Chapter 3: Petrochemical Manufacturing Schemes

- Diversity of petrochemical industry products
- Main manufacturing pathways in petrochemistry
- Examples of processes (PVC, Ammonia)

Petrochemistry is the study of reactions involving petroleum products and by-products, as well as the manufacturing and synthesis processes of basic chemical products derived from hydrocarbons.

I. Main production routes in petrochemistry:

After separation operations, the proportion of heavy hydrocarbons is still too high. To meet the demand for lighter products, these heavy molecules are "cracked" into two or more lighter molecules.

Here are the main production routes in petrochemistry, that is, the major industrial pathways used to produce chemical compounds from hydrocarbons (oil and natural gas).

II. Cracking and Desulfurization

II.1. Cracking

It’s the decomposition of a hydrocarbon into two other different hydrocarbons under the action of temperature and/or in the presence of a catalyst.

I.1.1. reactions

$$Paraffin \xrightarrow{(cracking)} Paraffin + olefin$$

Ex 1: $$\boldsymbol{C_8H_{18} \rightarrow C_4H_{10} + C_4H_8}$$

$$Olefin \xrightarrow{(cracking)} olefin + olefin$$

Ex 2: $$\boldsymbol{C_8H_{16} \rightarrow C_5H_{10} + C_3H_6}$$

$$Naphtene \xrightarrow{(cracking)} olefin + aromate$$

Ex 3: (desalkylation + aromatization)

-*Aromate* (*Cracking*) ⟶ *Aromate + Olefine*

Exemple : *Cumene* ⟶ *Benzene* + C_3H_6

II.1.2. Types of Cracking

II.1.2.1. Thermal Cracking

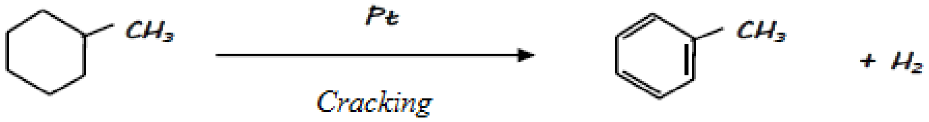
This is cracking that takes place at high temperatures.

- **Example 1:** Gas oil (cracking) → Naphtha (lighter)
- **Example 2:** Heavy fraction (500°C / 4 bars) → Naphtha + Gas oil
- **Example 3:** Production of coke by cracking heavy naphthenic petroleum

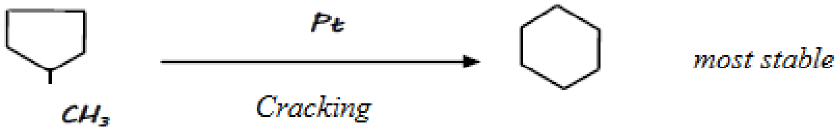
II.1.2.2. Catalytic Cracking

This type of cracking is carried out in the presence of platinum (Pt) as a catalyst. Catalytic cracking occurs at lower temperatures using a platinum catalyst. It has the advantage of requiring less energy and offers good yields. However, it requires desulfurized feedstocks to avoid catalyst poisoning and needs an additional step: catalyst regeneration by burning with air.

Ex1 : (Deshydrogénation)



Ex 2 : Isomérisation cyclic



II.1.2.3. Hydrocracking

This is cracking in the presence of hydrogen.

The presence of hydrogen prevents the formation of gums by the polymerization of olefins.

Example: Production of gasoline from gasoil

$$\mathbf{diesel} + \mathbf{H_2} \xrightarrow{\mathbf{500°C\ /\ 150\ bars\ /\ NiCO\ /\ Al_2O_3)}} \mathbf{Gasoline}$$

II.2. Desulfurization

This is the removal of sulfur compounds (**H_2S** and mercaptans (**R-S-H; RS-S-H**; ...)) which are corrosive and foul-smelling. There are several treatment processes:

II.2.1. Treatment with caustic soda (NaOH)

This is a limited treatment for light fractions (LPG, naphtha, etc.) because for radicals with ≥ 4 carbon atoms, the reactions become difficult.

$$\text{(Mercaptan)} + \text{NaOH (Basses T)} \longrightarrow \text{(Mercaptide)} + H_2O$$

$$R\text{-}S\text{-}Na + \text{NaOH (10 à 15\%)} \longrightarrow R\text{-}S\text{-}Na + H_2O$$

II.2.2. Sweetening Process

Two sweetening processes exist: the Doctor process and the copper chloride process. In general, the sweetening process can be summarized by the following overall reaction:

Mercaptans + Oxygen → Inert Disulfides + H_2O

$2R\text{-}S\text{-}H + \frac{1}{2} O_2 \rightarrow R\text{-}S\text{-}S\text{-}R + H_2O$

II.2.2.1. Doctor Process

This is a semi-regenerative process because sodium sulfate (**Na_2SO_4)** is purged each time, and sodium plumbite (**Na_2PbO_2)** and sulfur (S) are added.

$2R\text{-}S\text{-}H + Na_2PbO_2 \rightarrow (R\text{-}S)_2Pb + 2NaOH$

$(R\text{-}S)_2Pb + S \rightarrow R\text{-}S\text{-}S\text{-}R + PbS$

$PbS + 4NaOH + 2O_2 \rightarrow Na_2SO_4 + Na_2PbO_2 + 2H_2O$

Overall reaction:

$2R\text{-}S\text{-}H + S + 2O_2 + 2NaOH \rightarrow R\text{-}S\text{-}S\text{-}R + Na_2SO_4 + 2H_2O$

In summary, to convert mercaptans into inert disulfides, caustic soda (NaOH) and sulfur (S) are added, then oxygen (air) is blown in.

II.2.2.2. Copper Chloride Process

This is a process with regeneration of copper chloride by air blowing:

$4R\text{-}S\text{-}H + 4CuCl_2 \rightarrow 2R\text{-}S\text{-}S\text{-}R + 4CuCl + 4HCl$

Regeneration:

$4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O$

Overall reaction:

$4R\text{-}S\text{-}H + O_2 \rightarrow 2R\text{-}S\text{-}S\text{-}R + 2H_2O$

In summary, to convert mercaptans into inert disulfides, the compounds are passed through a fixed bed of copper chloride ($CuCl_2$), then oxygen (air) is blown in.

II.2.3. Catalytic Hydrotreatment

Desulfurization by hydrotreatment is carried out at high temperature and high pressure in the presence of hydrogen.

- R-S-H + H_2 → R-H + H_2S *(T and P)* ↗
- R-S-S-R + $3H_2$ → 2R-H + $2H_2S$ *(T and P)* ↗

$$\begin{matrix}\text{Naphta}\\ \textit{(Sulfured)}\end{matrix} \xrightarrow[100m^3\ H_2/\ \text{ton of loading}]{300^\circ C/30\ \text{bars}} \begin{matrix}\text{Naphta}\\ \textit{(desulfured)}\\ <1ppm\ \text{of sulfur}\end{matrix} + H_2S$$

$$\begin{matrix}\text{diesel}\\ \textit{(Sulfured)}\end{matrix} \xrightarrow[150m^3\ H_2/\text{ton of loading}]{350^\circ C/40\ \text{bars}} \begin{matrix}\text{Gasoil}\ \textit{(desulfured)}\\ <0{,}02\%\ \text{of sulfur}\end{matrix} + H_2S$$

II.2.3.1. Sulfur Recovery (Claus Process)

The hydrogen sulfide (H_2S) produced from the desulfurization reactions is treated using the **Claus process**, both to protect the environment from the impact of H_2S and to recover elemental sulfur (S).

- $H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$ *(at 200°C)*
- $SO_2 + 2H_2S \rightarrow 3S + 2H_2O$ *(with Al_2O_3 catalyst)*

Desulfurization can also be performed using another method: in a **counter-current absorption column** with a solution of monoethanolamine (MEA), at a concentration of **10 to 15% by mass**, operating at **low temperature and high pressure**.

III. Production of Polyvinyl Chloride (PVC)

III.1. Introduction

Polymerization is the reaction of **(n)** molecules of an organic compound containing a double bond (olefin) to form a new compound that is **(n)** times heavier than the original monomer. Polymerization takes place under well-defined conditions of pressure and temperature, in the presence of a catalyst—generally a **peroxide** or **percarbonate**.

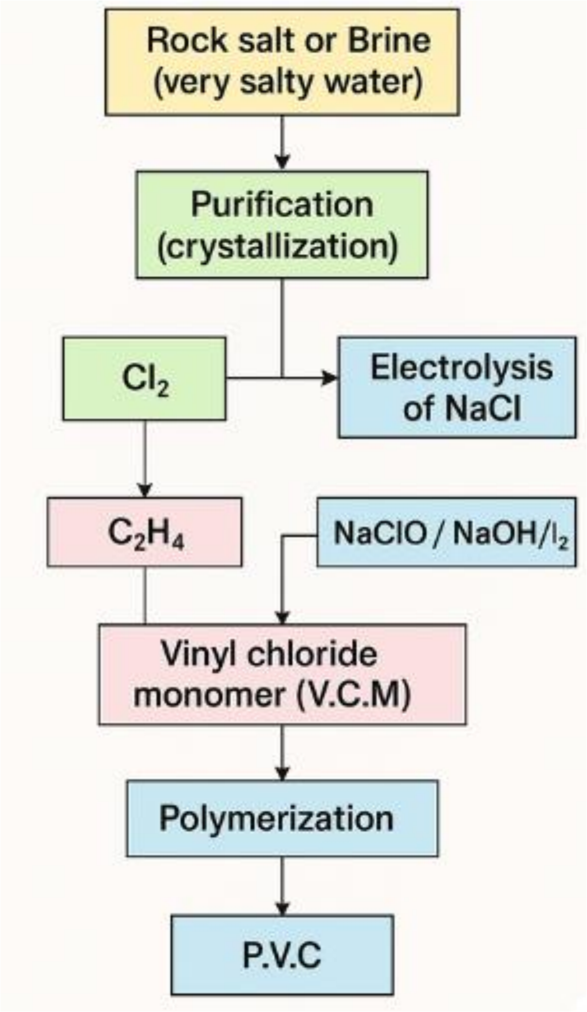
III.2. PVC Production

Polyvinyl chloride (PVC) is used in industries for the manufacturing of **pipes, packaging**, and various other **plastic products**.

PVC is based on the monomer **vinyl chloride monomer (VCM)**, also called **chloroethylene** (CH_2=CH-Cl).

The polymerization reaction takes place between **ethylene (C_2H_4)** and **chlorine (Cl_2)**, the latter being obtained from the **electrolysis of purified sodium chloride (NaCl) solution**.

The **production steps** of PVC are summarized in the following **flowchart** (not included here but can be created if needed).



III.2.1. Reactions

The synthesis of **vinyl chloride monomer (VCM)** takes place in **two main steps**:

1. **Formation of dichloroethane ($C_2H_4Cl_2$)**, either by:
    - **Direct chlorination**, or
    - **Oxychlorination**
2. **Thermal cracking** of dichloroethane ($C_2H_4Cl_2$)

1 / First Step

A. Direct Chlorination

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ (Catalyst: $CuCl_2$ / 50°C / 2 bars) ***$\Delta H < 0$ (exothermic reaction)***

After this reaction, the catalyst **($CuCl_2$)** becomes suspended in the **DCE ($C_2H_4Cl_2$)**. It is then separated by **settling and/or filtration**.

B. Oxychlorination

This occurs in the presence of **oxygen (O_2)** and **hydrogen chloride (HCl)** at **220°C** and under **3 bars of pressure**, using **$CuCl_2$** as a catalyst:

$C_2H_4 + 2HCl + \frac{1}{2} O_2 \rightarrow C_2H_4Cl_2 + H_2O$ (Catalyst: $CuCl_2$ / 220°C / 3 bars) $\Delta H < 0$

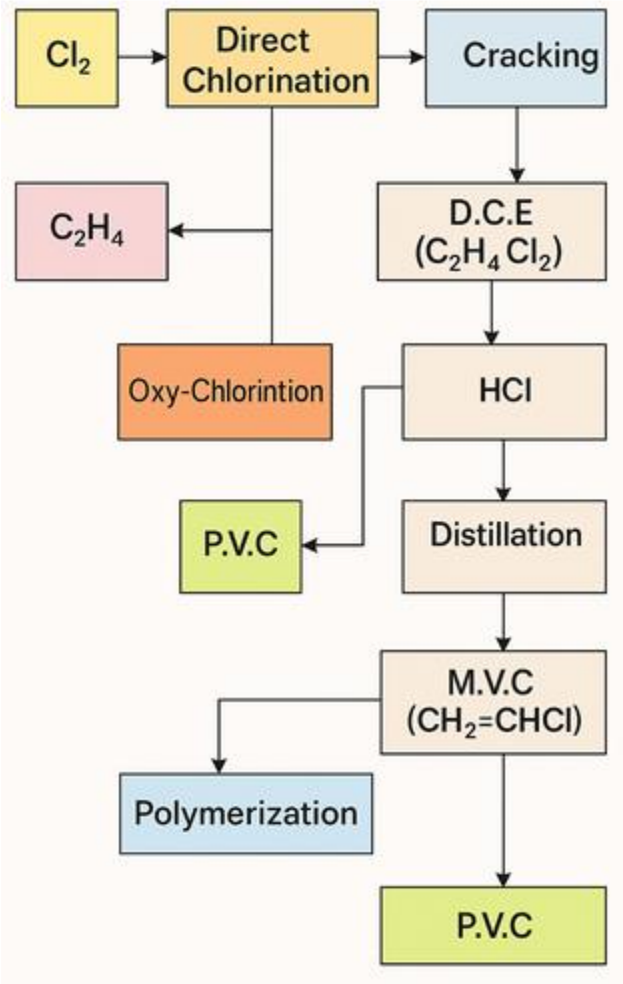
2 / Second Step: Thermal Cracking

This step involves the **thermal cracking** of dichloroethane at **550°C** and **25 bars** of pressure, where **dichloroethane ($C_2H_4Cl_2$)** is converted into **vinyl chloride ($CH_2{=}CH\text{-}Cl$)**:

$C_2H_4Cl_2 \rightarrow CH_2{=}CH\text{-}Cl + HCl$ ***(550°C / 25 bars)*** **$\Delta H < 0$**

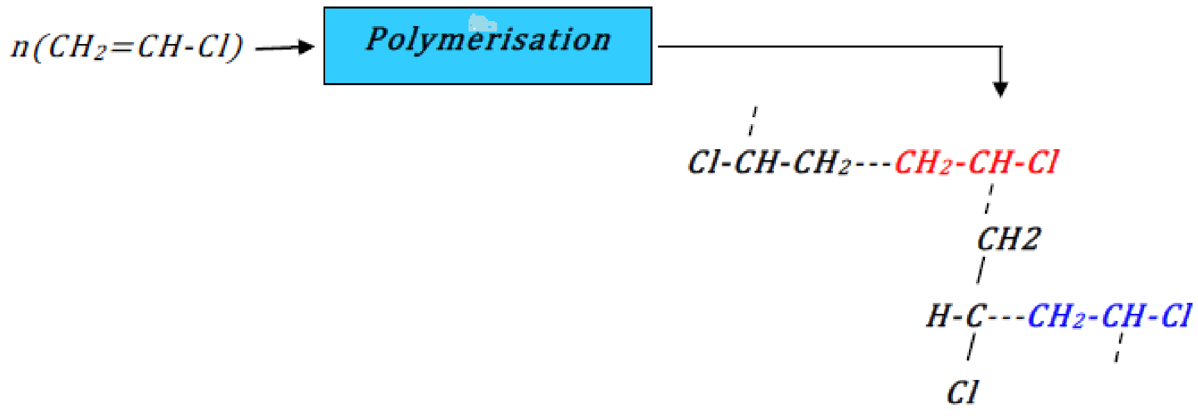
Overall Reactions:

- **$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$**
- **$C_2H_4 + 2HCl + \frac{1}{2} O_2 \rightarrow C_2H_4Cl_2 + H_2O$**
- **$2\, C_2H_4Cl_2 \rightarrow 2\, CH_2{=}CH\text{-}Cl + 2\, HCl$**
- **Net reaction:**
  $C_2H_4 + Cl_2 + \frac{1}{2} O_2 \rightarrow 2\, CH_2{=}CH\text{-}Cl + H_2O$



III.2.2. Polymerization

Several molecules of the monomer **(CH_2=CH-Cl)** react with each other under specific conditions of **pressure and temperature**, in the presence of a **catalyst**, which is generally a **peroxide** *(R-(CO)-O-O-(CO)-R)* or a **percarbonate** *(R-O-(CO)-O-O-(CO)-O-R)*, to form a large **polymer molecule (PVC)**.



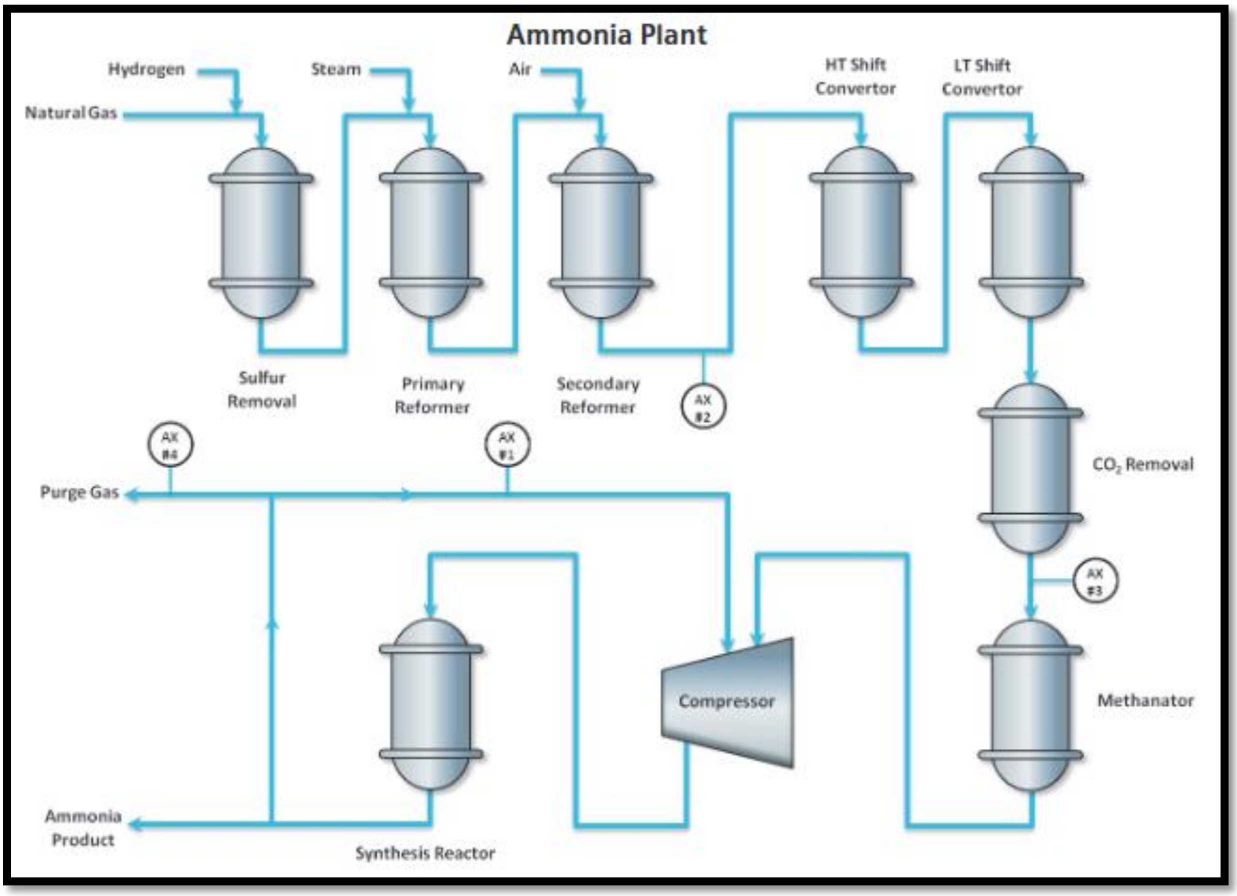
IV. Ammonia Production

Ammonia (NH_3) is a **key chemical** used in the production of fertilizers (like urea and ammonium nitrate), explosives, cleaning products, and in various chemical processes. In the petrochemical industry, ammonia is primarily produced via the **Haber-Bosch process**, using **hydrogen derived from natural gas**.

Industrial ammonia is synthesized from hydrogen (H_2) and nitrogen (N_2) via the Haber-Bosch process:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.4 \text{ kJ/mol}$$

IV.1. Process Steps



To produce **ammonia (NH_3)** from **natural gas (CH_4)** and **air (source of N_2)** via a series of reforming, purification, and synthesis steps.

1. Feed Preparation

- **Natural Gas + Steam + Hydrogen**: Enter the process.
- **Sulfur Removal Unit**:

Removes sulfur compounds (which poison catalysts later in the process).

2. Reforming Section

- **Primary Reformer**: Reforms methane (CH_4) with steam to produce syngas (H_2 + CO).

  $CH_4 + H_2O \rightarrow CO + 3\ H_2$
- **Secondary Reformer**: Air is added to introduce nitrogen (N_2). More H_2 and N_2 are formed here.

  $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2\ H_2$

3. Shift Conversion (Water-Gas Shift Reaction)

- **HT Shift Converter (High Temperature)**
- **LT Shift Converter (Low Temperature)**

  Converts CO to CO_2 and more H_2:

  $CO + H_2O \rightarrow CO_2 + H_2$

4. CO_2 Removal Unit

Removes CO_2 using a solvent (e.g., amine scrubbing).

5. Methanator

Removes remaining CO and CO_2 traces by converting them into methane:

$CO + 3H_2 \rightarrow CH_4 + H_2O$

$CO_2 + 4H_2 \rightarrow CH_4 + 2\ H_2O$

This protects the catalyst in the next step.

6. Compression

The purified gas (N_2 + H_2) is compressed to **high pressure** (150–250 bar).

7. Synthesis Reactor

Ammonia is synthesized over an iron-based catalyst:

$N_2 + 3H_2 \rightleftharpoons 2NH_3\ (\Delta H<0)$

Only part of the gas converts to NH_3; the rest is recycled.

8. Separation & Purge

- **Ammonia Product**: Ammonia is separated and collected.
- **Purge Gas**: A small portion is purged to remove inerts (e.g., Ar, CH_4) that would otherwise accumulate.

9. Cooling and Separation of Final Product

NH_3 is condensed and separated from unreacted gases.

IV.2. Environmental Considerations

- Large energy consumption
- Significant CO_2 emissions

- New research focuses on green ammonia using hydrogen from electrolysis of water powered by renewable energy.

IV.3. Applications of Ammonia

- Fertilizer production (urea, ammonium nitrate, ammonium sulfate)
- Explosives (TNT, nitramines)
- Refrigeration systems (as a refrigerant gas)
- Wastewater treatment
- Pharmaceutical and chemical industries