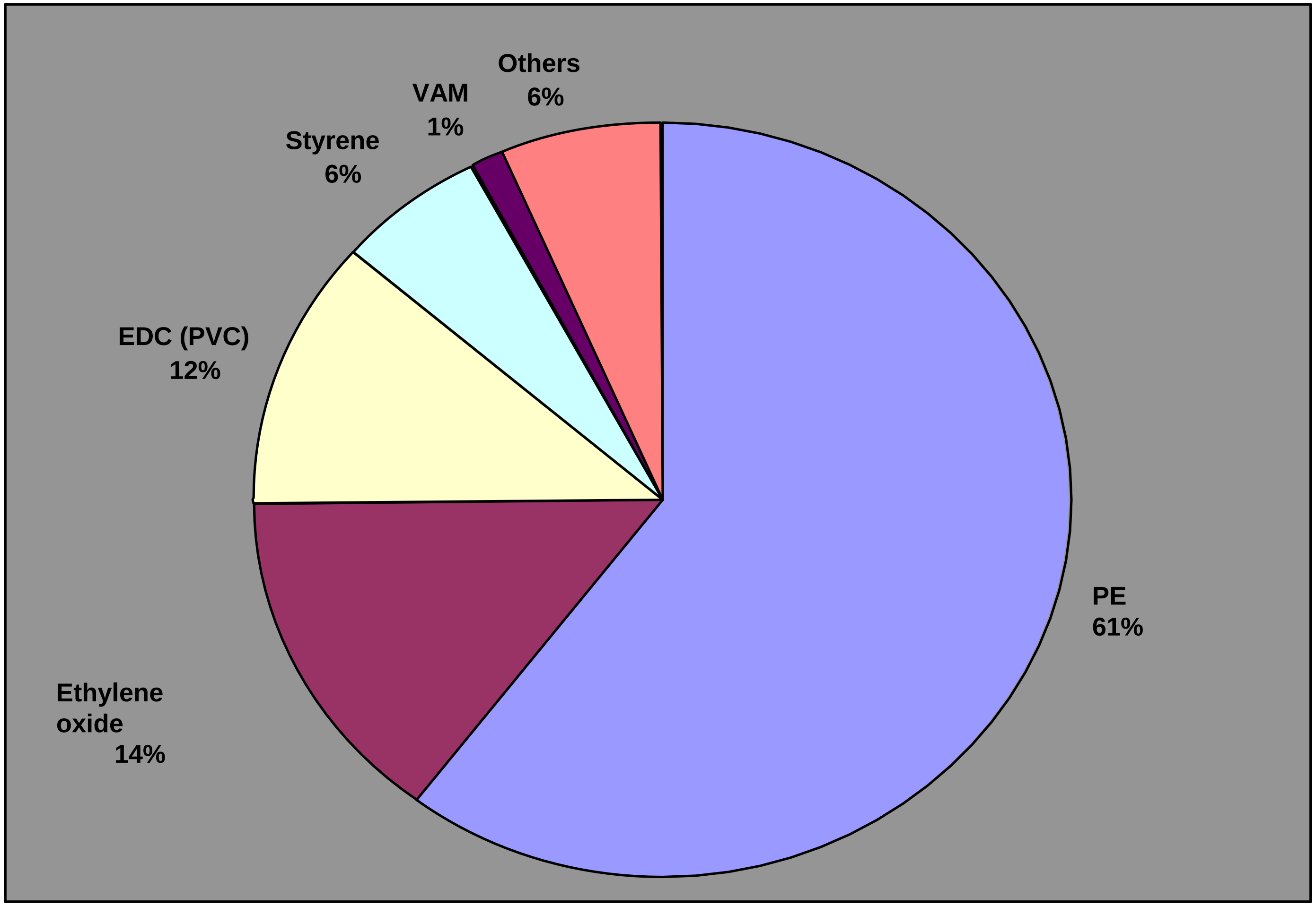
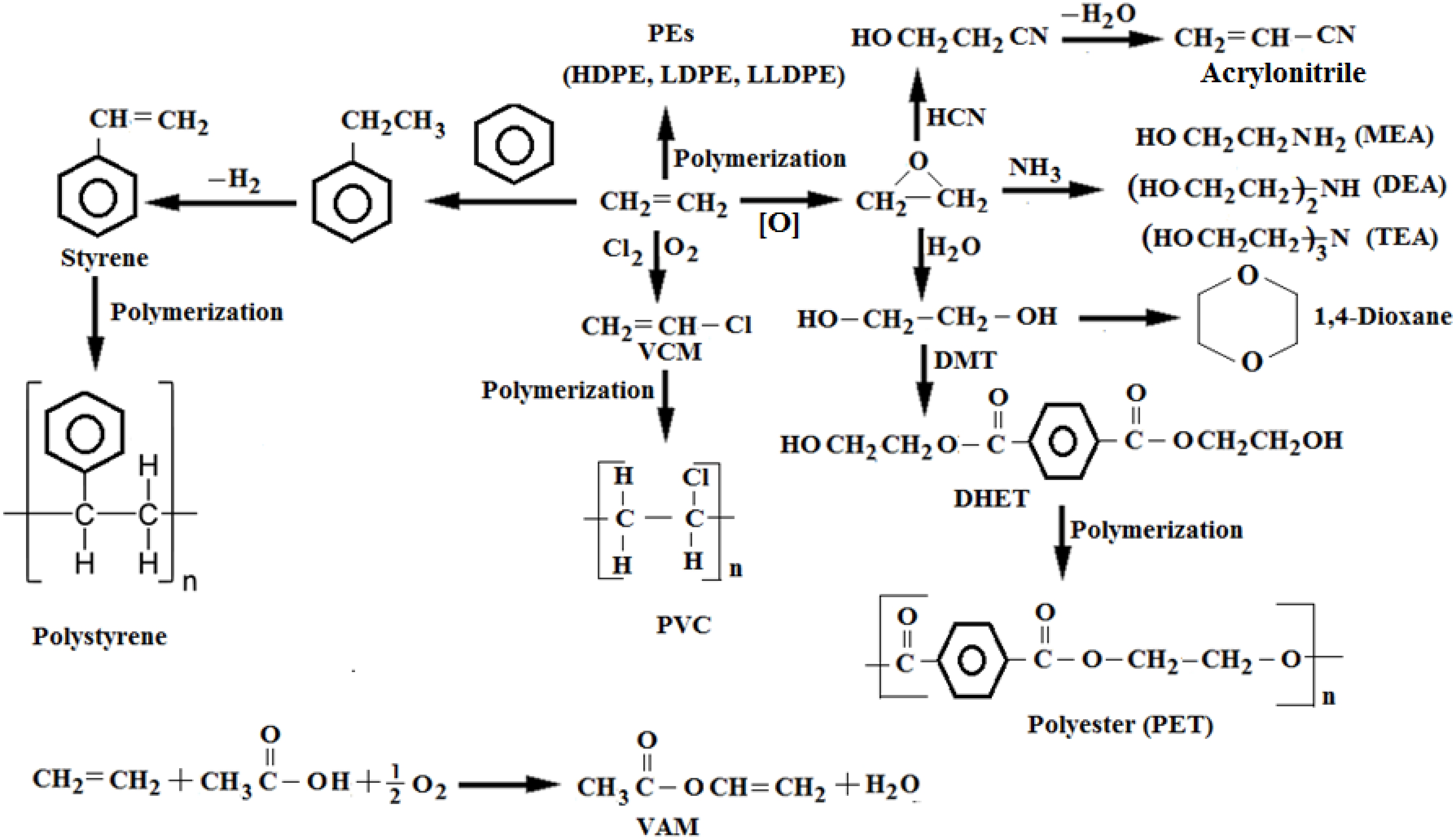
# Petrochemical Technology

**Chemicals from Ethylene**

# Ethylene Consumption Patterns



# Major Chemicals from Ethylene




**Vinyl Acetate Monomer** (VAM) is the precursor to **polyvinyl acetate (PVA)**. It is an intermediate used in the manufacture of a number of industrial polymers and resins for the production of adhesives, coatings, paints, films and textiles, as well as wire and cable insulation.

# Ethylene Oxide

**Ethylene Oxide (EO) is the second largest consumer of Ethylene. EO finds key applications in manufacturing Ethylene Glycol, the most common of which is monoethylene glycol (MEG). MEG is used for making PET resins which is used for making bottles and is also used in several antifreeze applications. Demand for several EO derivatives like ethyoxylates (used in shampoo, kitchen cleaners, etc.), glycol ethers (solvents, fuels, etc.) and ethanolamines (surfactants, personal care products, etc.) will always remain healthy.**

$$CH_2=CH_2 + \frac{1}{2}O_2 \longrightarrow \overset{O}{\overbrace{CH_2-CH_2}} \qquad \Delta H = -25\ \mathrm{kcal/mol}$$

$$CH_2=CH_2 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O \qquad \Delta H = -315\ \mathrm{kcal/mol}$$

Catalyst: **$Ag_2O/Al_2O_3$**

[Catalyst contains 10-15% of silver and promoters-compounds of alkalis or alkali earth metals, especially Cs and Ba.]

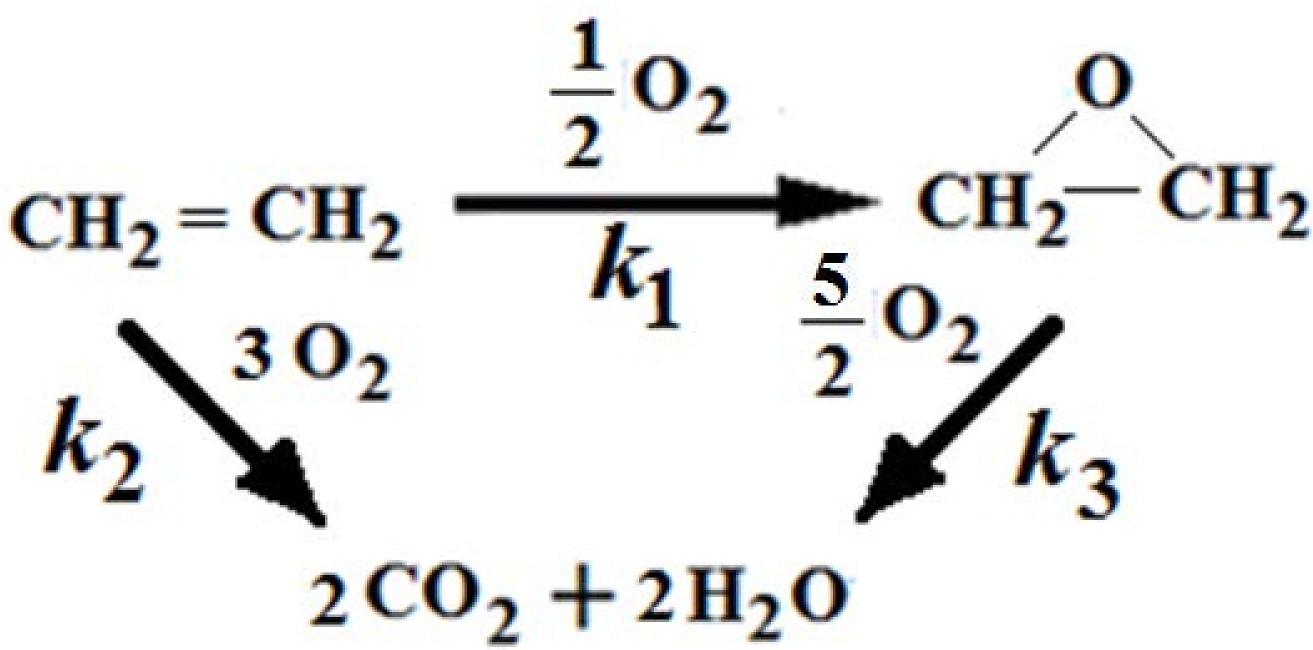
Oxidation with air : **260-280ºC**; Oxidation with oxygen: **230ºC**

Pressure: **10-30 atm**

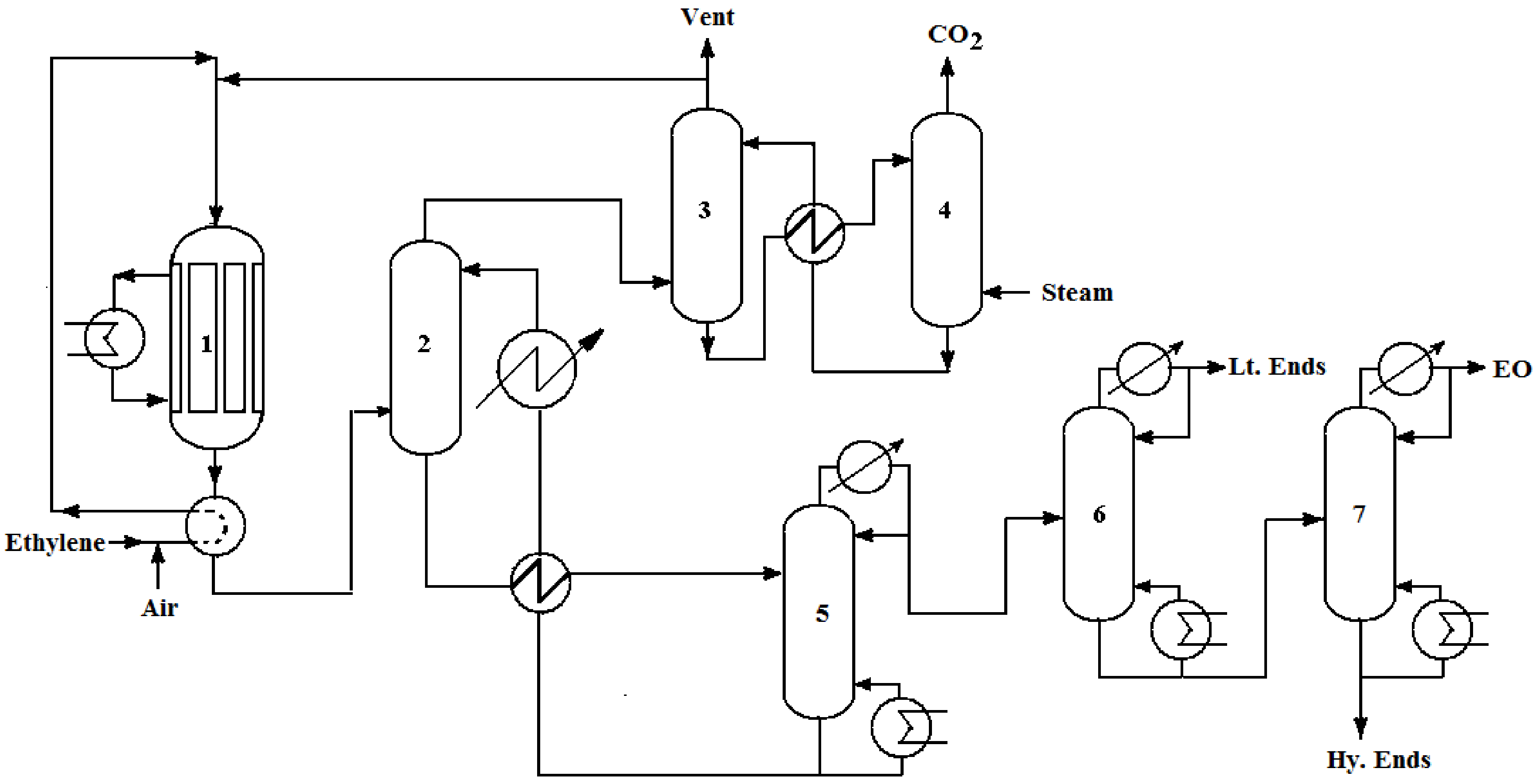
**High purity, sulphur-free ethylene** is required to avoid poisoning of the catalyst.

Ethylene concentration is about 20-30 vol% or 5 vol% when oxygen or air, respectively, is used as oxidant. The main byproducts are $CO_2$ and $H_2O$, and a very small amount of **acetaldehyde** is formed via isomerization of ethylene oxide.

**Selectivity to ethylene oxide is 65-75% (air process) or 70-80% ($O_2$ process).**
**Selectivity is improved by the addition of chlorine compounds (such as ethylene dichloride, ethyl and vinyl chloride), which reduce the production of byproduct $CO_2$ and ensure an even silver surface coating.**



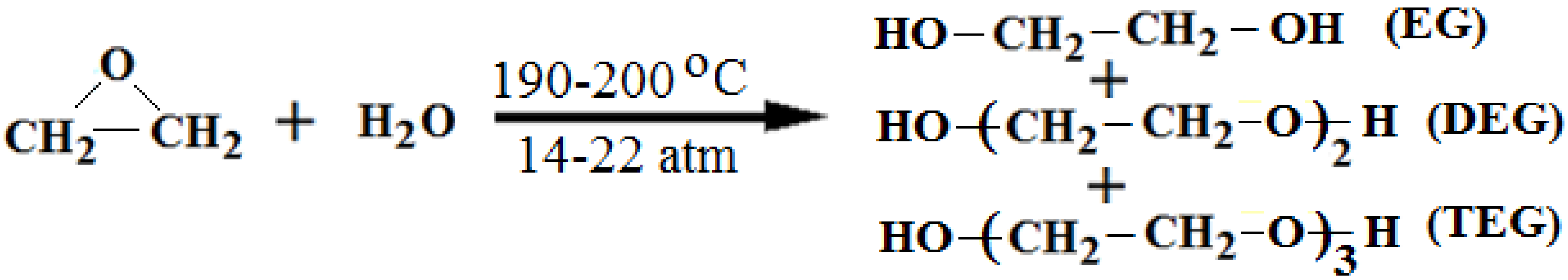

**On the best industrial catalysts $k_1/k_2$ is 6.0 and $k_2/k_3$ is 2.5.**




1: Reactor; 2: EO Absorber; 3: $CO_2$ Absorber; 4: $CO_2$ Stripper; 5: EO Stripper; 6: Lt. Ends Removal Column; 7: EO Column

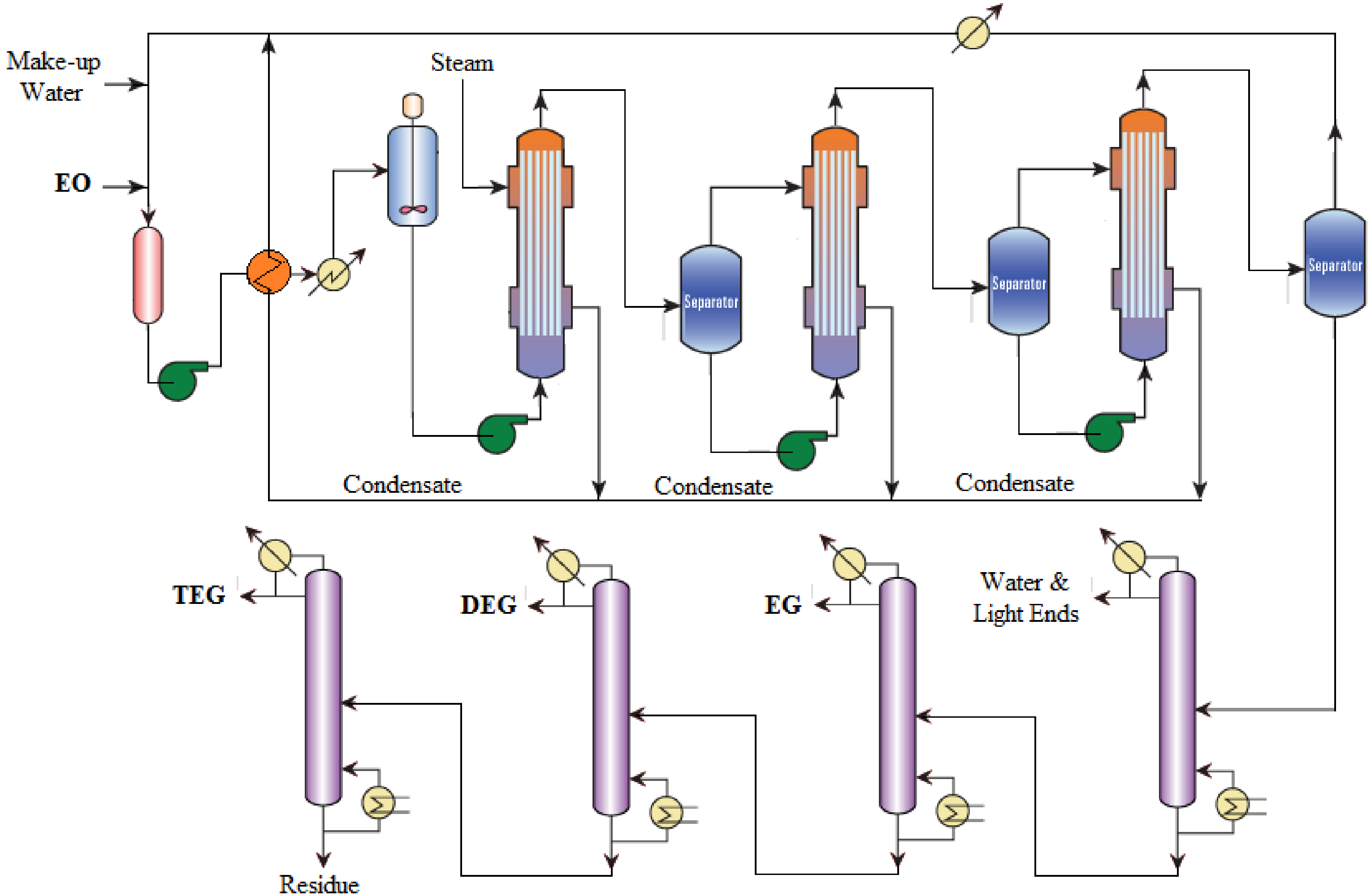
# Flowsheet for the production of Ethylene Oxide (EO)

# Ethylene Glycol




**A huge excess of water is used (18-24 moles of water/mole of EO) to prevent formation of di-, tri- and higher ethylene glycols.**

**Even with high water/EO ratio, mono- , di- and tri-ethylene glycols are obtained in a weight ratio of 91 : 8.6 : 0.4.**

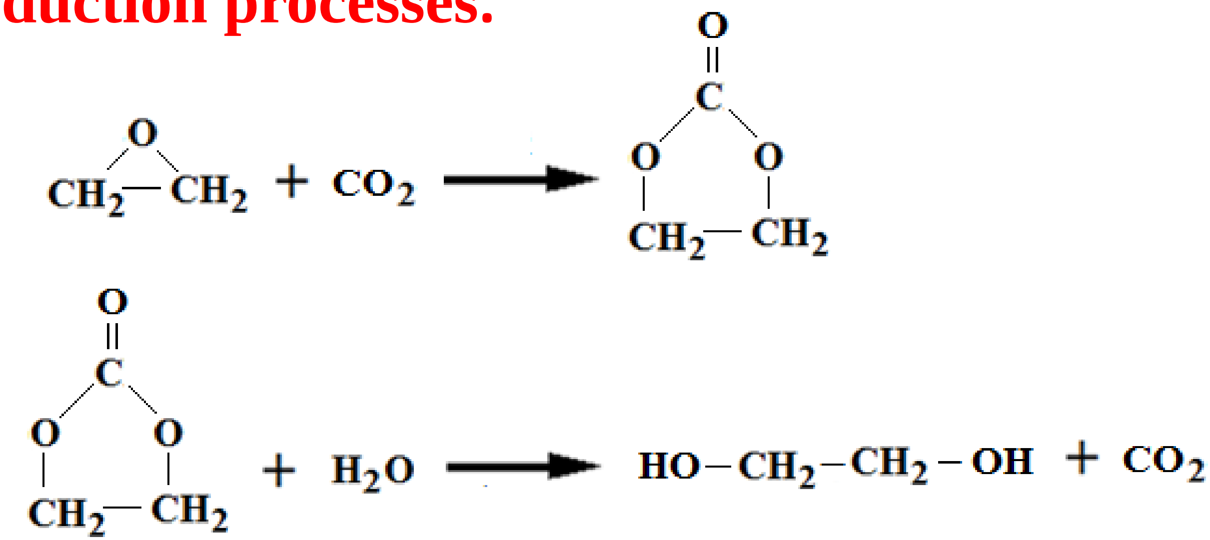



# Flowsheet for the production of Ethylene Glycol

# Monoethylene Glycol from EO

**Ethylene oxide is reacted with $CO_2$, forming ethylene carbonate, which is then hydrolyzed to form MEG and $CO_2$. Both reactions are carried out in the liquid phase using homogeneous catalysts.**

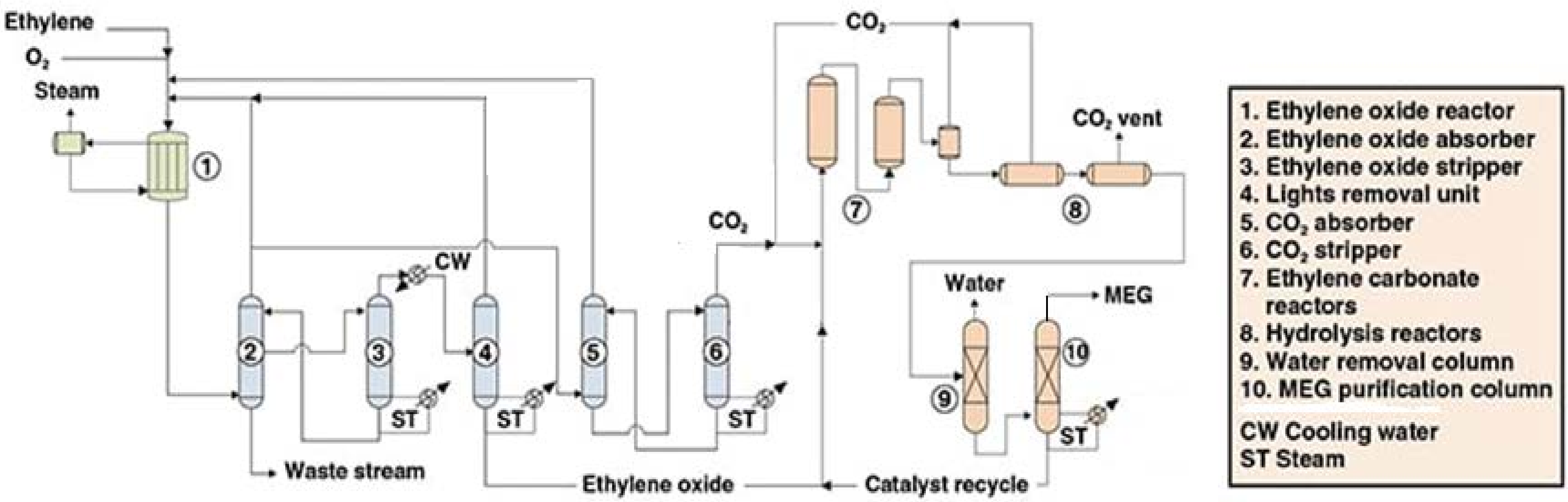
**An important feature of the process is the negligible production of diethylene glycol (DEG) and triethylene glycol (TEG), which occur as byproducts in other ethylene glycol production processes.**



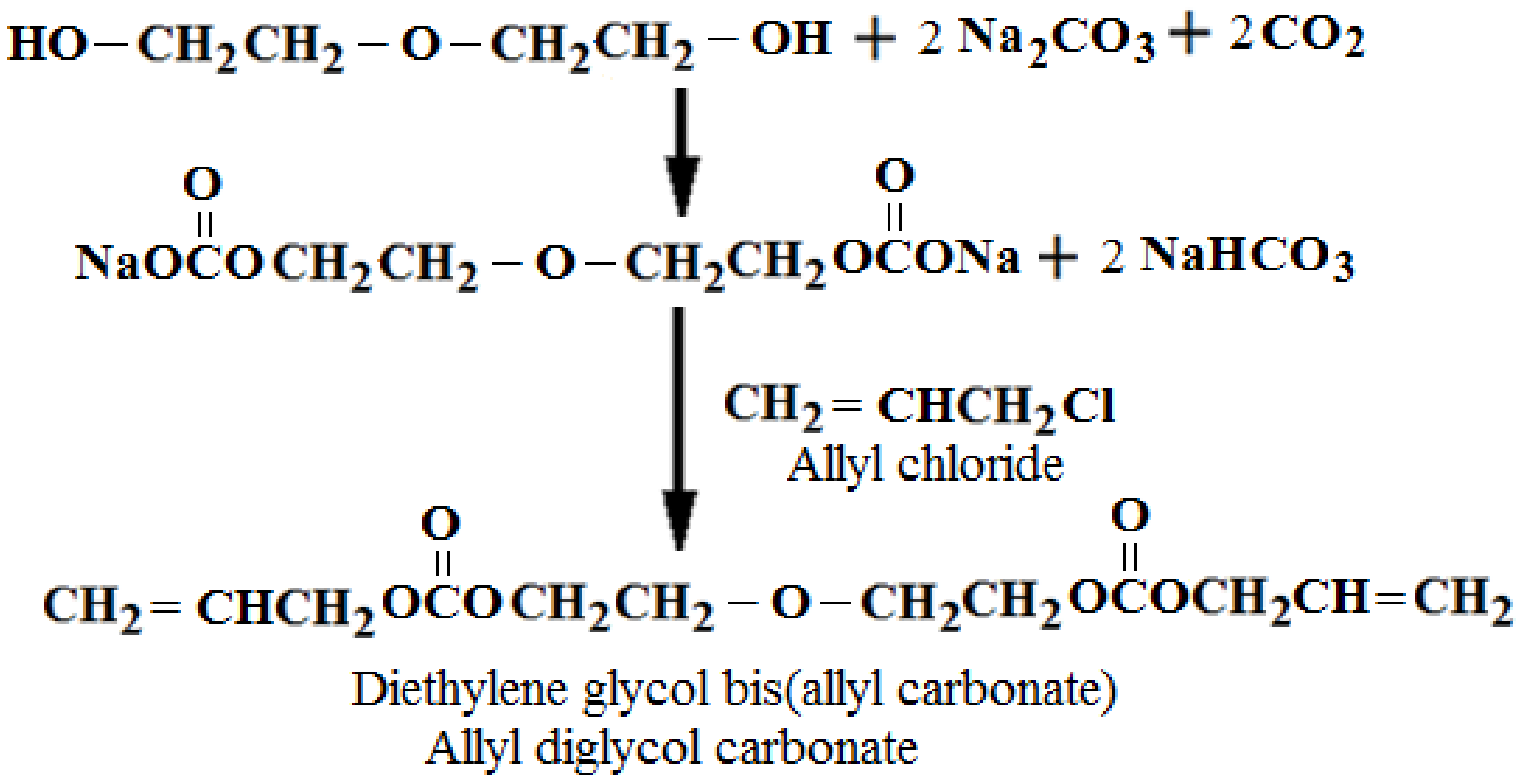
# Shell's OMEGA Process

## (OMEGA stands for "Only MEG Advantage")

Shell's OMEGA process for producing mono-ethylene glycol (MEG) from ethylene in a 2-stage, fully catalytic process, which has enabled many operators to achieve a conversion efficiency of over 99% compared to around 90% for conventional processes which utilise a thermal route to convert ethylene oxide (EO) into MEG.

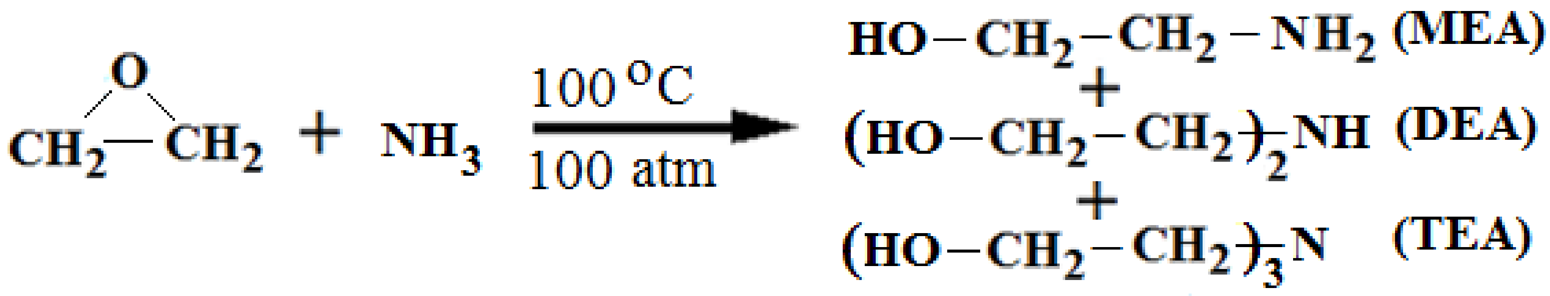



**Flowsheet for the production of Monoethylene Gylcol (OMEGA)**




**Diethylene glycol bis(allyl carbonate) is a specialty polycarbonate polymer whose major use is for molding eyeglass lenses by *in situ* polymerization.**

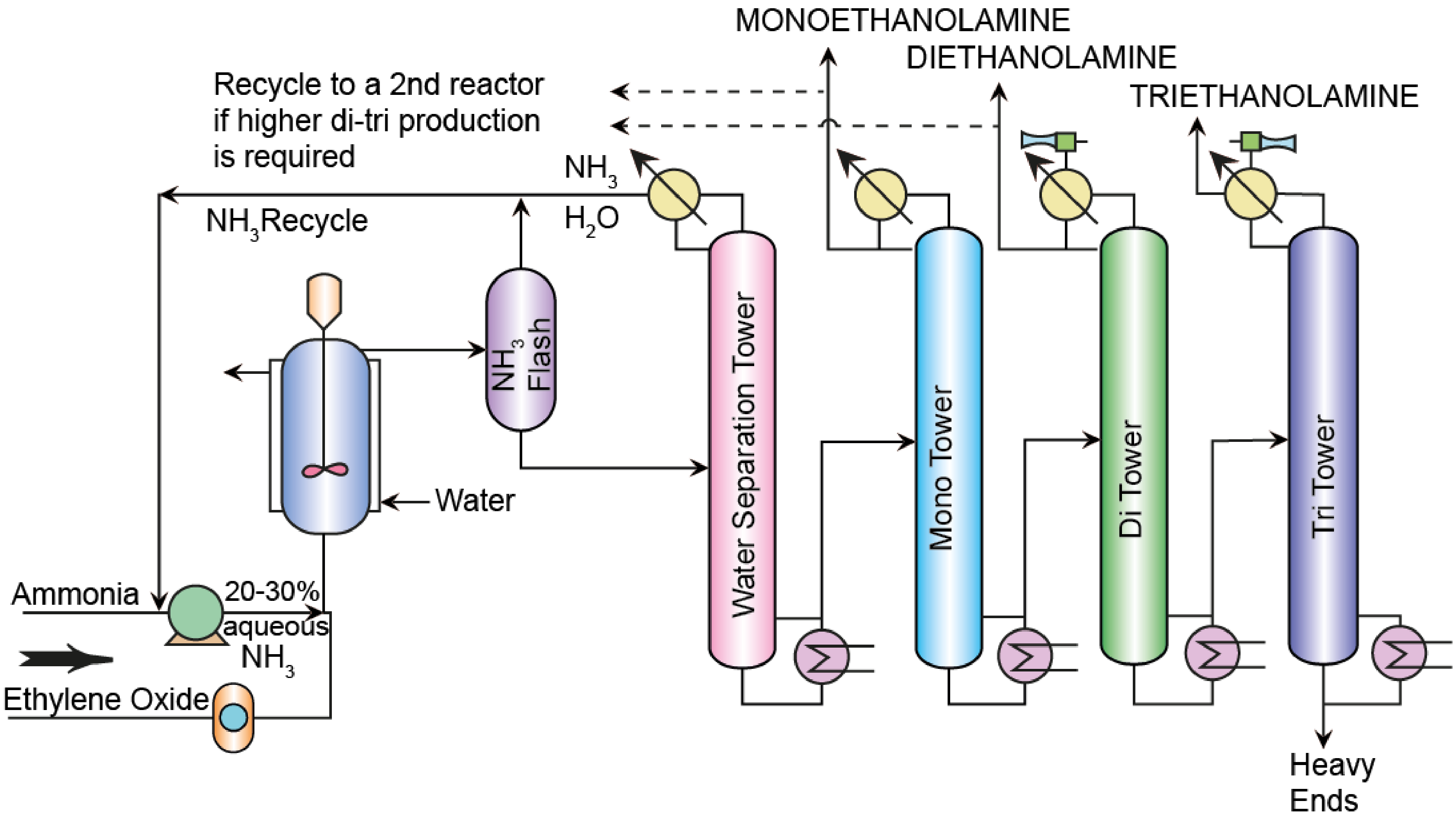
# Ethanol Amines




**$NH_3/EO = 0.5 – 3.0$,**

**Temperature = 35 – 275°C,**

**Pressure = 1 – 100 atm**




**Flowsheet for the production of ethanol amines from ethylene oxide**

The reaction of fatty acid methyl esters such as methyl laurate with ethanol amines provides fatty ethanol amides, widely used as foam stabilizers in detergent formulations.

$$\mathbf{CH_3(CH_2)_{10}COOCH_3 + NH_2CH_2CH_2OH \rightarrow}$$
$$\mathbf{CH_3(CH_2)_{10}CONH\ CH_2CH_2OH + CH_3OH}$$

N-hydroxyethyl lauramide

Of the three ethanol amines, triethanol amine enjoys about 40% of total demand, its major use being the formation of a quaternary salt with fatty acids to provide a surfactant useful in dry cleaning and cosmetic formulations.

$$\mathbf{(HOCH_2CH_2)_3N + C_{17}H_{35}COOH \rightarrow}$$
$$\mathbf{C_{17}H_{35}COO^{-}N^{+}H(CH_2CH_2OH)_3}$$

tris-Hydroxyethyl ammonium stearate

# Vinyl Chloride Monomer (VCM)

Global Vinyl Chloride Monomer (VCM) Market was valued at **USD 83.6 billion in 2023 and is expected to reach USD 164.2 billion by 2032**, registering a CAGR of 7.7% during the forecast period of 2024-2032.

The global VCM industry capacity was **52.38 mtpa** in **2022**.

Over 99% of total global VCM consumption is used for PVC production.

## Balanced Chlorination-Oxychlorination process:

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{50\text{-}70\,^{o}C} Cl{-}CH_2{-}CH_2{-}Cl \qquad \Delta H = -\,50 \text{ kcal/mol}$$

$$Cl{-}CH_2{-}CH_2{-}Cl \xrightarrow[25\text{-}30 \text{ atm}]{\geq 450\,^{o}C} CH_2{=}CH{-}Cl + HCl \qquad \Delta H = 17 \text{ kcal/mol}$$

$$CH_2{=}CH_2 + 2\,HCl + \tfrac{1}{2}O_2 \xrightarrow[1\text{-}15 \text{ atm/ } CuCl_2]{225\text{-}325\,^{o}C} Cl{-}CH_2{-}CH_2{-}Cl + H_2O \qquad \Delta H = -\,57 \text{ kcal/mol}$$

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$$2\,CH_2{=}CH_2 + Cl_2 + \tfrac{1}{2}O_2 \longrightarrow 2\,CH_2{=}CH{-}Cl + H_2O$$

# Mechanism of Oxychlorination

**Copper chloride is universally applied as catalyst. Known as the modified Deacon catalyst, $CuCl_2$ is supported on alumina and contains KCl.**

**Under operating conditions, a $CuCl_2$-$Cu_2Cl_2$-KCl ternary mixture, possibly in the molten state, is the active catalyst.**

**$CuCl_2$ is believed to be the active chlorinating agent producing EDC directly without the involvement of elemental chlorine.**

**The coupled oxidoreduction steps are indicated below:**

$$CH_2{=}CH_2 + 2\,CuCl_2 \longrightarrow Cl{-}CH_2{-}CH_2{-}Cl + Cu_2Cl_2$$

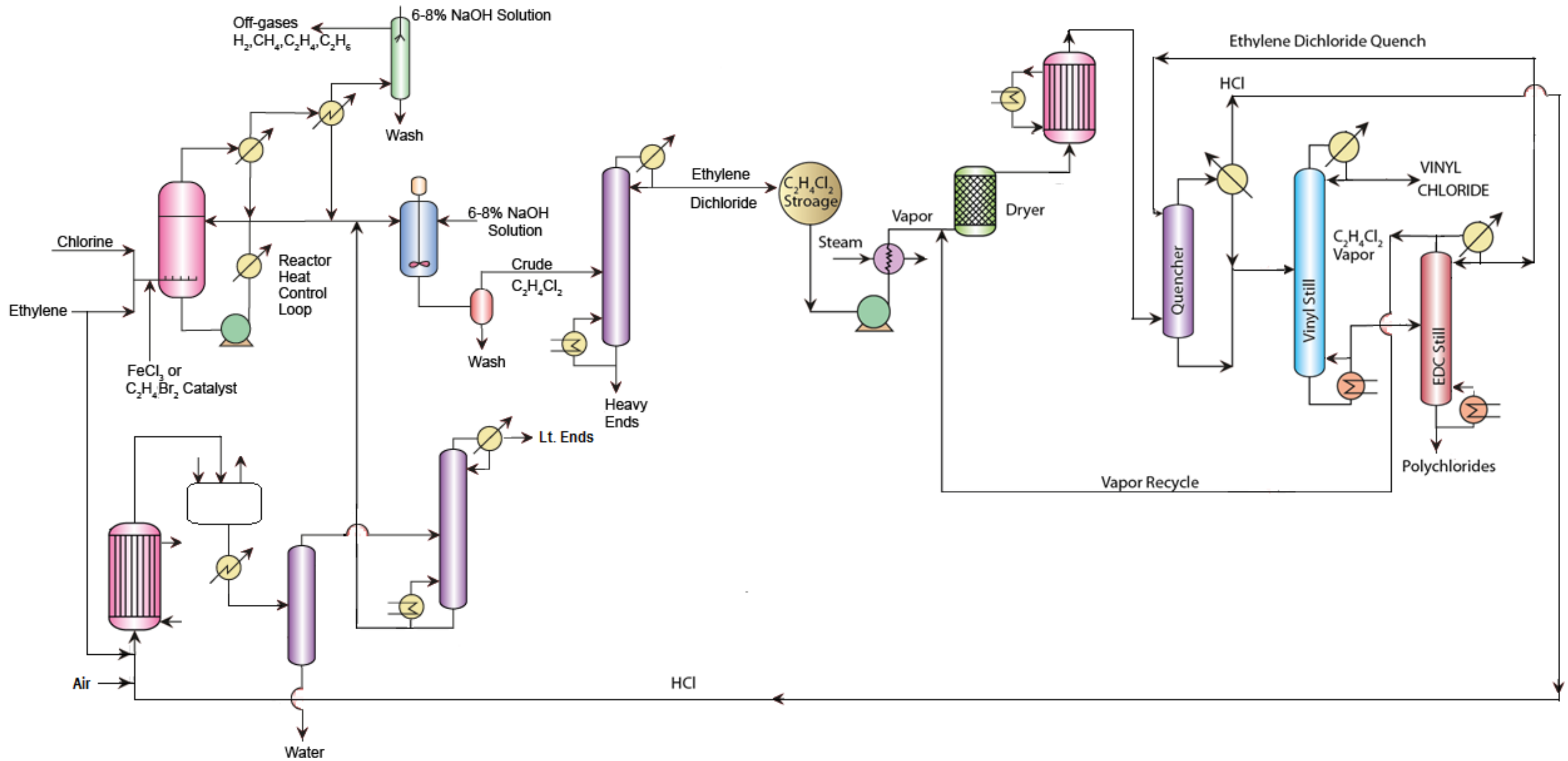
$$Cu_2Cl_2 + \frac{1}{2}O_2 \longrightarrow CuO.CuCl_2$$

$$CuO.CuCl_2 + 2\,HCl \longrightarrow CuCl_2 + H_2O$$

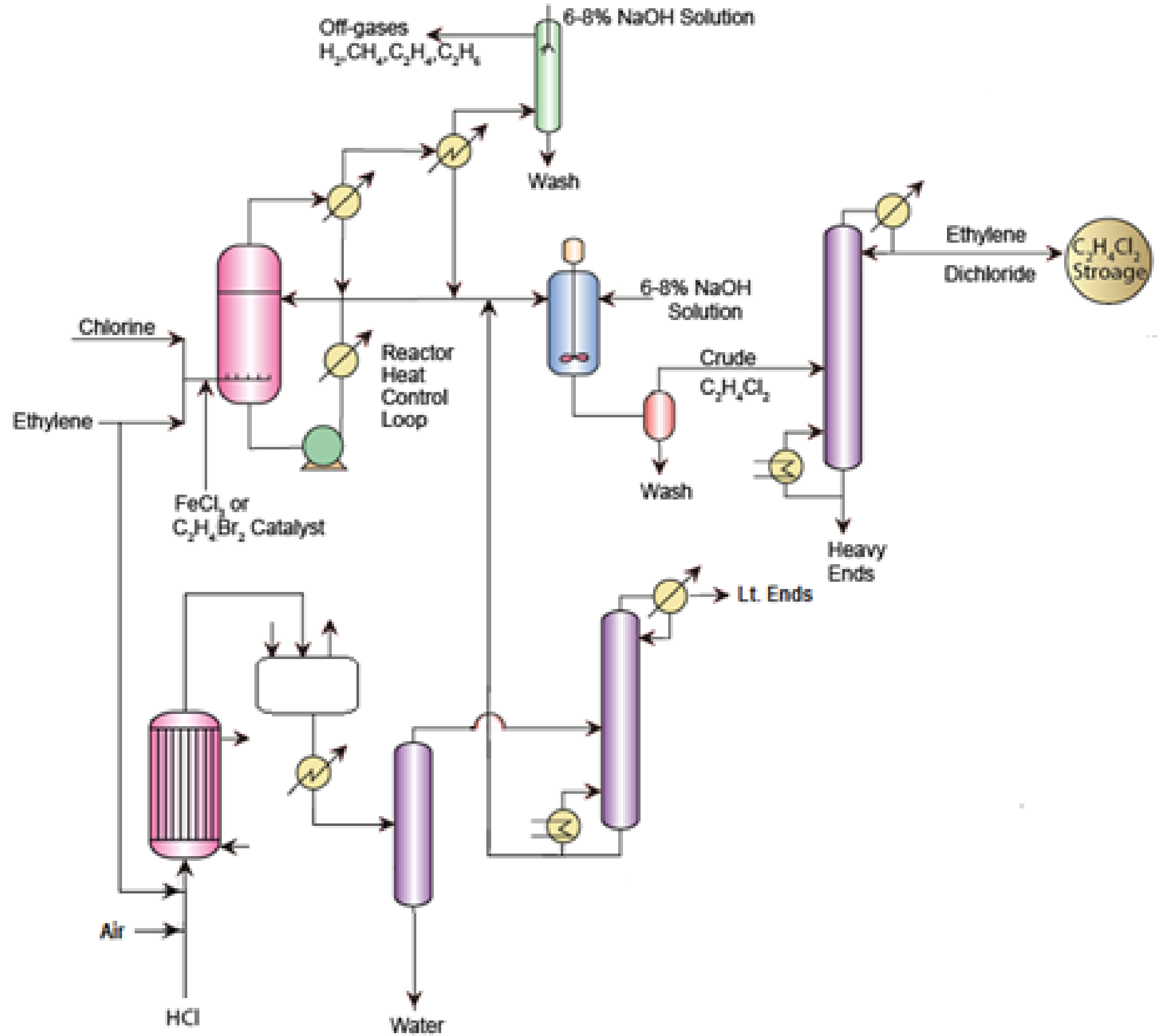
# Kellog's technology for oxidation of HCl to $Cl_2$

**A modified vinyl chloride process combines Monsanto's direct chlorination, cracking, and purification technologies and Kellog's proprietary technology for oxidation of HCl to $Cl_2$. In this process, the inefficient hazardous oxychlorination step is eliminated. Instead chlorine is recovered after the oxidation of HCl and used again in the direct chlorination of ethylene. This improved technology is more economical and less polluting and yields high purity vinyl chloride.**

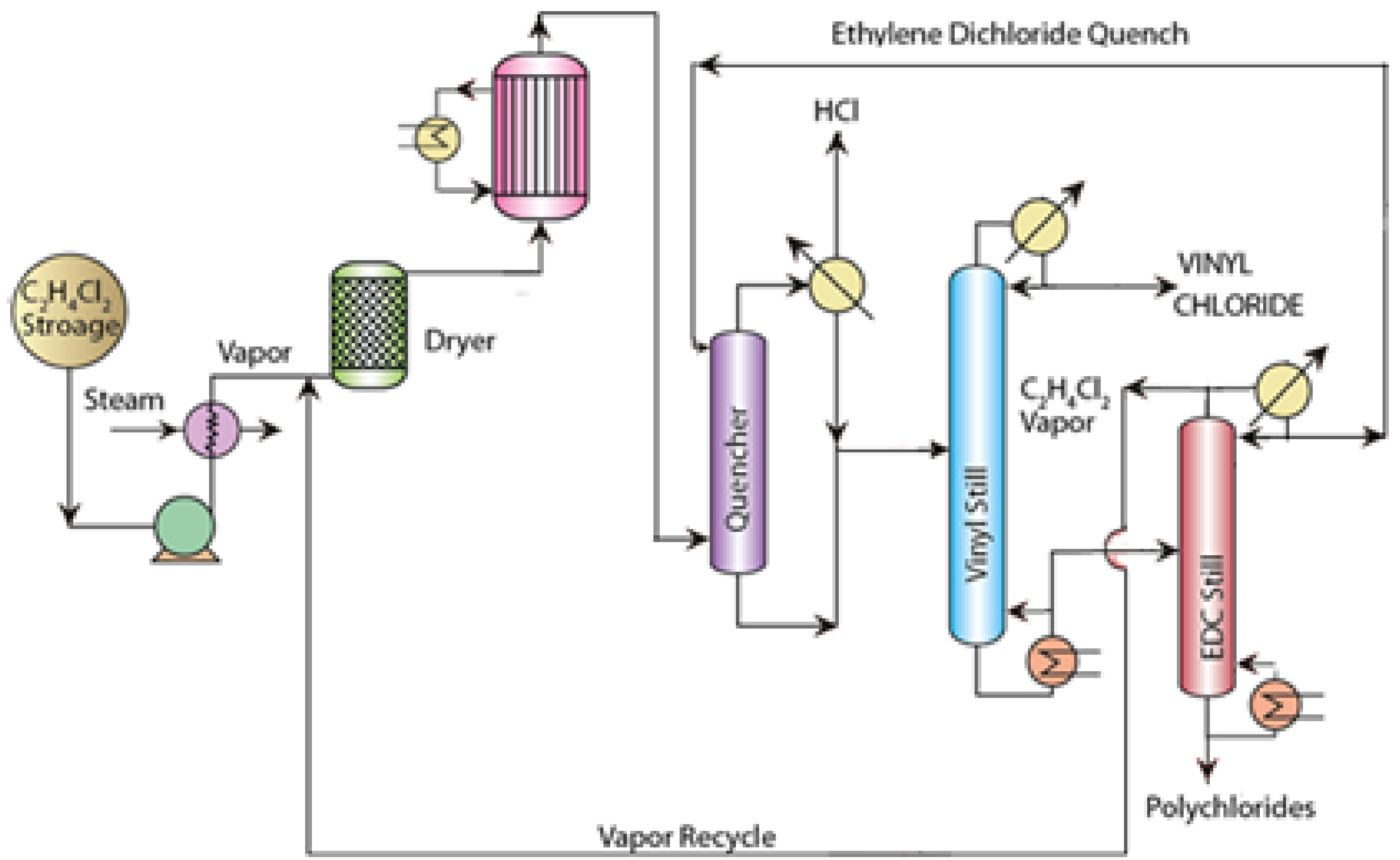
$$2\,HCl + \frac{1}{2}O_2 \xrightarrow[180^{o}C\,/\,20\text{ atm}]{CuCl_2/KCl} Cl_2 + H_2O$$




**Flowsheet for the Production of Vinyl Chloride Monomer (VCM) from Ethylene**




**Flowsheet for the Production of Ethylene Dichloride (EDC) from Ethylene**




**Flowsheet for the Production of Vinyl Chloride Monomer (VCM) from Ethylene Dichloride (EDC)**

# Thank you!