Lecture 6
Propylene, Propylene Oxide
And Isopropanol
Propylene, often referred as the crown prince of petrochemicals is superficially similar to ethylene but there are many differences in both production and uses [Hatch & Matar, 1978]. Propylene is used in many of the world’s largest and fastest growing synthetic materials and thermoplastics. The demand of propylene has increased rapidly during the last twenty years and primarily driven by polypropylene demand [Mall, 2007]. Product profile of propylene is given in Table M-VII 6.1.

According to SRI consulting 2010 global production and consumption of propylene in 2009 was both approximately 71 million tones with capacity utilization of 78.5%. Global propylene consumption is forecast to average growth of around 5.1% per year from 2009 to 2014 and 3.5% per year from 2014-19. Consumption of refinery grade propylene made up 9% of total consumption in 2009, chemical grade 23% and polymer grade 68%. Refinery grade propylene is consumed mainly for production of cumene and isopropyl alcohol. Chemical grade propylene mostly goes into o xo alcohol, propylene oxide and acrylonitrile.

### Table M-VII 6.1: Product Profile of Propylene

<table>
<thead>
<tr>
<th>Product</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscellaneous chemicals</td>
<td>1 butanol, 2-ethyl hexanol, Allyl chloride, Epichlorohydrin</td>
</tr>
<tr>
<td>Polymer</td>
<td>Polypropylene,, Polyacrylamide, nylon 66, acrylic sheets</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>Polyether-polyols, glycol ethers, isopropyl amines, propylene carbamate, surfactants</td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>Unsaturated polyester resins, food additives, cellophane, paints and coating, plasticisers, functional fluids, antifreeze, tobacco treatment</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>Acrylic fiber, acrylic acid, acrylates, methyl methacrylates, adiponitrile</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>Acetone, cosmetics, solvents, pharmaceuticals, isopropyl acetate</td>
</tr>
<tr>
<td>Polyols</td>
<td>Polyurethane and Polyester</td>
</tr>
</tbody>
</table>
Sources of Propylene
Propylene is a byproduct of steam crackers and varying amount of olefins is produced from steam crackers depending on the type of feedstock. Other sources of propylene may be recovery of propylene from FCC light ends, Propane dehydrogenation, Metathesis. Some of the major processes for production of propylene is given in Table M-VII 6.2. Typical Composition of FCC Gas Stream is given in Table M-VII 6.3.

Table M-VII 6.2: Propylene Production Technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Process</th>
<th>Licensor</th>
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<tbody>
<tr>
<td>Olefin conversion technology</td>
<td>This process involves production of propylene from ethylene and 2-butenes in a fixed bed metathesis reactor containing proprietary catalyst, which promotes reaction of ethylene and 2-butene to form propylene and simultaneously isomerises 1-butene to 2-butene.</td>
<td>ABB Lumus Global</td>
</tr>
<tr>
<td>Superflex Process</td>
<td>The process uses a fluidised bed catalytic reactor system using proprietary catalyst which converts low value feedstock to predominantly propylene and ethylene products. Low value light hydrocarbon streams from ethylene plant and refineries can be used, e.g. C₄ and C₅ olefin rich stream from ethylene plants, FCC naphtha, C₄ stream, thermally cracked naphtha from visbreakers or cokers.</td>
<td>Kellogg Brown &amp; Root, Inc.</td>
</tr>
<tr>
<td>Propylur Process</td>
<td>This process produces propylene beside ethylene from low value rich feeds ranging from C₄-C₈ from ethylene plant and refineries in a fixed bed reactor using proprietary catalyst. The process offers high selectivity towards propylene.</td>
<td>Lurgi Oel Gas Chemie GmbH</td>
</tr>
<tr>
<td>UOP Oleflex Process</td>
<td>This process produces polymer grade propylene from propane and the process consist of a reactor, catalyst regeneration section and product separation and fractionation section. The process uses platinum catalyst (DeH-12 catalyst).</td>
<td>UOP LLC</td>
</tr>
<tr>
<td>UOP/Hydro MTO Process</td>
<td>This process converts crude methanol (produced from synthesis gas using natural gas) to ethylene and propylene and can be operated either a maximum ethylene or a maximum propylene production mode using MTO-100 silicoaluminophosphate synthetic</td>
<td>UOP LLC and Hydro Norway</td>
</tr>
<tr>
<td>Technology</td>
<td>Process</td>
<td>Licensor</td>
</tr>
<tr>
<td>----------------------------------------</td>
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</tr>
<tr>
<td>Methanol to propylene (MTP) Technology</td>
<td>This process produces propylene through methanol route using natural gas. In this process propylene is produced in two steps. First methanol is converted to dimethyl ether in reactor followed by reaction of methanol/DME in second reactor. Methanol can be produced from methane from conventional method.</td>
<td>Lurgi Oel Gas Chemie GmbH</td>
</tr>
<tr>
<td>C4 hydrogenation and Meta-4 Process</td>
<td>This process involves production of polymer grade propylene plus an isobutylene rich stream or MTBE by upgrading low value C4 stream pyrolysis C4 cuts or butene rich cut. The process steps involve – butadiene and C4 acetylenes selective hydrogenation and butadiene hydroisomerisation, isobutylene removal or MTBE production and metathesis step for conversion of butene and ethylene to propylene. The two main equilibrium reactions taking place are metathesis and isomerisation.</td>
<td>Axens, Axens NA</td>
</tr>
<tr>
<td>Olefin Ultra ™</td>
<td>A new ultra high activity ZSM-5 additive that provides the highest activity has been developed by Davison catalysts.</td>
<td></td>
</tr>
<tr>
<td>KBR’s MAXOFIN-3 TECHNOLOGY</td>
<td>KBR’s MAXOFIN process is based on fluidised bed cracking of gas oils and residue feeds using ZSM catalyst and proprietary MAXOFIN-3 catalyst additive. The process gives 15% or higher propylene yield from gas oil.</td>
<td>Kellogg Brown &amp; Root, Inc.</td>
</tr>
</tbody>
</table>

Source: Pujaodo and Vora, 1990; Badoni et al., 1996; Meyers, 1986; Dunn et al., 1992; Venner & Kantorowicz, 2001; Petrochemical Processes 2003; Zinger, 2003; Nee, 2003; Dharia et al., 2004, Eng. et al., 2004

Table M-VII 6.3: Typical Composition of FCC Gas Stream

<table>
<thead>
<tr>
<th>Products</th>
<th>Yield weight (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry gas (including ethylene)</td>
<td>12.7</td>
</tr>
<tr>
<td>Propane</td>
<td>6.5</td>
</tr>
<tr>
<td>Propylene</td>
<td>21.0</td>
</tr>
<tr>
<td>Butene</td>
<td>35.8</td>
</tr>
</tbody>
</table>

Source: Badoni et al, 1996
Catalytic Dehydrogenation

Catalytic dehydrogenation of light paraffins is of increasing importance because of the growing demand of olefins such as propylene and isobutene [Reasco and Haller, 1994] and n-butene. Propane dehydrogenation accounts for 2 percent of the total world propylene production. Some of the commercial processes available for dehydrogenation of propane and n-butane are [Badoni et al., 1996]:

- Oleflex (UOP).
- Catofin (ABB Lumus).
- FBD-4 (Snamprogetti SPA).
- Star (Phillips Petroleum Company).

Catalytic dehydrogenation takes place at high temperature (650 °C) using platinum based or chromium-alumina or Fe, Cr/Al₂O₃ as catalyst. Reactor effluent treatment for the separation of hydrogen, propylene, and propane is not simple and total investment is high. These production units can be installed only in areas where field propane is available at low costs.

Methanol to Propylene:

This process produces propylene from natural gas via methanol by converting methanol to dimethyl ether in adiabatic reactor using high activity, high selectivity catalyst. The methanol, water, DME stream is then feed to series of MTP reactor where steam is added. The product stream is first processed for removal of traces of water, CO₂ and DME, followed by further processing for yielding polymer grade propylene.

PROPYLENE OXIDE, PROPYLENE GLYCOL AND POLYOLS

Propylene oxide, propylene glycols and polyols are important derivatives of propylene. Propylene oxide is used for the manufacture of propylene glycol and polyols. Major consumption of propylene oxide is manufacture of polyurethane and polyester resins. Propylene glycol find major application in the manufacture of unsaturated polyester resins, food additives, pharmaceuticals and personal care, tobacco humectants, cellophane, paints and coatings. Polyols major use is in the manufacture of polyurethane.
**Propylene Oxide**

Various route for making propylene oxide are

There are two major processes for the manufacture of propylene oxide: Propylene chlorohydrin process and propylene oxidation process using peroxides.

**Propylene Chlorohydrin Route:**

The chlorohydration process consists of formation of propylene chlorohydrin by the reaction between hypochlorous acid and propylene. The propylene chlorohydrin is epoxidised to propylene oxide by a 10% solution of milk of lime or NaOH. Various steps involved are

- **Propylene hypochlorination:** Propylene is reacted with aqueous chlorine resulting in the formation of propylene chlorohydrins. Unreacted propylene is recycled.

- **Neutralisation:** Neutralisation of propylene chlorohydrins containing hydrochloric acid which is formed during the process.

- **Dehydrochlorination:** Reaction of propylene chlorohydrin with milk of lime or caustic soda to produce propylene oxide

- **Purification:** Distillation of crude propylene oxide for separation heavy ends

**Reactions :**

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl} \\
\text{CH}_3\text{CH}==\text{CH}_2 + \text{HOCl} \underset{350^\circ \text{C}}{\rightarrow} \text{CH}_3\text{CH OH} -\text{CH}_2\text{Cl} \Delta H_{298}^0 = -225 \text{ kJ/mol} \\
\text{Propylene chlorohydrin} \\
2\text{CH}_3\text{CHOH-CH}_2\text{Cl} + \text{Ca(OH)}_2 \text{ or NaOH} \rightarrow 2\text{CH}_3\text{CH-CH}_2 + \text{CaCl}_2 \text{ or NaCl} + 2 \text{H}_2\text{O} \\
\Delta H_{298}^0 = 5 \text{ kJ/mol}
\]

Byproducts formed during the reaction are 1,2-dichloropropane and chlorinated di-isopropyl ether. Some of the disadvantages and major economic drawbacks of the process which led to the wide acceptability of epoxidation processes are use of costly chlorine, production of weak calcium chloride byproduct, and corrosion problem due to chlorine handling.

**Oxidation Route using peroxide Compounds:** In this process, propylene and peracetic acid (in ethyl acetate) which is produced by oxidation of acetaldehyde are reacted in a series of three specially designed reactors at 50-80 °C and 90-120 MPa pressure. The reaction products
are fed to the stripper where a mixture of propylene and propylene oxide are obtained as top product while mixture of ethyl acetate and acetic acid is obtained as bottom product. Both mixtures are fed to two separated columns where separation of propylene oxide, ethyl acetate, acetic acid, and heavy end takes place.

**Reaction**

**Peroxide from acetaldehyde**

\[
\text{CH}_3\text{CHO} + \text{O}_2 \xrightarrow{30-50 \degree C, 25-40 \text{ MPa}} \text{CH}_3\text{C} = \text{OOH} \quad \text{per acetic acid}
\]

Oxidation of propylene

\[
\text{CH}_3\text{C} = \text{CH}_2 + \text{CH}_3\text{C} = \text{O} \xrightarrow{50-80 \degree C} \text{CH}_3\text{C} = \text{CH}_2 + \text{CH}_3\text{COOH}
\]

**Propylene Glycol**

Propylene glycol is made by hydrolysis of propylene oxide. The process steps involve are:

**Reaction Section:** Hydrolysis of propylene oxide resulting in formation of mono propylene glycols (MPG). Small amount of di propylene glycol (DPG) and tri propylene glycol (TPG) s are also formed

**Concentration Section:** Concentration of glycol solution in multiple effect evaporator

**Distillation Section:** Separation of MPG, DIPG and TPG separated from MPG column. n series of distillation column where MPG is separated in first column.

**Polyols**

Polyols are made by polymerization of propylene oxide/ethylene oxide using an proprietary catalysed chain starter. The process consist of

- Raw material Preparation: Preparation of chain starter and addition in reactor along with EO/PO
- Reaction: Polymerisation using catalysed cahin extender
- Purification: Purification of raw polyol by neutralization

**ISOPROPANOL**
Ever since its first commercial introduction in 1920 as one of the first petrochemicals, isopropyl alcohol has found wide use as a solvent and raw material for other chemical products like acetone, isopropyl acetate, glycerol, isopropyl and disopropyl amines, corrosion inhibitor di-sopropyl ammonium nitrate, floatation agent isopropyl xanthate, isopropyl myristates etc. [Akiyama, 1974]

Process Technology:
Two major processes for isopropanol manufacture are

- **Esterification of propylene by sulphuric acid and hydrolysis**

  \[
  \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{SO}_4 \xrightarrow{\text{\text{\text{-}}}} (\text{CH}_3)_2\text{CH}\text{-O-SO}_3\text{H} \\
  (\text{CH}_3)_2\text{CH}\text{-O-SO}_3\text{H} + \text{H}_2\text{O} \xrightarrow{\text{\text{\text{-}}}} \text{CH}_3\text{-CH(OH)}\text{CH}_3 + \text{H}_2\text{SO}_4
  \]

- **Direct catalytic hydration of propylene (vapor phase, liquid phase and mixed phase)**

  \[
  \text{CH}_3\text{-CH}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{\text{\text{-}}}} \text{CH}_3\text{-CHOH}\text{-CH}_3 \quad \Delta H_{298K} = -51 \text{ KJ/mol}
  \]

Although originally isopropyl alcohol was made by esterification of propylene and hydrolysis, problems of corrosion and a high heat requirement has led to the use of direct hydration process.

**Direct Hydration of Propylene:** In liquid phase hydration of propylene (Tokuyama Process) silico tungstate is used. The catalytic hydration process takes at 250-27°C at 200 atm pressure. Propylene conversion has been reported around 60-70%.

**BUTANOLS (N-BUTANOL AND ISO-BUTANOL)**

Various routes for making butanol are

- Acetaldehyde route
- Hydroformylation of propylene
- Oxidation of Butane

**Condensation of Acetaldehyde:** The process involves Aldolization, dehydration, hydrogenation

\[
\text{2 CH}_3\text{CHO} \xrightarrow{\text{acetaldehyde}} \text{CH}_3\text{CH(OH)CHO} \\
\text{CH}_3\text{CH(OH)CHO} \xrightarrow{} \text{H}_3\text{C}==\text{C}==\text{CHO} + \text{H}_2\text{O} \\
\text{H}_3\text{C}==\text{C}==\text{CHO} \xrightarrow{\text{H}_2} \text{H}_3\text{C}==\text{C}==\text{C}==\text{C}==\text{OH}
\]
Hydroformylation of propylene

Butanol is manufactured from hydrogenation of n-butyraldehyde and iso-butyraldehyde mixture obtained by hydroformylation reaction of propylene and synthesis gas. Hydrogenation takes place at temperature 150-200 °C and 5-10 MPa pressure using copper or nickel catalyst. The butanols from the hydrogenation reactor go to a series of distillation columns for separation of light effluents and n-butanol and iso-butanol. About 88% of n-butanol and 12% iso-butanol are obtained.

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{C}=\text{H} + \text{CH}_3\text{CH}═\text{CHO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{CH}═\text{CH}_2\text{OH}
\]

BUTADIENE [\text{CH}_2═\text{CH}═\text{CH}_2]

Butadiene is one of the major petrochemicals with a wide range of uses as feedstock for production of a variety of synthetic rubbers and polymer resins, the bulk of which are related to styrene butadiene rubber (SBR), nitrile rubber, chloroprene rubber, polybutadiene rubber, and acrylonitrile butadiene styrene (ABS) resin. Another major use of butadiene is in the manufacture of adiponitrile which is a raw material for the production of Nylon 66. Global demand growth for butadiene is set to accelerate. Butadiene based synthetic rubbers are mainly used in the automotive industry. It is also widely used for manufacturing of engineering resins.

There are four major routes for production of butadiene:

- Steam cracking of naphtha
- Catalytic dehydrogenation of butenes
- Catalytic dehydrogenation of butanes
- Dehydrogenation-dehydration of ethanol (molasses route)

2-ETHYL HEXANOL
Major use of 2-ethyl hexanol is in the manufacture of di-2-ethylhexylphthalate which is used as plasticiser for vinyl resins. Other application are in synthetic lubricants, antioxidants and antifoams. 2-Ethyl hexanol is made either by the oxo-synthesis or from acetaldehyde route by condensation and hydrogenation. 2-Ethyl hexanol is also used in the manufacture of ethyl hexa acrylate. Ethyl hexaacrylate produces soft and tacky film with excellent low temperature flexibilities. Ethylhexanol also find application cable coating compositions, nitrocellulose lacquers, as softener in nitrile rubber compounds, in plastic compounds for water proof agents [Nandini Chemical journal, July 1998, p.21, mall 2007].

**Propylene Route:** In first step 4n-butyraldehyde is produced along with 1-isobutyraldehyde. 4n-butyraldehyde is further hydrogenated to 2-ethylhexanol

![Chemical Reaction Diagram]

**PROPYLENE CARBONATE** $[\text{C}_3\text{H}_6\text{CO}_3]\$

Propylene carbonate is prepared by reaction of propylene oxide and carbon dioxide in presence of ion-exchange resins [Mall, 2007]

![Chemical Reaction Diagram]

**Uses:** Propylene carbonate is used as special solvent. It is used in solvent extraction, plasticisers, organic synthesis, natural gas purification, and fiber spinning solvent.
ACRYLIC ACID

Acrylic acid is a versatile chemical which find application in the manufacture of glacial acrylic acid and acrylic esters (Acacrylates and metha acrylates), polyacrylic acid which is used in manufacture of super absorbent polymers, flocculants, detergents, paper chemicals and resin. SAP is used for water retention in infants diaper, adult in continence products and femininehygiene products [Nandini Chemical Journal, July, 1999]. Various acrylic esters are methyl acylate, ethyl acrylate, butyl acylate, 2-ethyl hexyl acrylate.

Process Technology:
Various routes for making acrylic acid are

- Acetylene route
- Ethylene Oxide Route
- Ethylene Route
- Chlorination of Propianic acid
- Propylene route
- Formaldehyde and Acetic Acid Route

Amongst the above process propylene oxidation through acrolein is commonly used

Propylene Route: In this route, acrolein is made in first stage by oxidation of propylene in presence of mixed catalysts (prepared from oxides of bismuth, potassium, cobalt, and iron, nickel, tin, tellurium, tungsten, etc). In the second stage, acrolein is oxidised to acrylic acid in the presence of mixed oxides of molybdenum and vanadium at 250-280 °C in the presence of steam.

\[ \text{CH}_2\text{CH} = \text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{CH} = \text{CHO} \]

Acrolein

REFERENCES
3. Akiyama, S. “Direct hydration of C3H6 yields Isopropyl alcohol”, Chemical Engineering, July 9,1973

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4. Austin, G.T., “Industrially significant organic chemicals part 6” Chemical engineering, May 27, 1974