

Chemicals From C₂ Compounds

Ethylene and Acetylene

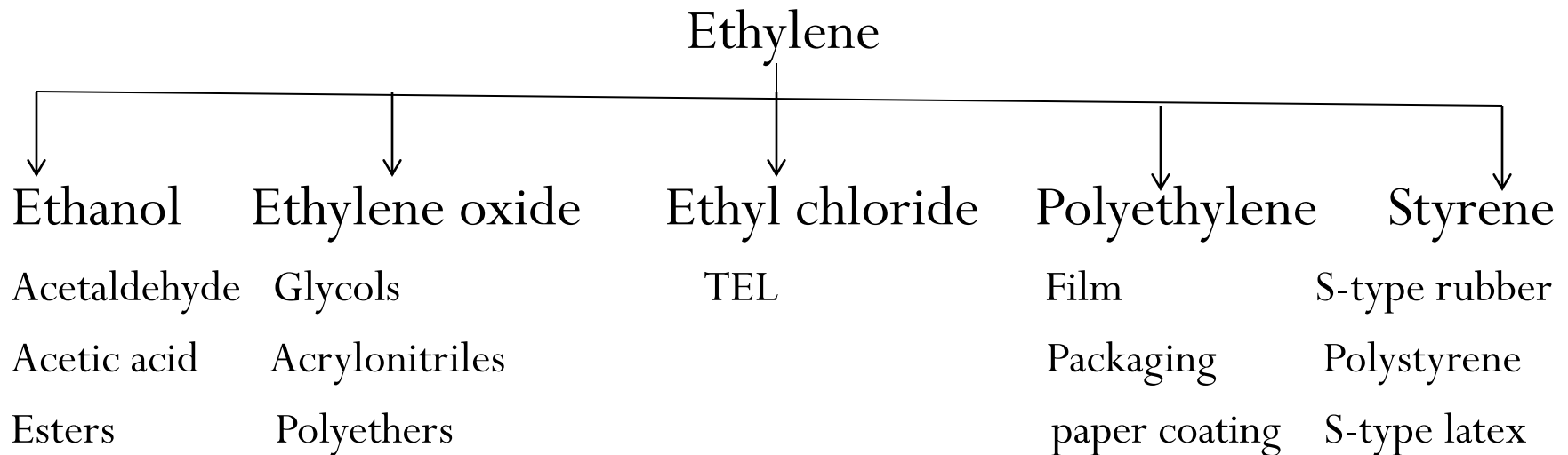
Ethylene Dichloride

Vinyl Chloride Monomer

Ethylene and Acetylene

(Via steam cracking of hydrocarbon)

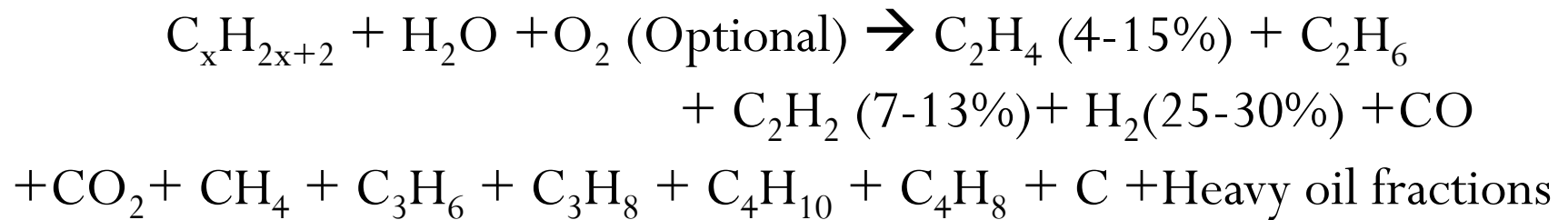
- The steam cracking process produces ethylene/acetylene in ratio of 0.3 to 2.0 depending on operating conditions.
- Consumption Pattern



Various methods of production

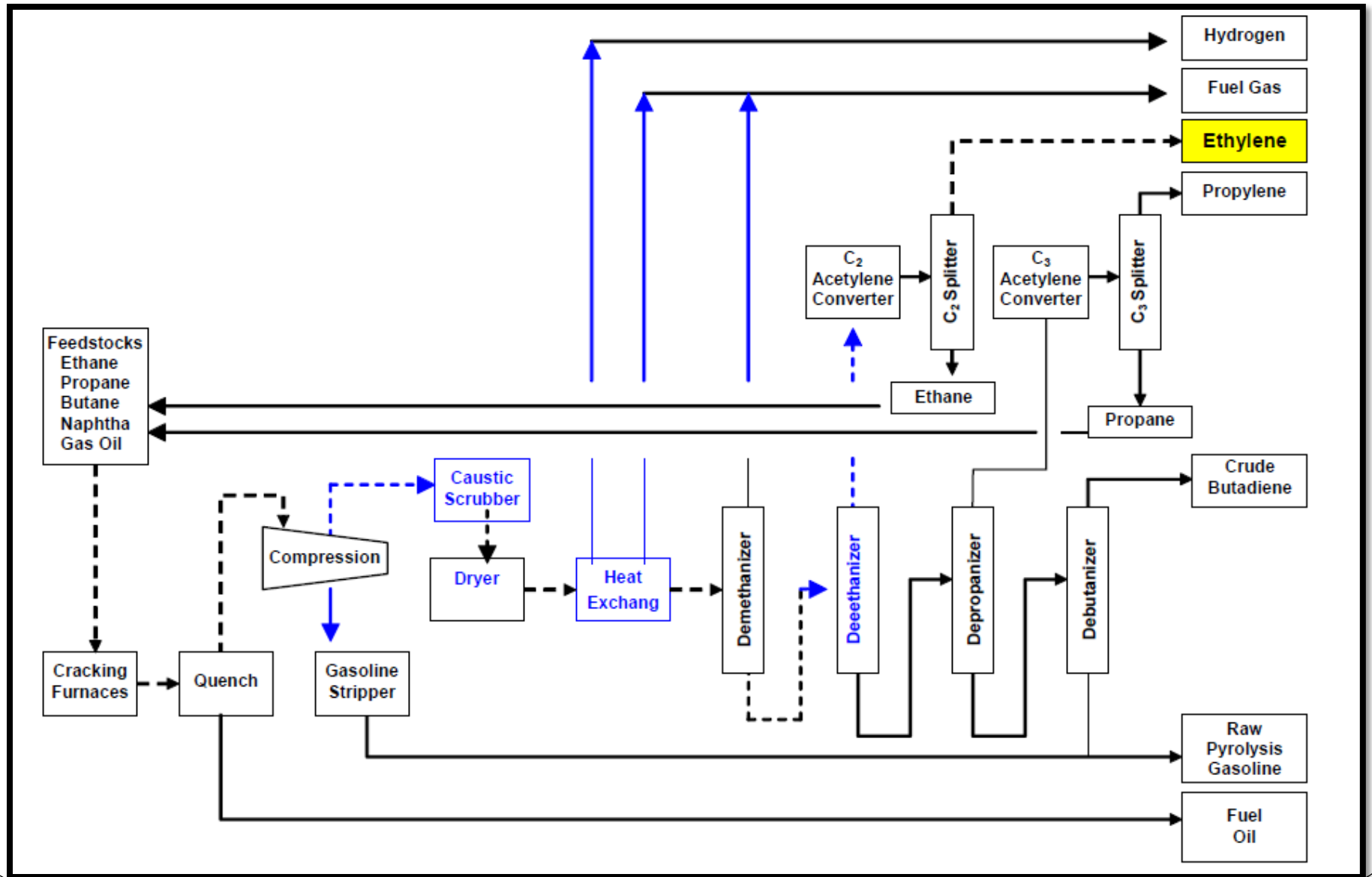
- Steam pyrolysis (cracking) of petroleum from LPG and naphtha feedstocks
- Thermal pyrolysis of ethane/propane
- Separation from refinery gases – Limited amount
- Dehydration of ethanol- not competitive for large-scale requirements

Steam Cracking of Petroleum Hydrocarbons

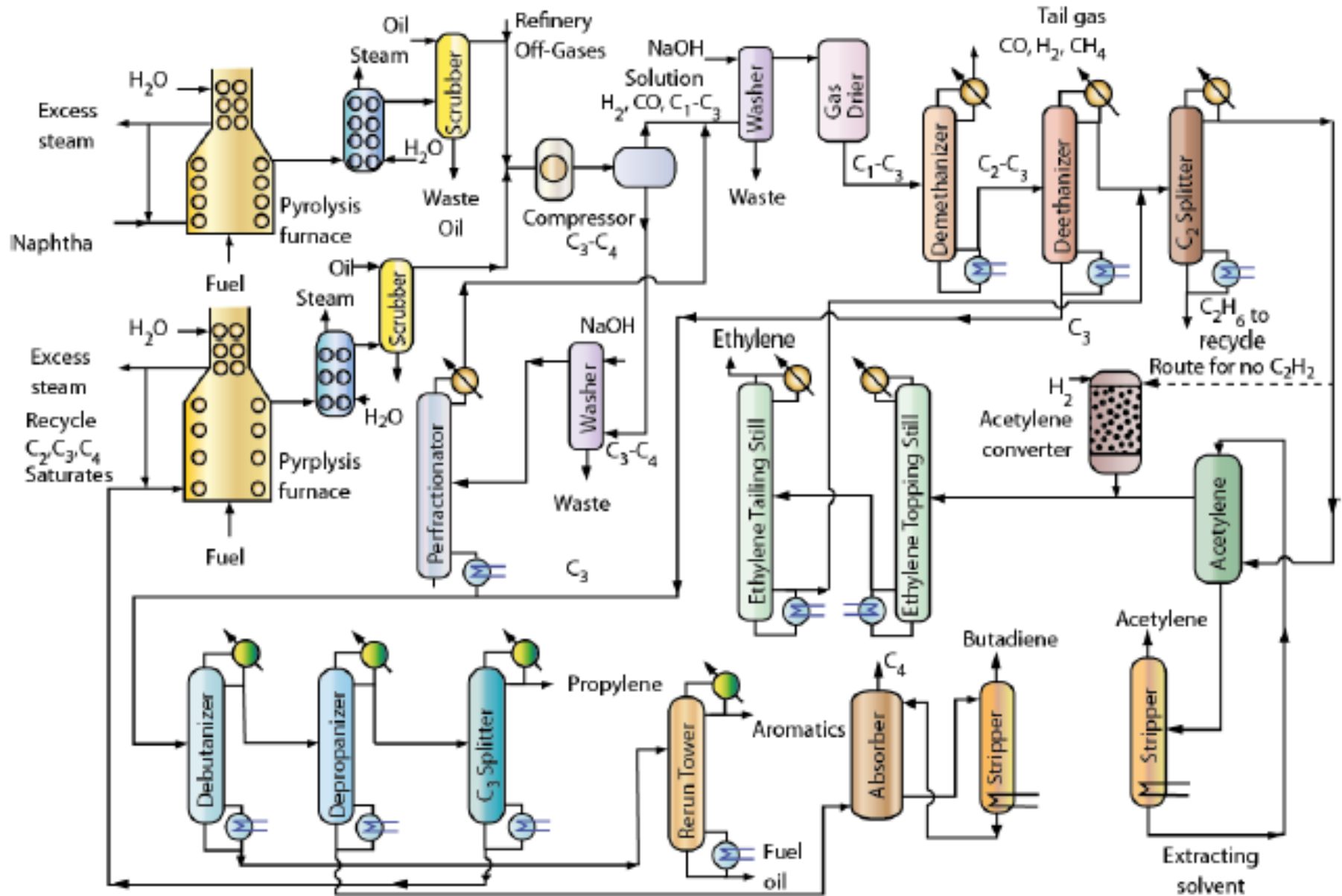


- The reaction is pretty complex as we produce about 10 to 12 compounds in one go.
- The flowsheet will be reaction-separation-recycle system only in its topology. But the separation system will be pretty complex.
- Important separation tasks: Elimination of CO and CO₂, Purification of all products such as ethylene, acetylene etc.
- Typical feed stocks are Ethane, LPG & Naphtha
- Reaction temperature is about 700 – 800 °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

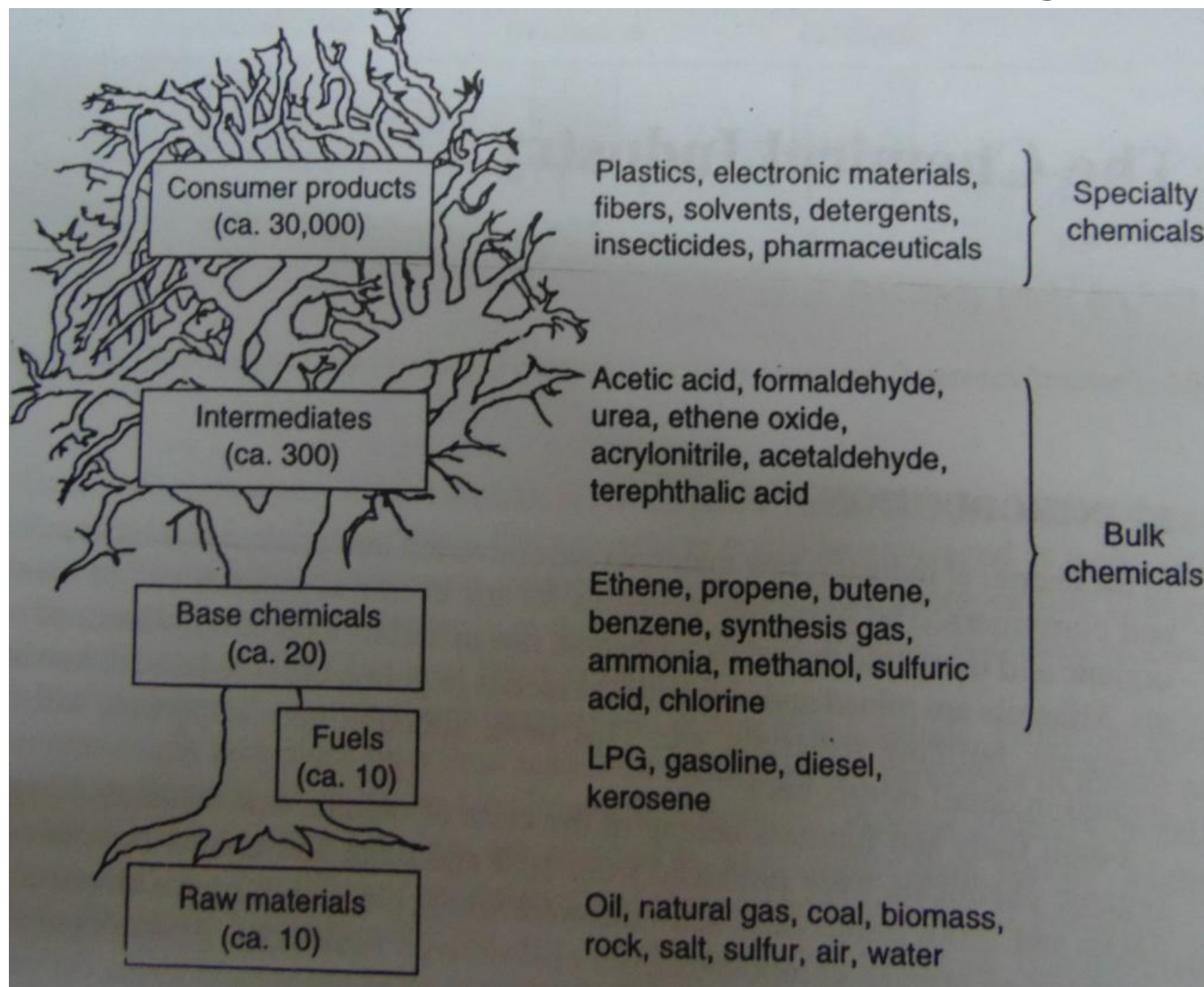
- Steam economy

- Heat added in pyrolysis section can be recovered by incorporating stack and quench boiler 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



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.

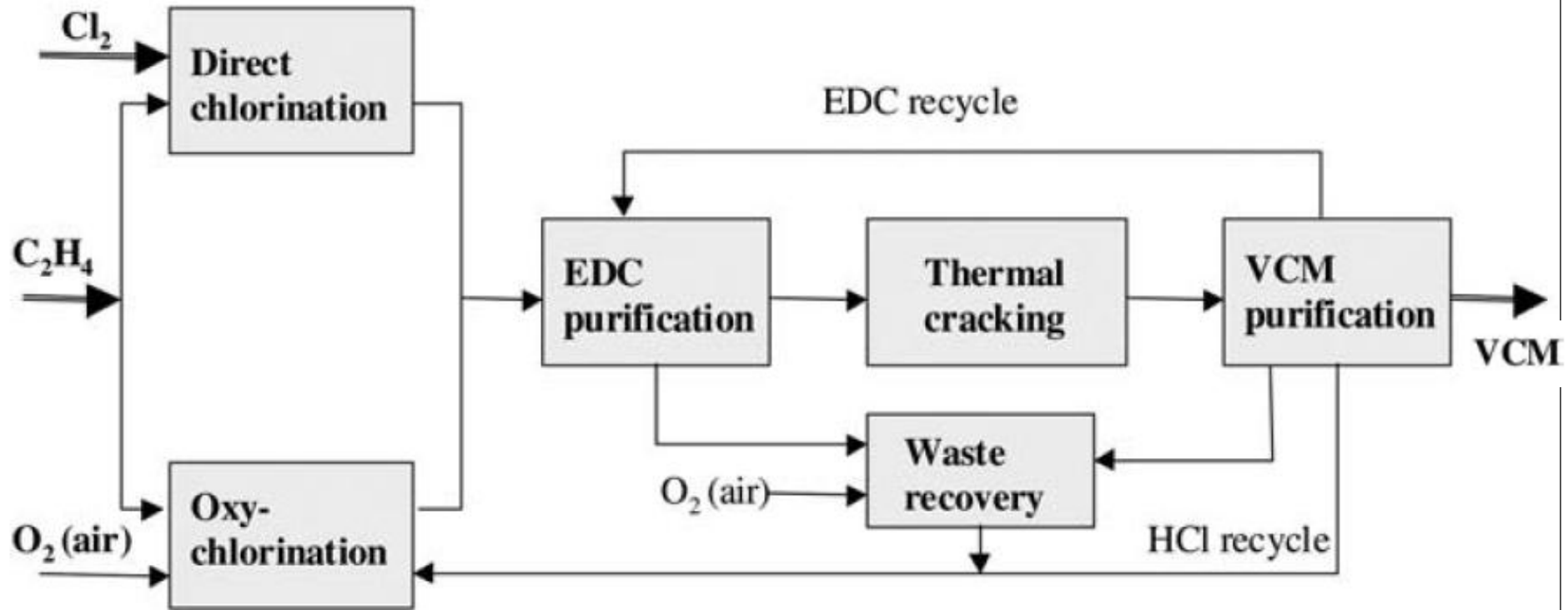
- **Use :** Mainly as precursor (monomer/ raw material) for poly vinyl chloride (PVC) polymer.

- **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 $\text{CH}_2\text{CH}_2 + \text{Cl}_2 \rightarrow \text{ClCH}_2\text{CH}_2\text{Cl}$ (EDC)
 - Oxychlorination $\text{CH}_2\text{CH}_2 + 2 \text{HCl} + \frac{1}{2} \text{O}_2 \rightarrow \text{EDC} + \text{H}_2\text{O}$
 - EDC pyrolysis $2 \text{EDC} \rightarrow 2 \text{CH}_2\text{CHCl}$ (VCM) + 2 HCl
 - **Overall reaction**
$$2 \text{CH}_2\text{CH}_2 + \text{Cl}_2 + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{CH}_2\text{CHCl} + \text{H}_2\text{O}$$
 - No generation of HCl
 - 95% of the world's VCM is produced utilizing the balanced process

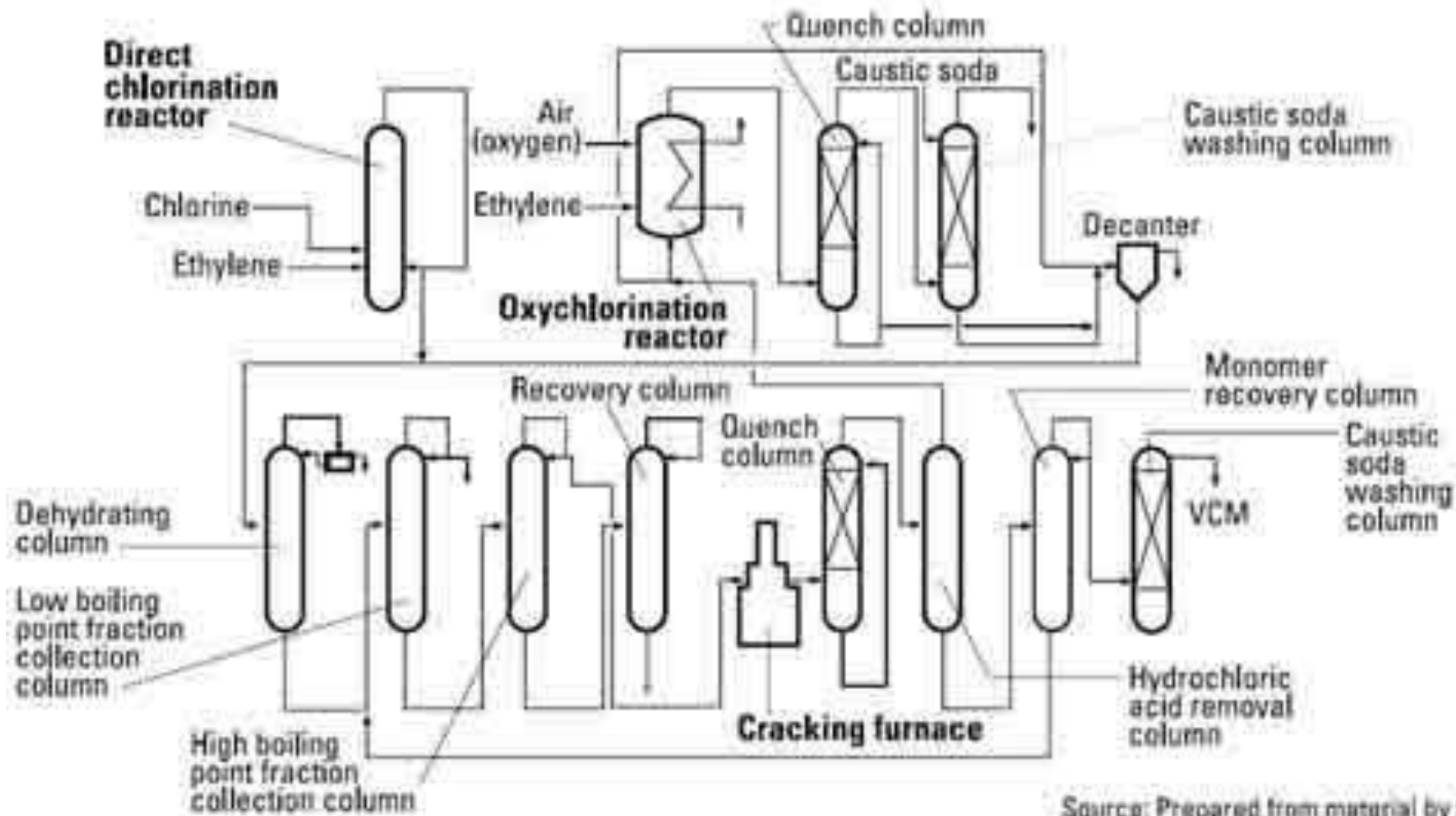
Balanced Process for VCM



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.
 - $T = 50\text{-}90\text{ }^{\circ}\text{C}$
- 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.
- $T = 200^{\circ}\text{C}$ 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 $480\text{-} 550^{\circ}\text{C}$ 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 (+C₂H₂)/bottoms (VCM + EDC)
 - Split 2: top crude VCM/bottoms crude EDC
 - Split 3: top Lights (C₄H₅ Cl)/bottoms crude EDC
 - Split 4: top pure EDC/bottoms TCE and heavies



Source: Prepared from material by the JPI

Major engineering problems

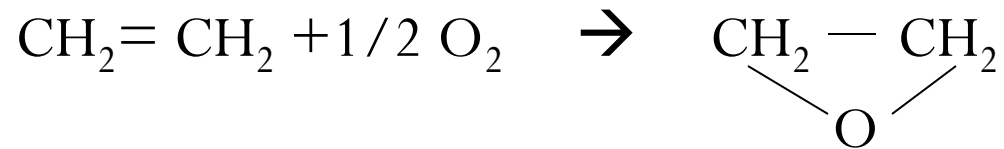
- **Carbon formation**
 - Occurs steadily until reactor has too high a pressure drop
 - Causing shut-down and periodic cleaning
 - Increasing conversion beyond 50% by longer residence time or higher temperature increase carbon formation and polymerization
 - Reactor conditions need to be worked out to 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

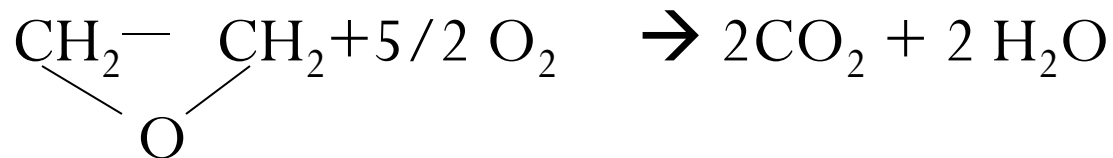
- Properties :
 - Mol wt : 44.05 B.P. = 10.7 °C
- Highly reactive chemical; an important raw material for production of ethylene glycol, ethanolamines, surfactant.
- Reaction is a good example of selective oxidation.
- Silver is the only metal known to catalyze this reaction with sufficient selectivity.
- Methods of production
 - Direct oxidation of ethylene (Air or oxygen)
 - Chlorohydrination of ethylene (Inefficient, cause major pollution problems)

Reactions & Kinetics

- Basic reaction



- Side reaction

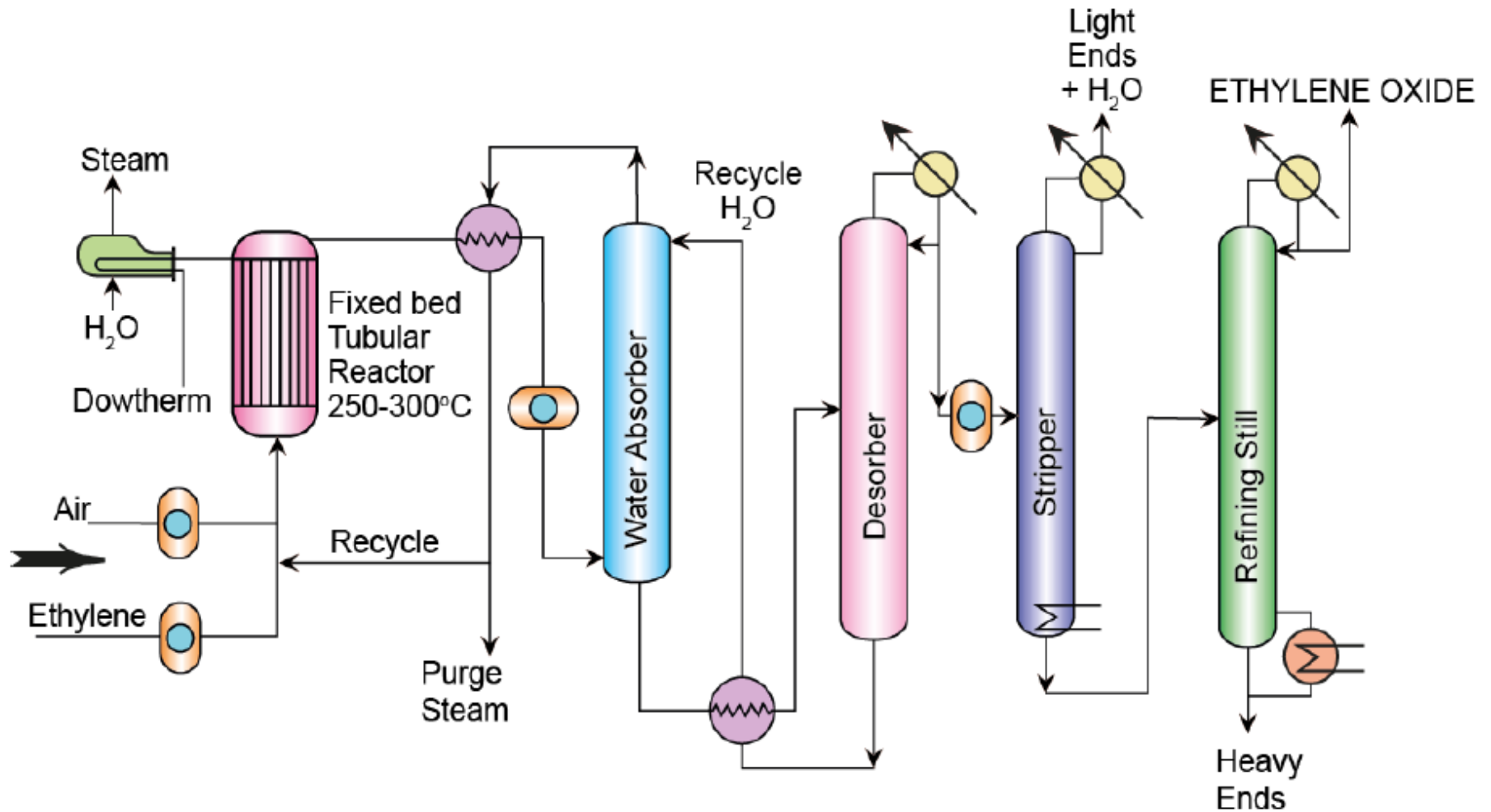


All 3 reactions are highly exothermic

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 $\text{CO}_2 + \text{H}_2\text{O}$
 - 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 ($T=150^{\circ}\text{C}$)
- Water is used in absorbing-desorbing train to maintain temperature $20-30^{\circ}\text{C}$.

Ethanolamines

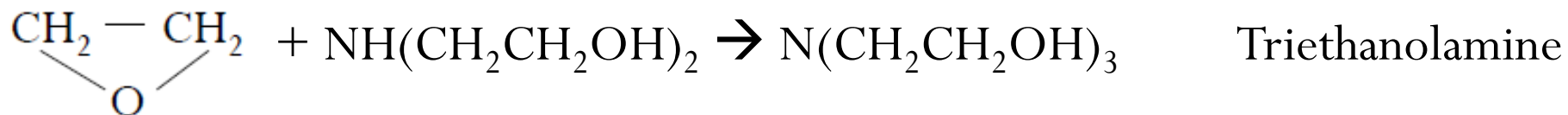
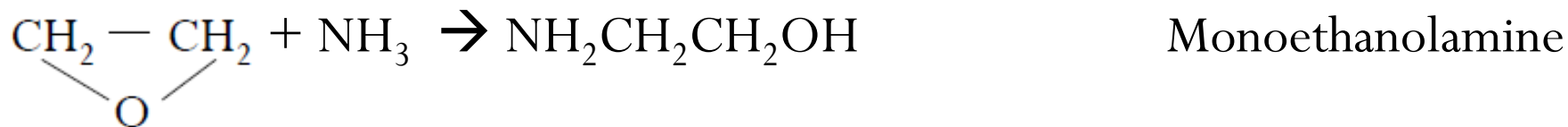
- In the industry received as a result of synthesis of ethylene oxides and ammonia. In the course of the further rectification Monoethanolamine (MEA), Diethanolamine (DEA), Triethanolamine (TEA) are separated out.
- Properties

	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

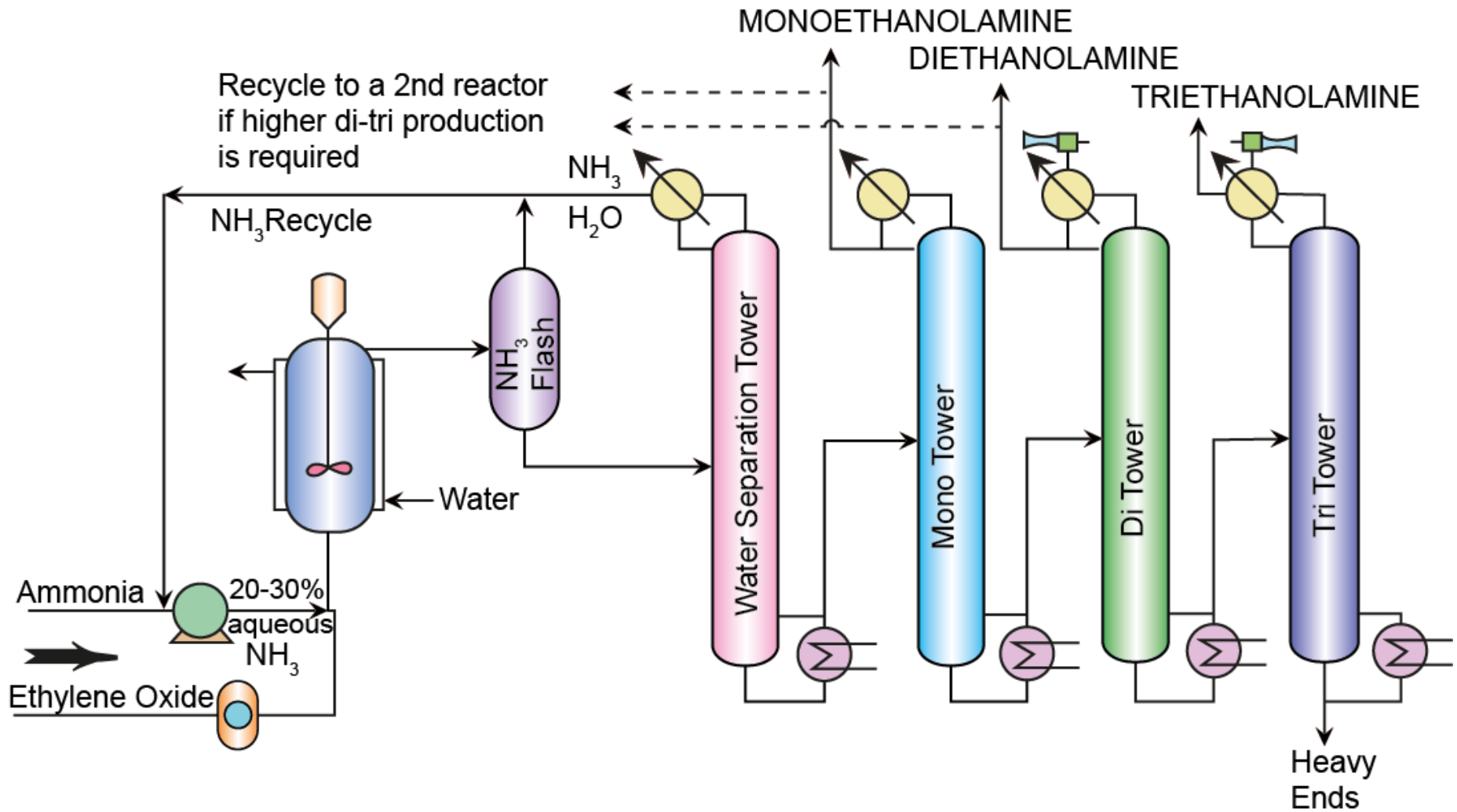


- The above reactions are series reaction scheme.
- Reactions are exothermic.
- Ammonia is in aqueous phase and ethylene oxide is in vapor state. Therefore, the reaction will be gas-liquid reaction.

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 40-80°C 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; $T = 35-275\text{ }^{\circ}\text{C}$; $P_r = 1-100\text{ atm}$.

- **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

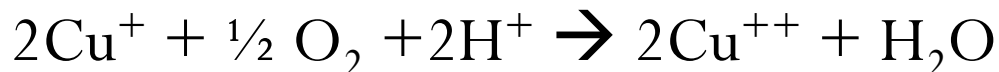
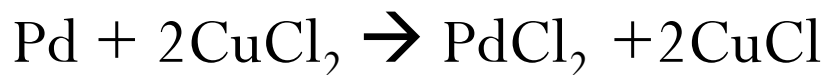
Acetaldehyde (CH₃CHO)

- 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



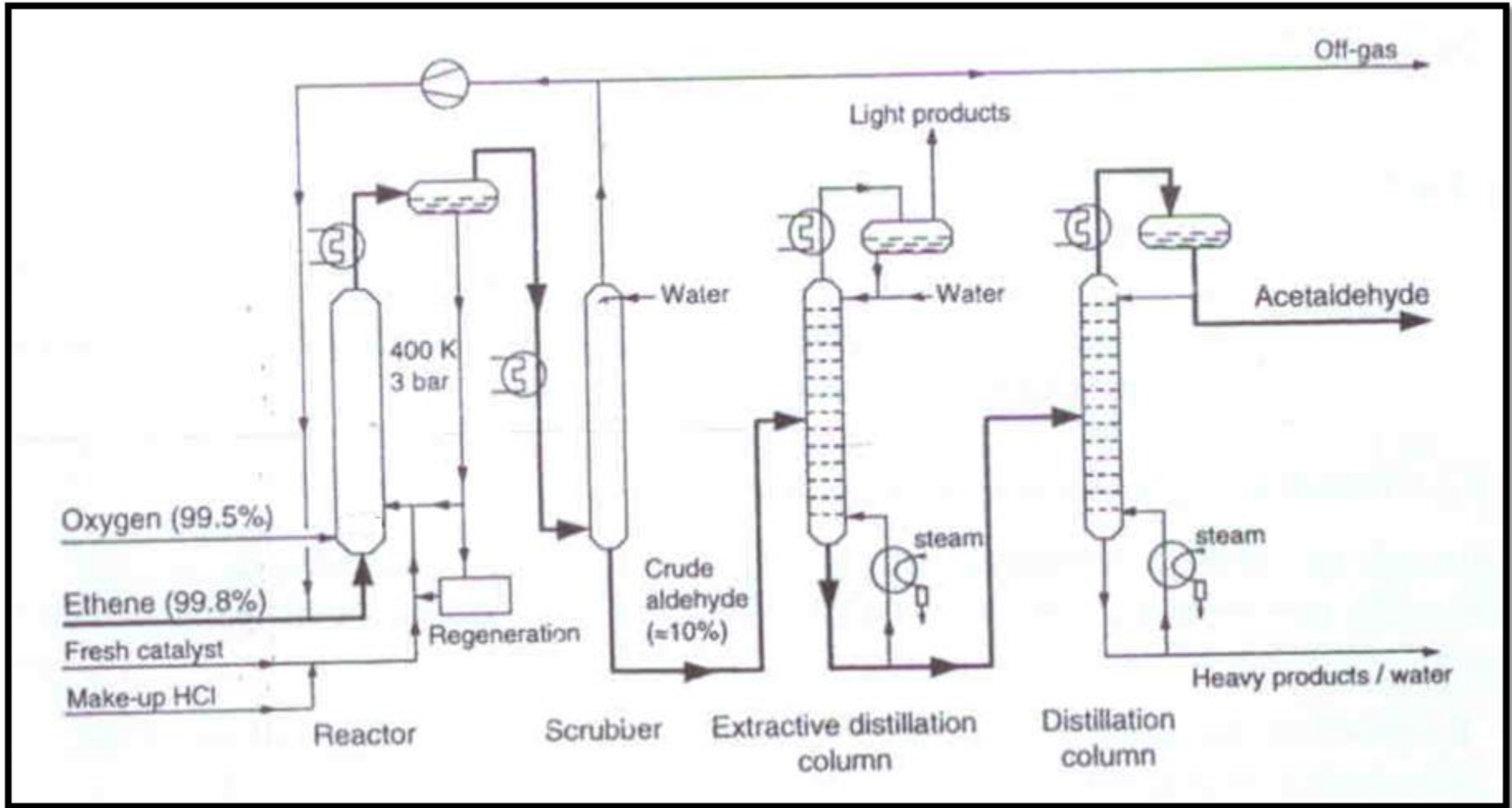
- Series of oxidation-reduction reaction



Process description

- Ethene and oxygen are fed into the lower part of reactor in which the circulation occurs by the upward movement of the gas bubbles.
 - Catalyst 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 be 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.