INTRODUCTION

Every industrial chemical process is designed to produce economically a designed product or range of products from a variety of starting materials (i.e. feed, feedstocks, or raw materials). Figure 1 shows the typical structure of a chemical process.

![Figure 1: Typical structure of a chemical process.]

**Steps involved in a chemical process:**

1. **Feed pretreatment:** The feed usually has to be treated. It may undergo a number of physical treatment steps (e.g. liquid feedstocks may have to be vaporized, water is removed from benzene by distillation before its conversion to ethylbenzene, removing of sulfur from naphtha.)

2. **Reaction section:** The treated feed is usually sent to the reactor for the chemical conversion.

3. **Product separation:** The reaction products need to be separated and purified. Distillation is still the most common separation method, but extraction, crystallization, membrane separation, etc. can also be used.

**Base Chemicals**

- The vast majority of chemicals, about 85%, is produced from a very limited number of simple chemicals called *base chemicals*. The most important hydrocarbon base chemicals being oil, natural gas, and coal. Conversion of base chemicals can produce about 300 different intermediates, which are relatively
simple molecules. The base chemicals and the intermediate can be classified as *bulk chemicals*. A wide variety of *consumer products* can be obtained by further reaction steps. These products include:

- Plastics: e.g. polyvinylchloride (PVC), polyacrylonitrile
- Synthetic fibers: e.g. polyesters like polyethylene, nylon-6, polyesters
- Fertilizers: e.g. ammonium nitrate
- Vitamins
- Pharmaceuticals
- Detergents

**Petrochemical Industry**

- Petrochemicals, i.e. oil derived chemicals are the major raw materials for the chemical industry.
- The most important petrochemicals are:
  - Lower alkenes (olefins): e.g. ethylene, propylene and butadiene.
  - Aromatics: benzene, toluene, xylene (BTX)
  - Ammonia, methanol, synthesis gas (H2 & CO)
- Most final products are produced directly or indirectly from the previous compounds (building blocks).
- The feedstock chosen for the production of the chemical products depends on 1) availability 2) prices 3) production units.
- For the production of light alkenes, there is a difference, for example, between the USA and the rest of the world (e.g., Europe and Japan). In the USA, the production of light alkenes is from alkanes such as ethane and propane. In Europe and Japan, the production of light alkenes is from naphtha. In Saudi Arabia, ethane is the main source for the production of lower alkenes. Figures 2 and 3 show the production of lower alkenes from crude oil and natural gas, respectively.
Figure 2: Lower alkenes (olefins) production from oil.

Figure 3: Lower alkenes production from natural gas.
**Natural Gas**
- Natural gas is a mixture of hydrocarbons with methane as the main constituent. It can be found in porous reservoirs, either associated with crude oil (associated gas) or in reservoirs in which no oil is present (non-associated gas).
- Natural gas is important as a source of energy and also as a raw material for the petrochemical industry.
- Natural gas usually contains small amounts of non-hydrocarbon gases such as carbon dioxide, nitrogen, and hydrogen sulfide.
- Natural gas classifies as ‘dry’ or ‘wet’ natural gas. Dry natural gas contains only small amounts of condensable hydrocarbons (at ambient temp.). Non-associated gas is usually dry.
- Natural gas contains substantial amounts of ethane, propane, butane, and C5+ hydrocarbons, which liquefy on compression at ambient temperature (natural gas liquids, NGL).
- The terms ‘sweet’ and ‘sour’ natural gas denote the absence or presence of H₂S and CO₂.
- Condensable hydrocarbons are removed from a wet natural gas and part can be sold as liquefied petroleum gas (LPG).

**Crude Oil**
- Crude oil is not a uniform material with a simple molecular formula. It is a mixture of gaseous, liquid, and solid hydrocarbon compounds.
- Crude oil contains alkanes, cycloalkanes (naphthenes), aromatics, poly-cyclic aromatics, sulfur-containing compounds, nitrogen-containing compounds, oxygen-containing compounds, … etc.
- The presence of sulfur in crude oil is highly undesirable because it leads to corrosion, poison catalysts and is environmentally harmful.
- Nitrogen compounds can disturb major catalytic processes, such as catalytic cracking and hydrocracking.
STEAM CRACKING
PRODUCTION OF LOWER ALKENES (OLEFINS)

Introduction

- Steam cracking is the process used to convert the un-reactive alkanes (e.g. ethane) into much reactive alkenes (e.g. ethylene).
- This process produces mainly ethylene, but valuable co-products such as propylene, butadiene, and pyrolysis gasoline with benzene as the main constituent are also produced.
- In steam cracking (also called thermal cracking), a hydrocarbon feed is thermally cracked in the presence of steam, yielding a complex product mixture.
- Steam is not cracked but it functions primarily as a diluent, allowing higher conversion.
- Feedstocks range from light saturated hydrocarbons such as ethane and propane to naphtha and light and heavy gas oil.
- In USA, ethane (from natural gas) is the primary feedstock for the production of ethylene. In Europe and Japan, naphtha is the major feedstock.
- In Saudi Arabia, ethane is the primary feedstock for the ethylene production.

Product processing (process description)

- Cracked gas is based on either gas or liquid feedstocks (see Figures 4 and 5).
- The conventional flow scheme (process flow sheet [PFS]) for the production of olefins varies from one process to another and depends on the type of feedstock and the degree of recovery desired for the different products.
- The separation section on an olefin plant is based on compression and cooling. Normal and cryogenic distillation processes are usually used.
Figure 4: Simplified process flow diagram for producing ethene via gas cracking.
Figure 5: Simplified process flow diagram for producing ethene via liquid cracking.
• The cracked gas from gaseous feedstocks (ethane, propane, butane) begins with its entry into the transfer-line exchanger (TLE), followed by direct quench with water, and multistage compression, typically in four to six stages with intermediate cooling. Before the last compressor stage, acid gas (mainly hydrogen sulfide and carbon dioxide) is removed.

• After the last compressor stage, water removal takes place by chilling and drying over zeolites. Subsequent fractionation of the cracked gas is based on cryogenic (temp < 273 k) and conventional distillation under pressure (15-35 bar). Cryogenic distillation requires large amount of energy due to the need for a refrigeration system. In the purification section, separation of ethane/ethylene and propane/propylene is difficult.

**Cracking Reactions**

Cracking occurs by free-radical reactions. The simplest feedstock is ethane. The reaction is initiated by cleavage of the C-C in an ethane molecule resulting in the formation of two methyl radicals.

Initiation: $\text{H}_3\text{C} - \text{CH}_3 \rightarrow \text{H}_3\text{C}^* + \text{H}_3\text{C}^*$

Propagation:
- $\text{H}_3\text{C}^* + \text{H}_3\text{C} - \text{CH}_3 \rightarrow \text{CH}_4 + \text{H}_3\text{C} - \text{C}^*\text{H}_2$
- $\text{H}_3\text{C} - \text{C}^*\text{H}_2 \rightarrow \text{H}_2\text{C} = \text{CH}_2 + \text{H}^*$
- $\text{H}^* + \text{H}_3\text{C} - \text{CH}_3 \rightarrow \text{H}_2 + \text{H}_3\text{C} - \text{C}^*\text{H}_2$
- $\text{H}_3\text{C} - \text{C}^*\text{H}_2 \rightarrow \text{etc.}$

Termination:
- $\text{H}^* + \text{H}^* \rightarrow \text{H}_2$
- $\text{H}_3\text{C} - \text{C}^*\text{H}_2 + \text{H}_3\text{C}^* \rightarrow \text{H}_2\text{C} = \text{CH}_2 + \text{CH}_4$
- etc.

**Industrial process**

The main requirements for the steam cracking process are:

• Considerable heat input at a high temperature level.
- Limitation of hydrocarbon partial pressure.
- Very short residence times (<1 s).
- Rapid quench of the reaction product to preserve the composition.

**Steam Crackers**

A mixture of hydrocarbons and steam is passed through tubes placed inside furnaces heated by combustion of natural gas, LPG or fuel oil. The furnaces consist of a convection zone in which hydrocarbon feed and steam are preheated and a radiation zone in which the reactions take place. The hydrocarbons undergo pyrolysis, and subsequently the products are rapidly quenched to prevent further reaction, and thus preserve the composition. The residence time in the tube is very short (≈ 1 s). the temperature is chosen as high as possible.

**Future Developments**

Cracking furnaces are very capital intensive and it is expected that, in the next decades, many have to be replaced because of their age. Therefore, direct production methods for these specific alkenes receive increasingly more attention. A logical choice of process is the selective dehydrogenation of the corresponding alkanes.

Some characteristics of the catalytic dehydrogenation of alkanes are:

1. The reaction is endothermic and high temperatures are required.
2. At high temperatures, secondary reactions such as cracking and coke formation are possible.
3. The thermodynamic equilibrium limits the conversion per pass so that a substantial recycle stream is required.
4. Several catalytic dehydrogenation processes are available, which differ in the type of catalyst used, the reactor design, the method of heat supply, and the method used for catalyst regeneration.
Example: Overall Material Balances for the Ethylene Process

The ethylene process includes various unit operations designed to perform different tasks. Rigorous mass and energy balances using advanced computer programs are necessary to determine mass and energy flows throughout the plant. To meet the desired annual production capacity of the plant (500,000 tons per year) the feed (propane) flowrate to the plant must be determined. The initial estimate is attained by conducting an overall material balance based on the actual outlet yields from an industrial thermal cracking unit as presented in Table 1. The estimated component mass balance is then fed to a rigorous simulator (e.g. HYSIS) that recognizes both major and minor reactions occurring in the ethylene plant to determine the precise flow rates of each component for the detailed process flow sheet. Determine the product distribution of the ethylene process based on propane feedstock for an annual capacity of 500,000 tons.

Solution

Figure 6 illustrates a simple flow diagram for the ethylene process. For a feed F of 100 lb/hr as a basis, utilizing the nomenclature of Figure 6, and assuming theoretical separation in the purification processes,

Overall material balance

\[ F = E - (R_1 + R_2) = P \]  \hspace{1cm} (1)

Ethane material balance

\[ R_1 = 0.4 \times R_1 + 0.044 \times (100 + R_2) \]  \hspace{1cm} (2)

Note that 40% of the ethane is unreacted and theoretically would return in \( R_1 \) and 4.4% of the ethane obtained from the propane reaction is theoretically returned in \( R_1 \).
Table 1: Actual furnace outlet yields under the same cracking severity for either pure ethane or propane feedstock.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Ethane Conversion (wt %)</th>
<th>Propane Conversion (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Furnace outlet yields (wt% of feed)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.55</td>
<td>1.29</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Methane</td>
<td>4.17</td>
<td>24.67</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.25</td>
<td>0.33</td>
</tr>
<tr>
<td>Ethylene</td>
<td>48.20</td>
<td>34.50</td>
</tr>
<tr>
<td>Ethane</td>
<td>40.00</td>
<td>4.40</td>
</tr>
<tr>
<td>Propadiene/methylacetylene</td>
<td>0.02</td>
<td>0.34</td>
</tr>
<tr>
<td>Propylene</td>
<td>1.11</td>
<td>13.96</td>
</tr>
<tr>
<td>Propane</td>
<td>0.17</td>
<td>10.00</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>1.07</td>
<td>2.65</td>
</tr>
<tr>
<td>Isobutene</td>
<td>0.11</td>
<td>0.52</td>
</tr>
<tr>
<td>Butene-1</td>
<td>0.10</td>
<td>0.48</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.27</td>
<td>0.05</td>
</tr>
<tr>
<td>C_{6-8} PON*</td>
<td>0.27</td>
<td>1.81</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.48</td>
<td>2.20</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.06</td>
<td>0.48</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Heavy Gasoline C_{6-8} PON*</td>
<td>0.14</td>
<td>1.44</td>
</tr>
<tr>
<td>Fuel oil</td>
<td>0.00</td>
<td>0.85</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

* PON (Paraffin, Olefin, Naphthene).
Figure 6: Diagram of the overall material balances for the ethylene process.
Propane material balance

\[ R_2 = 0.0017 \times R_1 + 0.1 \times (100 + R_2) \quad (3) \]

The propane in \( R_2 \) is obtained from a 0.17% conversion from ethane and a nonreaction of 10% of the propane fed to the thermal reactor and therefore would theoretically be returned in \( R_2 \).

Solving Equations 1 and 2 simultaneously gives,

\[ R_1 = 8.15 \text{ lb/hr} \]
\[ R_2 = 11.13 \text{ lb/hr} \]

Ethylene material balance

\[ P_{C_2H_4} = 0.482 \times R_1 + 0.345 \times (100 + R_2) \quad (4) \]

Note that the ethylene yield is 48.2% from the ethane conversion and 34.5% from the propane conversion (See Table 1).

From Equation 4,

\[ P_{C_2H_4} = 42.26 \text{ lb/h} \]

This indicates that each unit of ethylene produced in this ethylene process requires about 2.36 units of fresh propane feed.

Propylene material balance

\[ P_{C_3H_6} = 0.0111 \times R_1 + 0.1396 \times (100 + R_2) \quad (5) \]

Again, note that the propylene yield is 1.11% from the ethane conversion and 13.96% from the propane conversion (See Table 3-1).

From Equation 5,

\[ P_{C_3H_6} = 15.60 \text{ lb/hr} \]

A similar procedure is followed to attain the material balances for the other by-
products. Table 2 shows the calculated product distribution that is obtained with the previous procedure.

Table 2: Calculated product distribution of the base-case ethylene process.

<table>
<thead>
<tr>
<th>Product</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>42.263</td>
</tr>
<tr>
<td>Propylene</td>
<td>15.604</td>
</tr>
<tr>
<td>Tail gas</td>
<td>29.480</td>
</tr>
<tr>
<td>Acid gas</td>
<td>0.036</td>
</tr>
<tr>
<td>C2H2</td>
<td>0.387</td>
</tr>
<tr>
<td>C3H4</td>
<td>0.380</td>
</tr>
<tr>
<td>C4's</td>
<td>4.238</td>
</tr>
<tr>
<td>Gasoline</td>
<td>6.667</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>0.945</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>
PRODUCTION OF SYNTHESIS GAS

- Synthesis gas (or syngas) is a general term used to describe mixtures of hydrogen (H₂) and carbon monoxide (CO) in various ratios.
- Synthesis gas is used for the production of different materials and is also a source of pure hydrogen and pure carbon monoxide.

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>Main uses</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>Refinery hydrotreating and hydrocracking</td>
<td>( C_6H_6OH + H_2 \rightarrow C_6H_6 + H_2O )</td>
</tr>
<tr>
<td>3H₂:1N₂</td>
<td>Ammonia</td>
<td>( 3H_2 + N_2 \rightarrow 2NH_3 )</td>
</tr>
<tr>
<td>2H₂:1CO</td>
<td>Methanol</td>
<td>( 2H_2 + CO \rightarrow CH_3OH )</td>
</tr>
<tr>
<td>1H₂:1CO</td>
<td>Aldehydes (Hydroformylation)</td>
<td>( CH_2CH = CH_2 + CO + H_2 \rightarrow )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \overset{O}{CH_3}CH_3CH_2CH_3 )</td>
</tr>
<tr>
<td>CO</td>
<td>Acids (formic and acidic)</td>
<td>( CH_3OH + CO \rightarrow CH_3\overset{O}{C}=OH )</td>
</tr>
</tbody>
</table>

- Syngas may be produced from a variety of raw materials ranging from natural gas to coal. The choice for a particular raw material depends on cost and availability of feedstock.
- Syngas can be produced by one of three processes:
  1. Steam reforming of natural gas or light hydrocarbons, optionally in the presence of oxygen or carbon dioxide.
  2. Partial oxidation of (heavy) hydrocarbons with steam and oxygen.
  3. Partial oxidation of coal (gasification) with steam and oxygen.

Definitions:

Steam reforming: is the reaction of hydrocarbons with steam in the presence of a catalyst.
Reforming: (in gas industry) is commonly used for the conversion of a hydrocarbon by reacting it with O-containing molecules, usually H2O, CO2 and/or O2.

Partial oxidation: (also called steam/oxygen reforming) is a non-catalytic reaction of hydrocarbons with oxygen and usually also steam.

Coal gasification: is more common term to describe partial oxidation of coal. A combination of steam reforming (endothermic reaction) and partial oxidation (exothermic reaction) is often referred to as (autothermic reforming).

\[
e.g. \quad CH_4 + H_2O \nrightarrow CO + 3H_2 \quad \Delta H_{298} = 206 \text{ KJ/mol}
\]

\[
e.g. \quad CH_4 + 1/2 O_2 \rightarrow CO + 2H_2 \quad \Delta H_{298} = -36 \text{ KJ/mol}
\]

Figure 7: General flow schemes for the production of syngas
**Process Discussion**

- The steam reforming feed usually has to be desulfurized. Sulfur is a poison of metal catalysts because it can block active sites by the formation of sulfides.
- In steam reforming and in downstream, many reactors based catalysts are used, therefore sulfur compounds must be removed to less than 1 ppm.
- When sulfur is present as H$_2$S, it can be removed by:
  1. Adsorption (e.g. activated carbon)
  2. Reaction with an oxide (for example, ZnO)
  3. Scrubbing with a solvent (e.g. NaOH)
- Feed purification of coal and heavy hydrocarbon is not possible, therefore partial oxidation process is used for such feeds. Sulfur compounds are then removed after the formation of syngas.
- Depending on the use of syngas, the syngas may be treated in several ways to adjust the ratio of H$_2$ to CO. Examples: (1) water-gas shift reaction may be used to reduce the contents of CO and increase the ratio of hydrogen: CO + H$_2$O = CO$_2$ + H$_2$. (2) Separation of H$_2$ from CO can be applied using distillation process.

**Synthesis Gas from Natural Gas**

- Natural gas consists mainly of methane and higher alkanes. For methane in presence of steam, the most important reactions are:
  1. The steam reforming reaction

\[
CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{298}^o = 206 \text{ kJ/mol}
\]

  2. The water-gas shift reaction

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_{298}^o = -41 \text{ kJ/mol}
\]

  3. The CO2 reforming reaction: some processes require synthesis gas with a high CO content. This might be produced from methane and CO2 in a reaction known as CO2 reforming:
The CO\textsubscript{2} reforming is also referred to as “dry reforming”, because of the absence of steam.

The main reactions may be accompanied by carbon formation which leads to deactivation of the catalyst. Carbon may be formed by:

1. decomposition of methane

\[
CH_4 \rightleftharpoons C + 2H_2 \quad \Delta H^0_{298} = 75 \text{ kJ/mol}
\]

2. disproportionation of CO, the Boudouard reaction

\[
2CO \rightleftharpoons C + CO_2 \quad \Delta H^0_{298} = -173 \text{ kJ/mol}
\]

In the presence of oxygen, methane undergoes partial oxidation to produce CO & H\textsubscript{2}

\[
CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \quad \Delta H^0_{298} = -36 \text{ kJ/mol}
\]

Side reactions such as the complete oxidation of methane to CO\textsubscript{2} and H\textsubscript{2}O may occur:

\[
CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \quad \Delta H^0_{298} = -803 \text{ kJ/mol}
\]

Oxidation of the formed CO & H\textsubscript{2} may also occur

\[
CO + \frac{1}{2}O_2 \rightleftharpoons CO_2 \quad \Delta H^0_{298} = -284 \text{ kJ/mol}
\]

\[
H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \quad \Delta H^0_{298} = -242 \text{ kJ/mol}
\]

Steam Reforming Process

Steam reforming is carried out at high temperature (> 1000 K). A catalyst (supported nickel) is required to accelerate the reaction due to the very high stability of methane. The catalyst is contained in tubes, which are placed inside a furnace that is heated by combustion of fuel. The steam reforming (as shown in the Figure) consists of two
sections: (1) convection section and (2) Radiation section. In the convection section, heat recovered from the hot flue gases is used for preheating of (1) the natural feed process, (2) the process steam and (3) for generation of superheated steam. In the radiant section of the furnace, the reforming reactions take place.
Methanol (CH$_3$OH)

1- Background Information

- Methanol (CH$_3$OH) is the second large-scale process involving catalysis at high pressure & temp. (BASF, 1923)
- The same team that developed the ammonia synthesis process also developed a commercial process for the production of methanol based on synthesis gas (H$_2$/CO/CO$_2$)

2- Thermodynamics

The main reactions for the formation of methanol from synthesis gas are:

\[
\begin{align*}
\text{CO} + 2\text{H}_2 & \rightarrow \text{CH}_3\text{OH} \quad \Delta H_{298}^o = -90.8 \text{ KJ/mol} \\
\text{CO}_2 + 3\text{H}_2 & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H_{298}^o = -49.6 \text{ KJ/mol}
\end{align*}
\]

The two methanol reactions are coupled by the water-gas-shift reaction:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298}^o = -41 \text{ KJ/mol}
\]

- For higher conversion of CO & H$_2$ to CH$_3$OH, the temperature should be low and the pressure should be high (as shown in the CO equilibrium conversion Table).

<table>
<thead>
<tr>
<th>CO equilibrium conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (k)</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>525</td>
</tr>
<tr>
<td>575</td>
</tr>
<tr>
<td>625</td>
</tr>
<tr>
<td>675</td>
</tr>
</tbody>
</table>
Catalyst development for methanol synthesis was more difficult than ammonia synthesis. This is because the selectivity is low due to the other products that can be formed such as higher alcohols and hydrocarbons.

The original catalysts (ZnO-Cr_2O_3) were only active at high temperature. Therefore, the pressure has to be high (250-350 bar) to reach acceptable conversions. The catalysts that active at low temperature were not resistance to impurities.

The catalysts (CU/ZnO/AL_2O_3) is very selective. In modern plants, the catalysts are active at low temperature which led to "low-pressure plants".

The reaction temperature is critical. A low temperature is favorable from thermodynamic point of view, but the rate of reaction is also low at lower temperature. The pressure for modern plant is usually in the range of 50-100 bar.

3- Synthesis gas for methanol production

The ideal synthesis gas for CH_3OH production has a H_2/CO ratio of about 2. A small amount of CO_2 (about 5%) increases the catalyst activity. When H_2/CO ratio is lower than 2, it leads to increased by product formation (higher alcohols, …etc.) A higher ratio results in a less efficient plant due to the excess hydrogen present in syngas which has to be purged.
4- Methanol synthesis

- The first industrial plants were based on a catalyst that was resistant to impurities but not very active and selective. Therefore, to achieve a reasonable conversion to methanol, these plants were operated at high pressure!
- All modern processes are low-pressure processes with plant capacities ranging from 150 to 6000 t/d.

Process steps:
1. In a modern plant, an adiabatic reactor is used with a single recycle gas.
2. The reaction is quenched by adding cold reactant gas at different heights in the catalyst bed.
3. The product is quenched and the methanol is separated from the syngas in the flash drum. The syngas is recycled back to the reactor.
4. The crude methanol is separated in two columns. The first column removes gases and other light impurities. The second column separates methanol from heavy alcohols (side stream) and water.
Inorganic Bulk Chemicals

1- Sulfuric Acid

- Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) is the largest-volume chemical produced (> 130 million ton/year).
- It is used in the production of all kinds of chemicals, of which fertilizers are the most important. E.g. super phosphate fertilizer, triple super phosphate, phosphoric acid/Ammonium Sulfate.

Manufacturing

- Two methods are used to produce the sulfuric acid:
  1- "Contact Process" (modern process)
  2- "Lead Chamber process" (obsolete process)

1- The contact process

- The contact process is a catalytic oxidation process where catalyst such as vanadium pentoxide (V\textsubscript{2}O\textsubscript{5}) is used.
- Elemental sulfur is the most widely used for the production of sulfuric acid:
  \[ S + O_2 \rightarrow SO_2 \]
  \[ SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \]
  \[ SO_3 + H_2O \rightarrow H_2SO_4 \]

Since both the oxidation of sulfur and sulfur dioxide require oxygen, excess air is used to burn S, which has the advantage of complete oxidation of sulfur.

- Sulfuric acid commercially produced in various acid strengths, ranging from 33.33 to 114.6 wt%. Sulfuric acid with strength of over 100% is referred to as oleum, which consists of sulfuric acid with dissolved sulfur trioxide (SO\textsubscript{3}). The concentration of oleum is expressed as wt% dissolved SO\textsubscript{3} ("free SO\textsubscript{3}") in 100 wt% sulfuric acid.
**Manufacturing steps (starting from sulfur)**

1- melt sulfur.
2- Clean and dry the combustion air.
3- Burn the sulfur with combustion air to obtain SO$_2$.
4- Recover the heat from the hot SO$_2$ to produce steam. Steam is used in step (1) {melting of sulfur}.
5- Purification of SO$_2$ to remove inerts in coke filters.
6- \[ SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \]

This reaction is carried out in CONVERTERS.

7- Removal of O$_2$, N$_2$ and SO$_2$ .
8- Absorption of SO$_3$ in H$_2$SO$_4$ solution.

**The problem of conversion and kinetics (reaction rate)**

As in all processes, the ultimate goal is high conversion (i.e. high yield) coupled with rapid conversion (i.e. high rate of reaction).

\[ SO_2 + \frac{1}{2}O_2 \rightarrow SO_3 \]

**Effect of temperature:**

➢ To obtain a high conversion we required a temperature of about 400 °C (673 K) during the oxidation of SO$_2$.
But at 400 °C, the rate of reaction is very low compared with what it is at 500-600 °C. The rate at which equilibrium is established at 550-600 °C is 50 to 100 times as high as it is at 400 °C.

As with all exothermic equilibrium reactions, however, the ideal temperature must be a compromise between achievable conversion (thermodynamics) and the rate at which this conversion can be attained (kinetics). To solve this problem, three approaches are usually applied:

1- **Searching a good catalyst:**
Catalyst does not change conversion but it can increase the kinetic rate and hence the rate of production. Effective catalysts such as V$_2$O$_5$ or platinum are used in the production of sulfuric acid.

2- **Multiple catalyst beds:**
The oxidation of SO$_2$ is exothermic equilibrium reaction. With increasing conversion the temperature increases, leading to lower attainable equilibrium conversions. For example, the equilibrium conversion at 710 K is about 98%, but due to the adiabatic temperature rise conversions of only 60-70% are obtainable in a single catalyst bed. This is overcome by using multiple catalyst beds (usually four) with intermediate cooling. Cooling can be achieved by heat exchanger or by quenching with air.
Absorption of SO$_3$:

The lowering of temperature between the beds ensures an overall conversion of 98-99%. Still this is not enough to meet current environmental standards (~99.7% acid). Therefore, modern sulfuric acid plants use intermediate SO$_3$ absorption after the second or third catalyst bed.

The intermediate removal of SO$_3$ enables the conversion of SO$_2$ "beyond thermodynamic equilibrium".
Effect of pressure:

\[ SO_2 + \frac{1}{2} O_2 \rightarrow SO_3 \]

The equilibrium constant is:

\[ K_p = \frac{P_{SO_3}}{P_{SO_2} \times P_{O_2}^{1/2}} \]

if \( n \) = total moles of gas present
\( n_{O_2} \) = moles of oxygen ……etc.

\( P \) = total pressure

Dalton's law:

\[ P_A = y_A P = \frac{n_A}{n} P \]

\[ K_p = \frac{(\frac{n_{SO_3}}{n}) P}{(\frac{n_{SO_2}}{n}) P \times \sqrt{\frac{n_{O_2}}{n}} P} \]

\[ K_p = \left( \frac{n_{SO_3}}{n_{SO_2}} \right) \frac{1}{\sqrt{n_{O_2} P}} \]

\[
\left( \frac{n_{SO_3}}{n_{SO_2}} \right) = K_p \sqrt{n_{O_2} P}
\]

The conversion ratio \( \frac{n_{SO_3}}{n_{SO_2}} \) can be increased by:

1- increasing total pressure, \( P \)
2- increasing \( O_2 \), i.e. use excess pure \( O_2 \).
3- increasing \( K_p \).