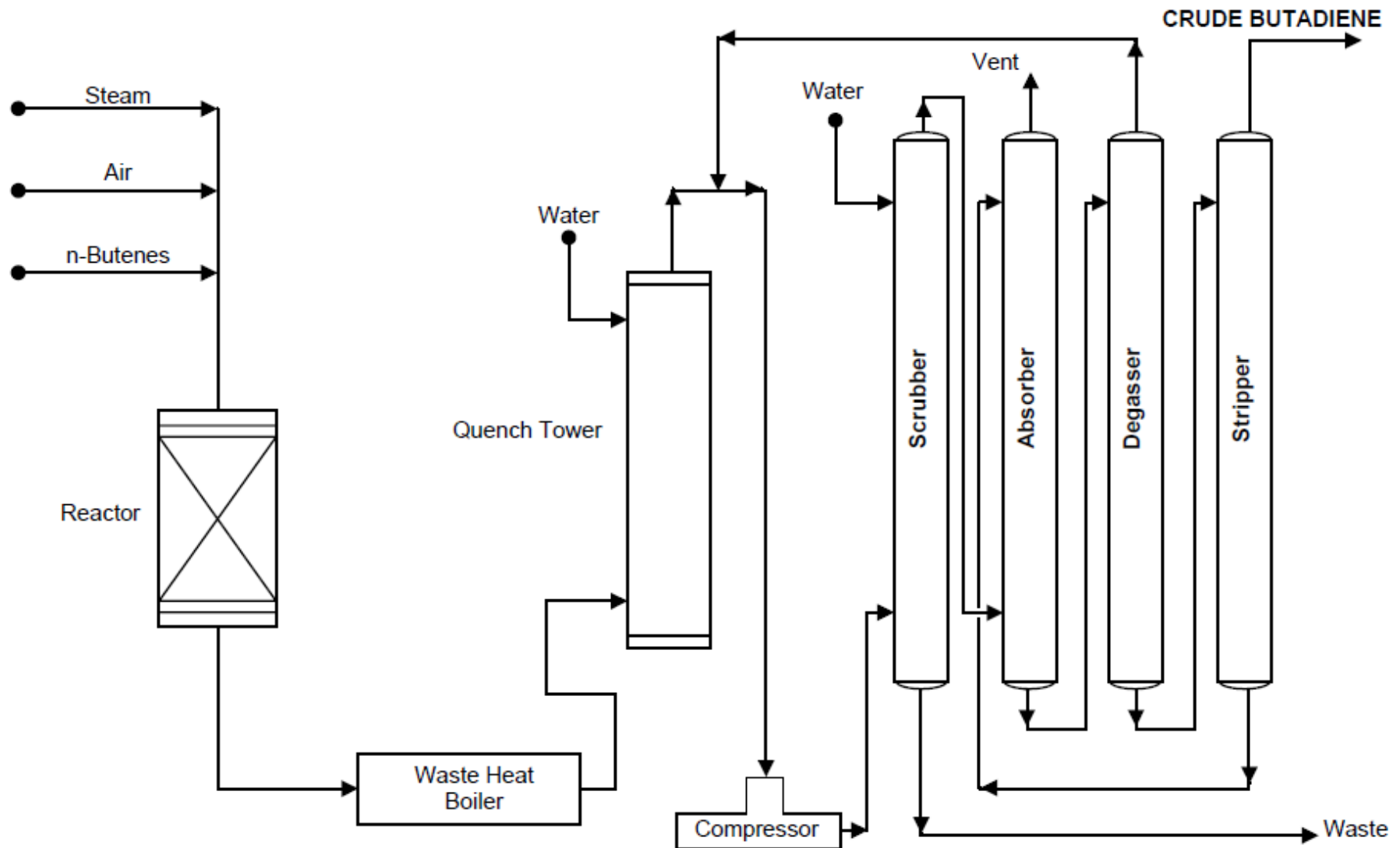
- Oxidative dehydrogenation of n-butenes has replaced many older processes for commercial (on-purpose) production of butadiene.

- In this process, the dehydrogenation equilibrium between butenes and butadiene is displaced by the addition of oxygen towards greater formation of butadiene.

- Butenes are much more reactive, however, and they require less severe operating conditions than that of n-butane to produce an equivalent amount of product. Therefore, the use of n-butane as a feedstock in this process may not be practical.

- In industrial operation, a sufficient quantity of oxygen (as air) is introduced so that the heat supplied by the exothermic water formation roughly equals the heat required for the endothermic dehydrogenation. In this way the butene conversion, the selectivity to butadiene, and the lifetime of the catalyst can be improved. By using an excess of air, the maximum temperature can be controlled by addition of steam. Mixed oxide catalysts based on Bi/Mo or Sn/Sb are most often used.

- In general, in an oxydehydrogenation process, a mixture of n-butenes, air and steam is passed over a catalyst bed generally at low pressure and at temperature approximately 500-600 °C.

- The heat from the exothermic reaction can be removed by circulating molten heat transfer salt, or by using the stream externally for steam generation. The air feed rate is such that an oxygen/butene molar ratio of approximately 0.55 is maintained, and the oxygen is totally consumed. A steam to butene ratio of 10:1 has been reported as necessary to absorb the heat of reaction and to limit the temperature rise

- The reactor effluent is cooled and the C_4 components are recovered in an absorber/degasser/stripper column combination. The lean oil flows from the bottom of the stripper back to the absorber, with a small amount passing through a solvent purification area. Crude butadiene is stripped from the oil, recovered in the overhead of the stripper, then it is sent to a purification system to recover the butadiene product.

Processing of Crude

Butadiene Streams

Process Description

Petrochemical from Aromatics

Aromatics
- Benzene
  - Styrene $\longrightarrow$ Polystyrene, Rubber
  - Phenol $\longrightarrow$ Resin, Polymer
  - Dichlorobenzene $\longrightarrow$ DDT
- Toluene
  - Benzoic Acid
  - Solvent
- Xylene $\longrightarrow$ o-Xylene, m-Xylene, p-Xylene
- Naphthalene
  - Phthalic anhdride
  - Dyes, Drug, Insect repellent