

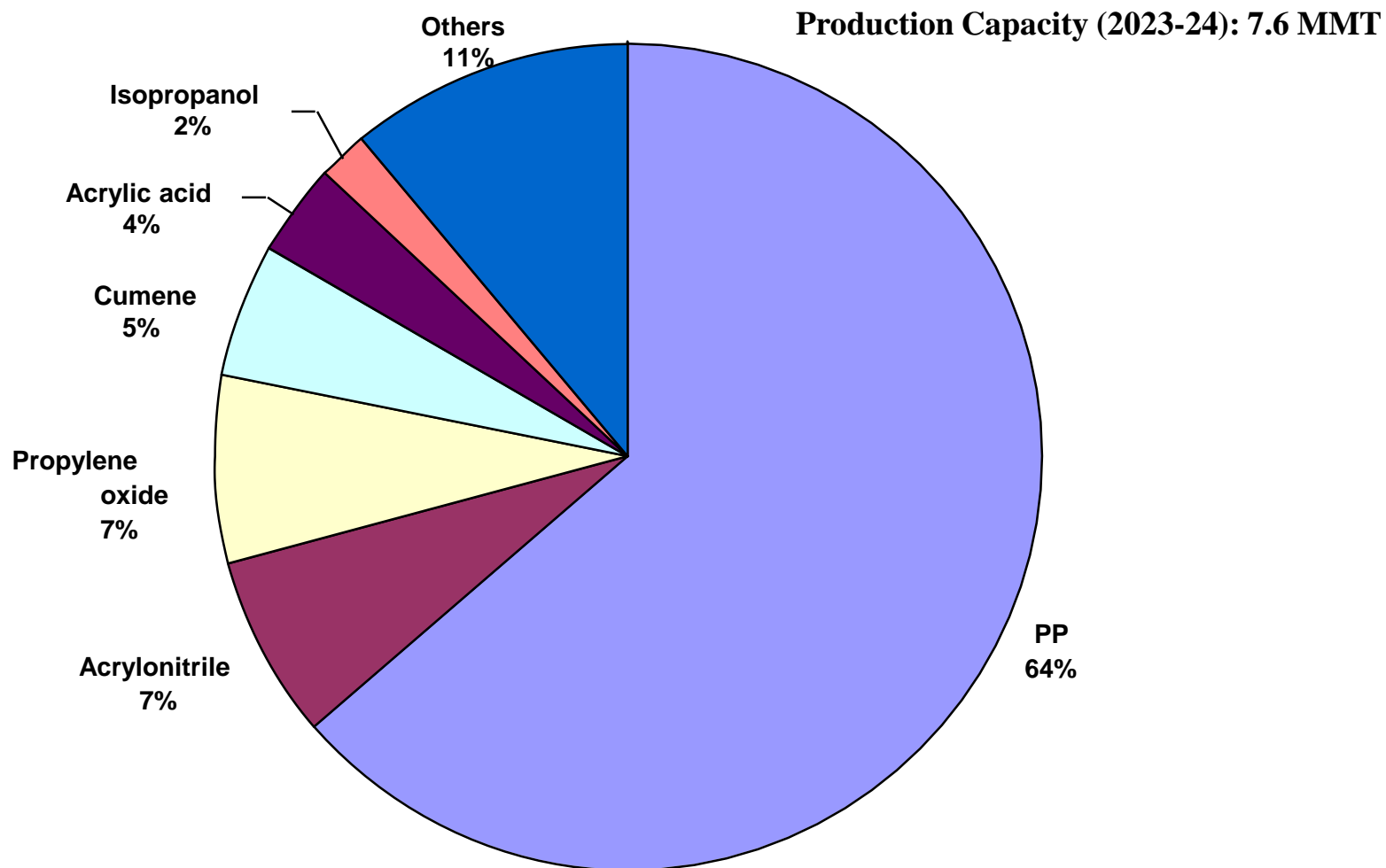
# **Petrochemical Technology**

## **Chemicals from Propylene**

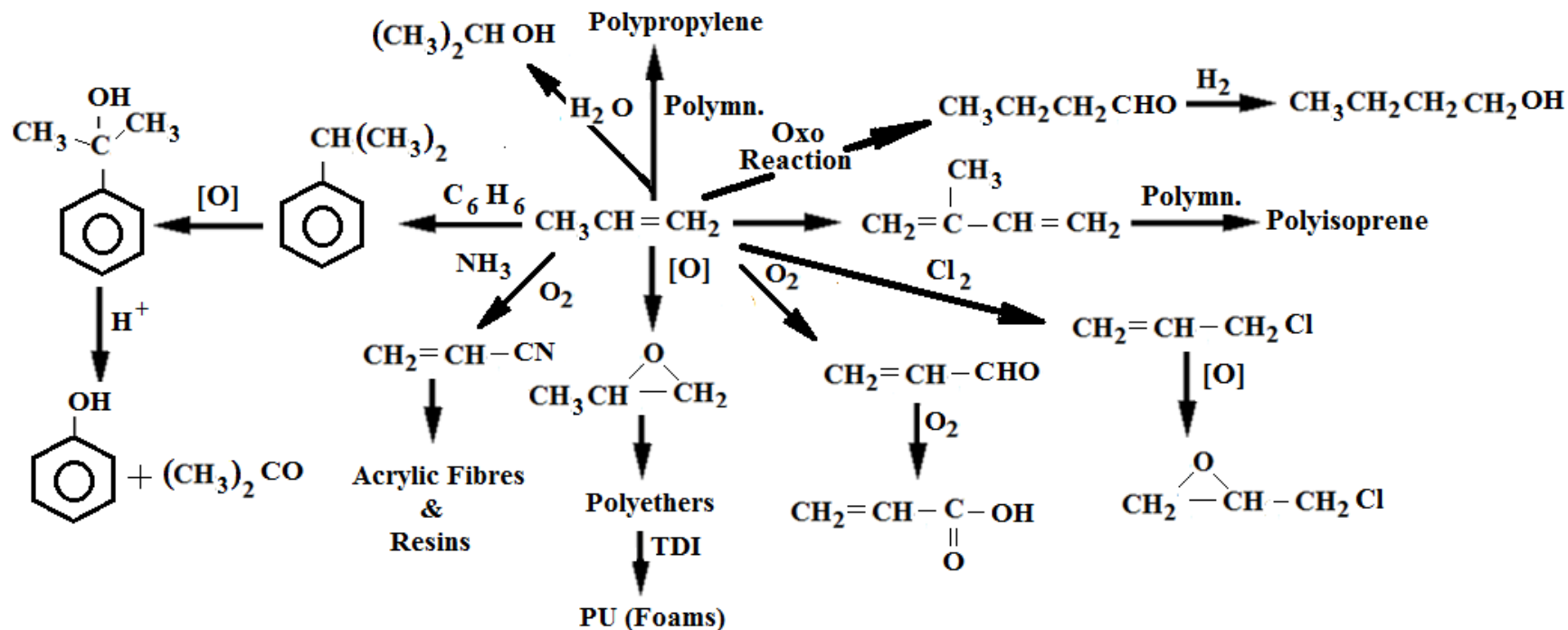
# Propylene Consumption Patterns

**Global propylene capacity could increase from 150.3 MTPA in 2023 to 199.35 MTPA in 2030.**

**India Polypropylene market demand stood at 5.9 Million Tonnes in FY2023 and is forecast to reach 10.29 Million Tonnes by FY2030, growing at a healthy CAGR of 7.25% until FY2030.**



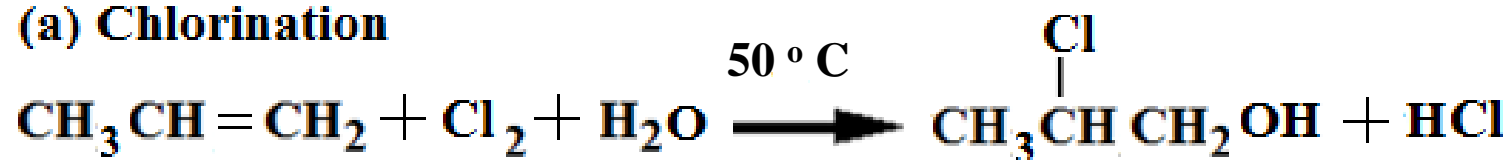
# Major Chemicals form Propylene



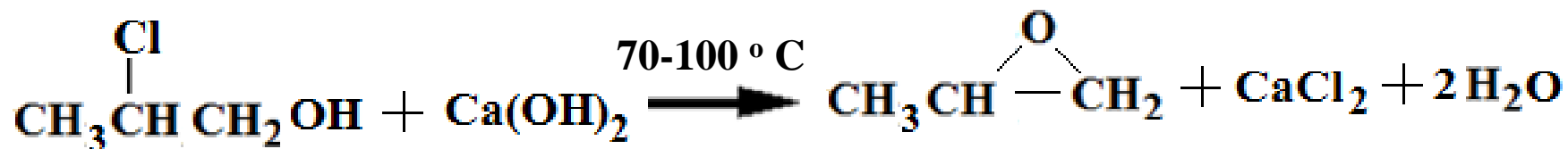
# Propylene Oxide

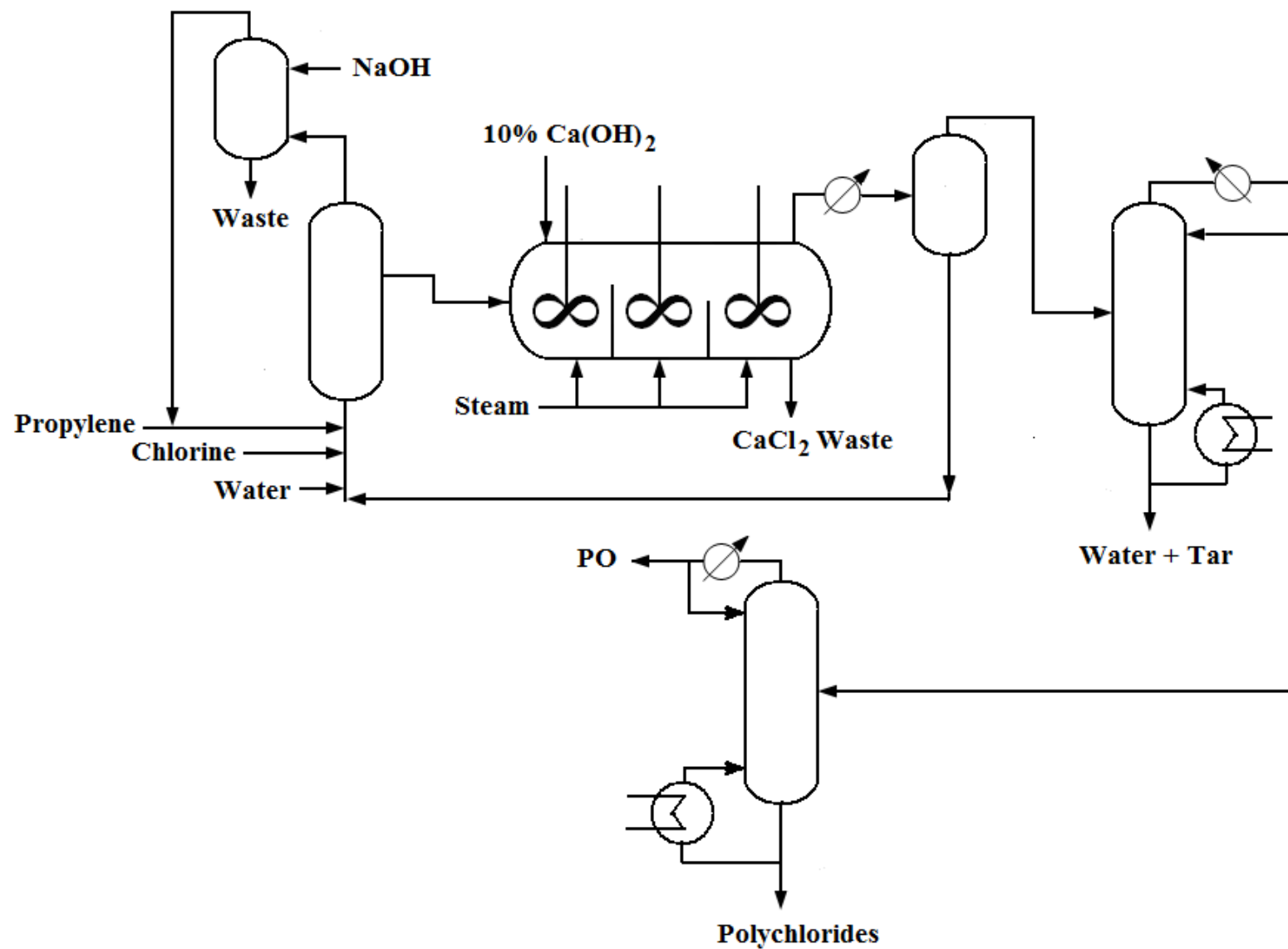
## Chemical Reactions

### (a) Chlorination



### (b) Dehydrochlorination





**Flowsheet for the Production of Propylene Oxide**

## ACRYLONITRILE ( $\text{CH}_2=\text{CH-CN}$ )

**Ammoxidation** of propylene to acrylonitrile is usually carried out in fluid-bed reactors converting a nearly stoichiometric mixture of propylene, air and ammonia at about **400-500°C**, **1.5-3.0 atm** pressure. Practically complete conversion of propylene and ammonia is achieved to produce acrylonitrile in **65-75% selectivity**.

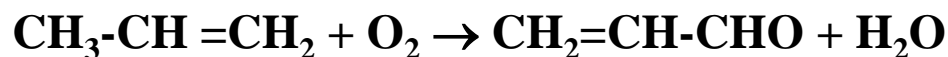
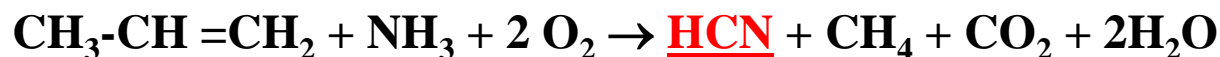
**Acetonitrile** and **HCN** are the main byproducts. The **Sohio process** originally used **Oxides of Bi, Co, and Mo, and bismuth and cobalt molybdates**. Other catalysts developed later (uranyl antimonite, antimony oxide-iron oxide, oxides of Fe, Ce, and Mo, mixed oxides of Sb and Sn) produce fewer byproducts and ensure higher yields of acrylonitrile.

**Silica supported oxides of Selenium, Iron and Tellurium** have also been used as catalysts. It gives **100% conversion of propylene with 86.9% selectivity for acrylonitrile** and 2.9% selectivity for HCN in 2-5 s of contact time at 320 °C.

### Main Reaction:



### Side reactions in ammoxidation process:



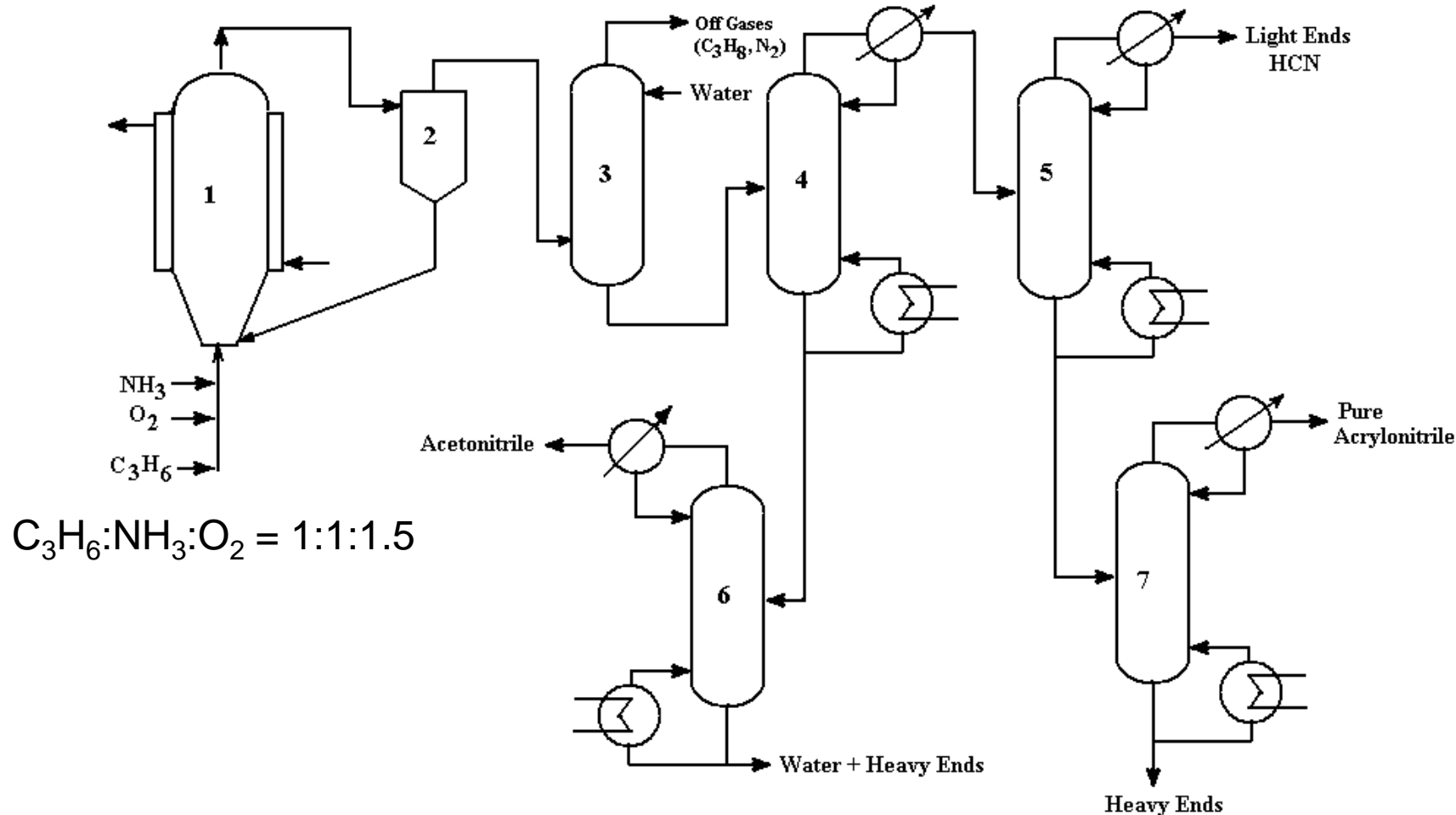
## **Propane Ammoxidation – BP Process**

**Processes based on propane ammoxidation to manufacture acrylonitrile have also been developed and commercialized by BP. Dehydrogenation at high reaction temperature (485-520 °C), which is about 100 °C higher than that for propylene ammoxidation, results in the formation of propylene, which subsequently undergoes normal ammoxidation.**

**Despite higher investments and markedly lower selectivity (30-40%), the process can be economical because of the price difference between propylene and propane.**

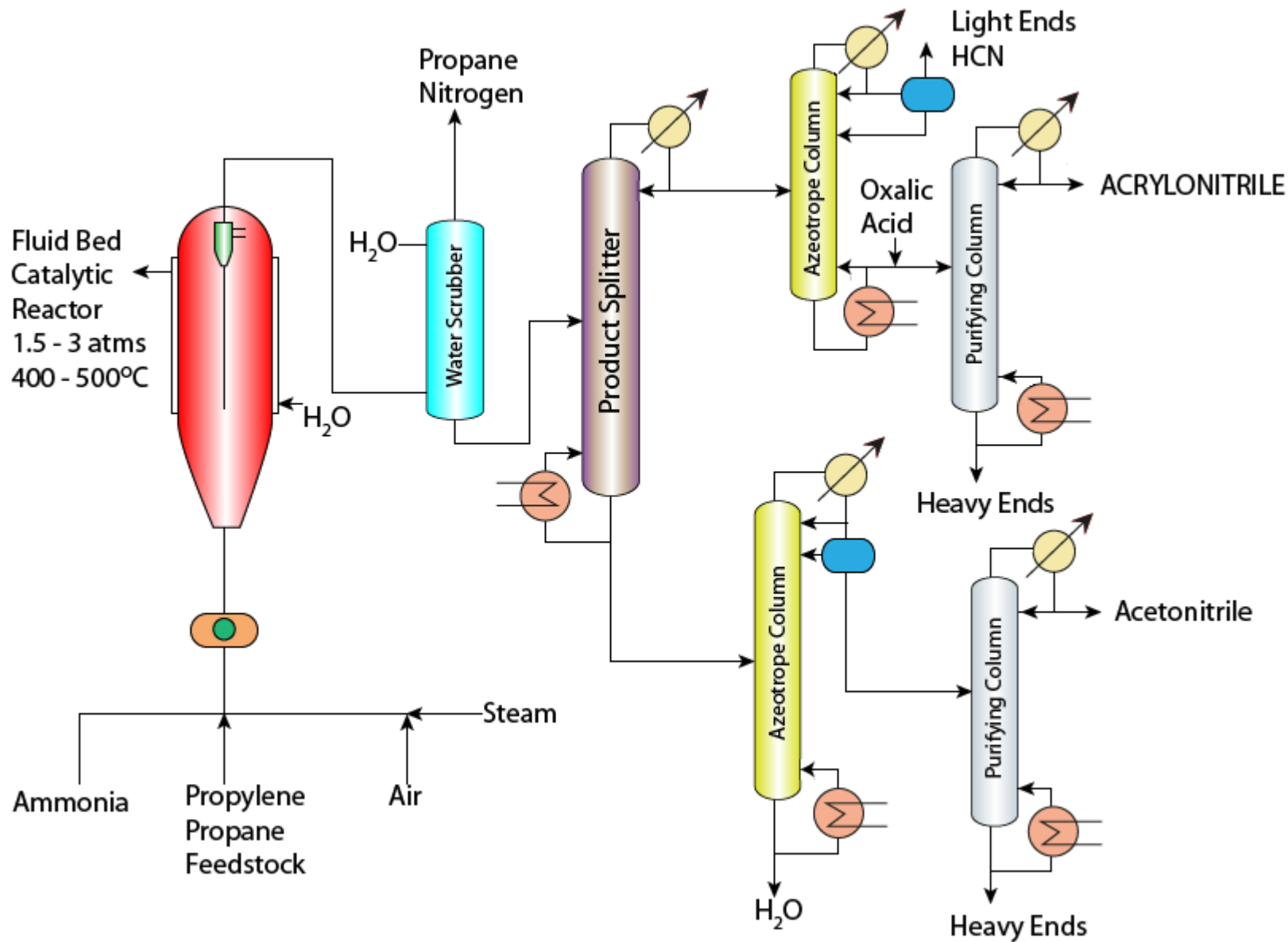
**Better selectivities can be achieved at lower (40-60%) conversions.**



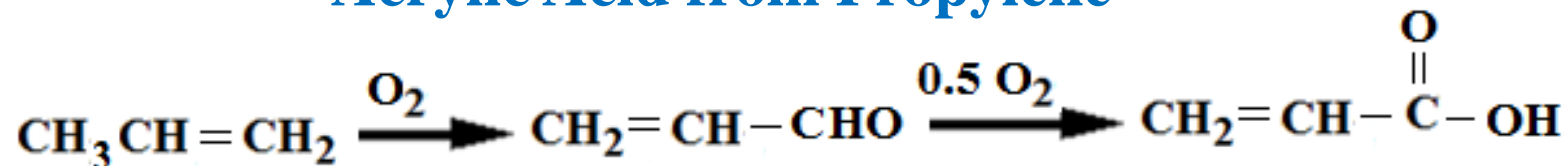


1: Fluidized bed reactor; 2: Cyclone separator; 3: Water scrubber; 4: Product stripper;  
 5: Light ends column; 6: Acetonitrile column; 7: Acrylonitrile column

## Flowsheet for the production of Acrylonitrile by Ammoxidation of Propylene



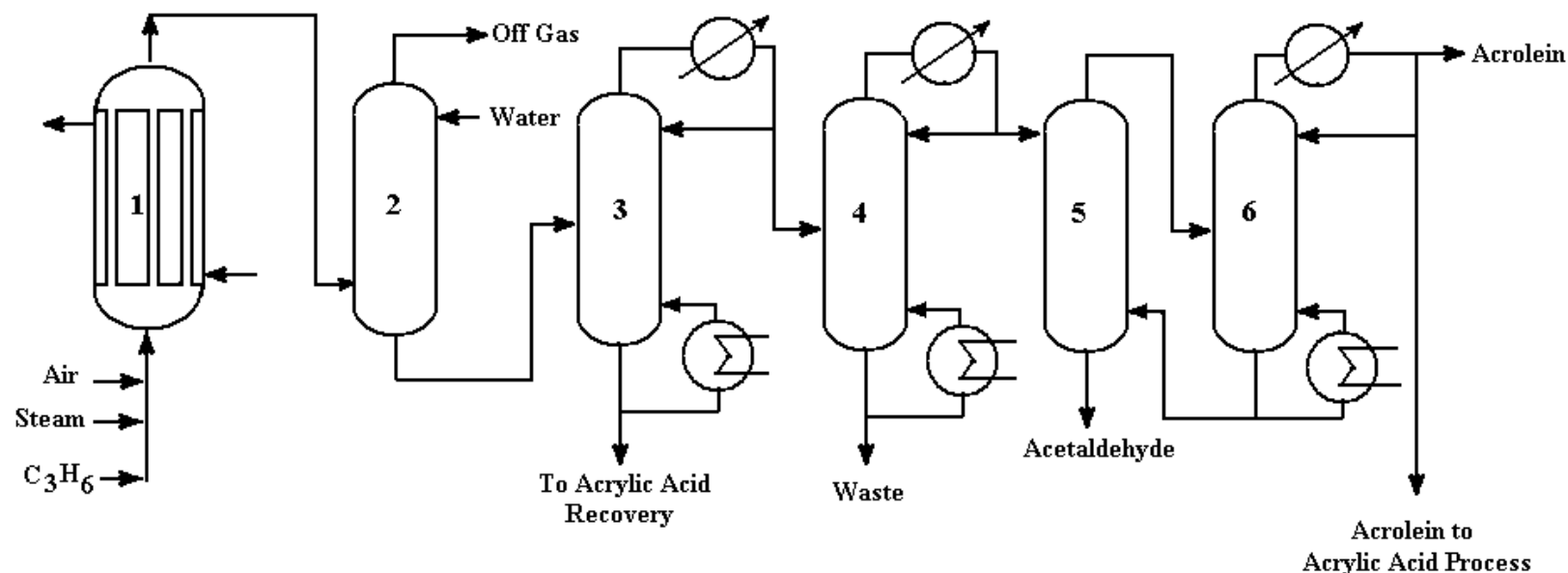
## Acrylic Acid from Propylene



The two-step process yields acrolein as an intermediate that can be isolated, if desired. Optimum catalyst and temperatures are different for each of the two steps, the first step requiring much higher temperature than the second.

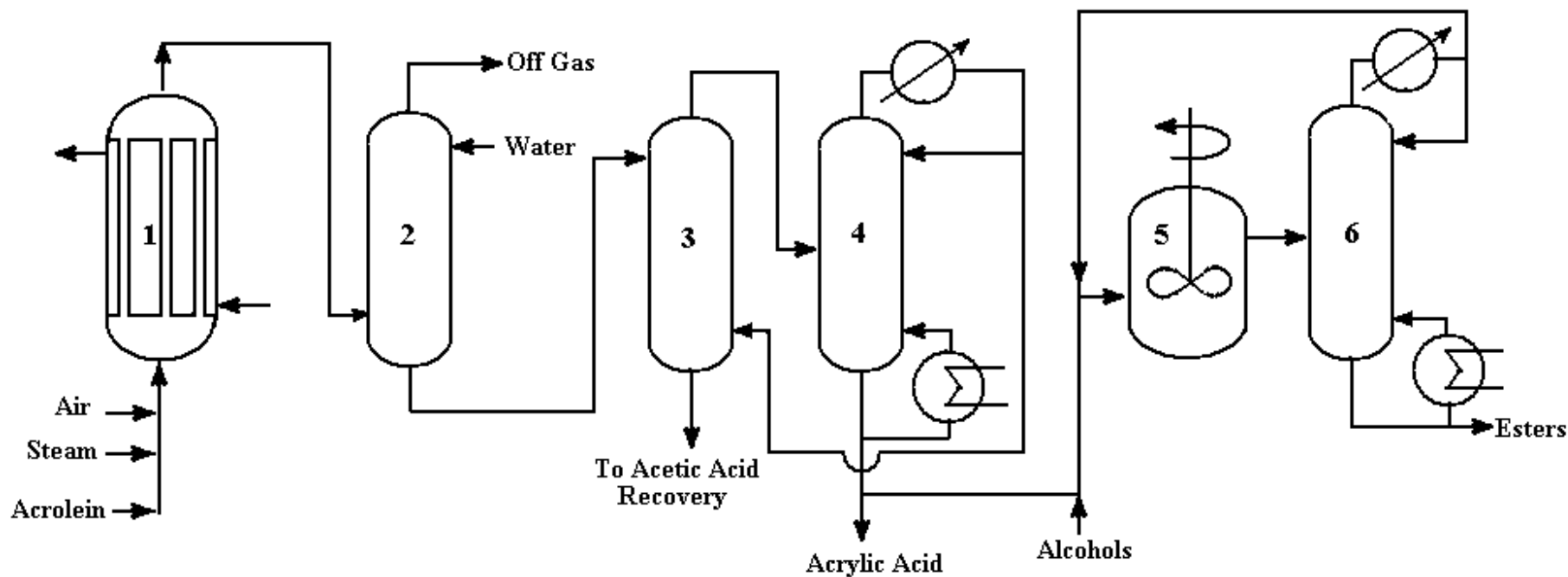
Molybdenum based catalysts predominate and a typical catalyst for the first step of the two-step conversion is  $\text{Fe}_4\text{BiW}_2\text{Mo}_{10}\text{Si}_{1.35}\text{K}_{0.6}$ . With the catalyst at 320 °C, propylene conversion is 97% and acrolein selectivity is 93%. In addition, however, there is a 6% selectivity to acrylic acid making the useful selectivity 99%. These results are typical of what can be achieved with modern sophisticated catalyst.

In the second stage, the catalyst used is  $\text{Mo}_{12}\text{V}_{4.6}\text{Cu}_{2.2}\text{Cr}_6\text{W}_{2.4}$ . The catalyst is supported on alumina and at 220 °C, a 98% selectivity for acrylic acid is obtained.



**1: Reactor; 2: Quench tower; 3: Acrylic acid recovery column;  
4: Heavy ends column; 5: Extraction column; 6: Acrolein column**

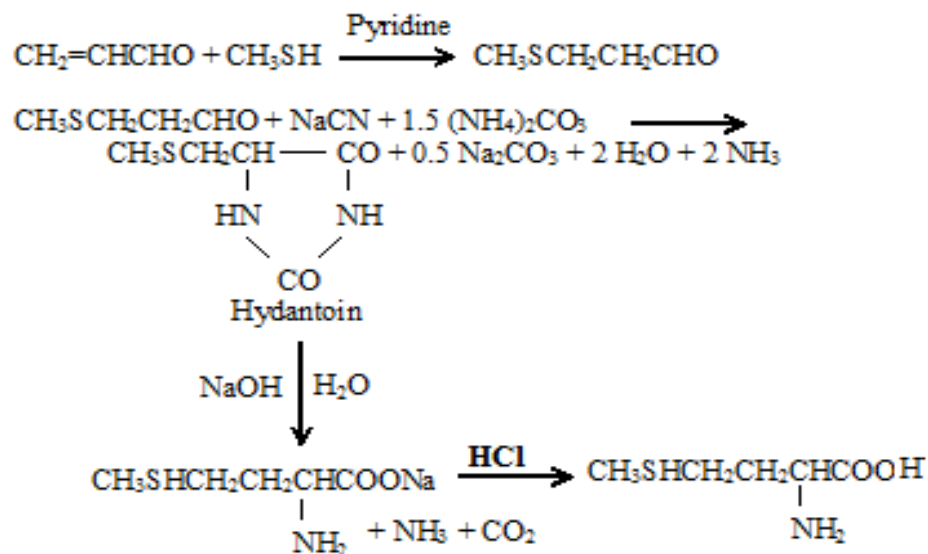
**Flow sheet for the production of acrolein from propylene**



**1: Reactor; 2: Quench tower; 3: Extraction column; 4: Acrylic acid column;  
5: Esterification reactor; 6: Ester column**

**Flow sheet for the production of acrylic acid/acrylates  
from acrolein**

The most important use of acrolein is for the production of D,L-methionine, an essential amino acid added to poultry feeds. Methionine is the amino acid produced in third largest volume after L-glutamic acid, whose monosodium salt is a flavor enhancer in foods, and L-lysine, also used in feeds. In the methionine synthesis, acrolein reacts almost quantitatively with methyl mercaptan in the presence of pyridine to yield  $\beta$ -methylthiopropionaldehyde. The aldehyde is converted to a hydantoin with sodium cyanide and ammonium carbonate. Hydrolysis of hydantoin with aq. NaOH gives sodium salt of methionine, which on acidification produces methionine.



## Oxo Process

An oxo process involves the substitution of HCHO across a double bond, hence the name **Hydroformylation**. The reactants are an  $\alpha$ -olefin and synthesis gas ( $\text{CO} + \text{H}_2$ ). The primary product is an aldehyde with one additional carbon atom. The process is capable of producing the following compounds of commercial interest:

### (a) Long chain alcohols:

*Isooctyl alcohol* – used in the synthesis of dioctyl phthalate, a plasticizer for polymers, principally polyvinyl chloride.

*Decyl alcohol* – made from nonene, a trimer of propylene; sulfated straight chain derivative is a good biodegradable detergent; esterified for plasticizer use.

*Tridecyl alcohol* – made from dodecene, a tetramer of propylene; sulfated derivatives used for detergents.

**(b) Short chain alcohols:**

*n-Butanol* – plasticizer; converted to butyl acetate and other solvent derivatives

*2-Ethyl hexanol* – dimerized via butyraldehyde, used in plasticizers and synthetic lubricants.

**(c) *n-Butyraldehyde*** – converted to butyric acid and anhydride for making cellulose acetate butyrate, a high strength thermoplastic; reacts directly with polyvinyl chloride to make polyvinyl butyral film, used for safety glass.



## Butyraldehyde and n-Butanol from Propylene: Oxo Process

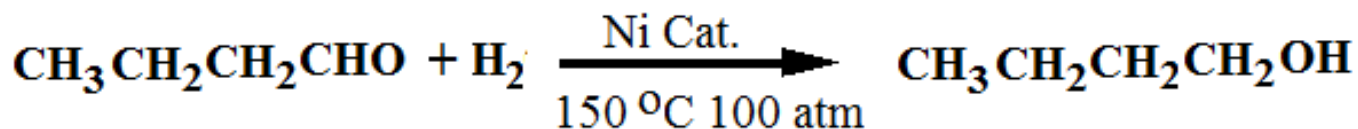
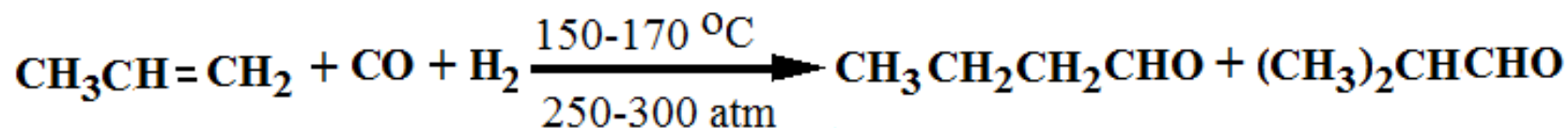
The olefin in the liquid state is reacted at 250-300 atm and 150-170 °C in the presence of a soluble cobalt catalyst (usually, cobalt carbonyl).

The aldehyde and lesser amount of alcohol are formed.

With the Co-catalyst, the ratio of n- to i- isomers of aldehyde is 3-4:1.

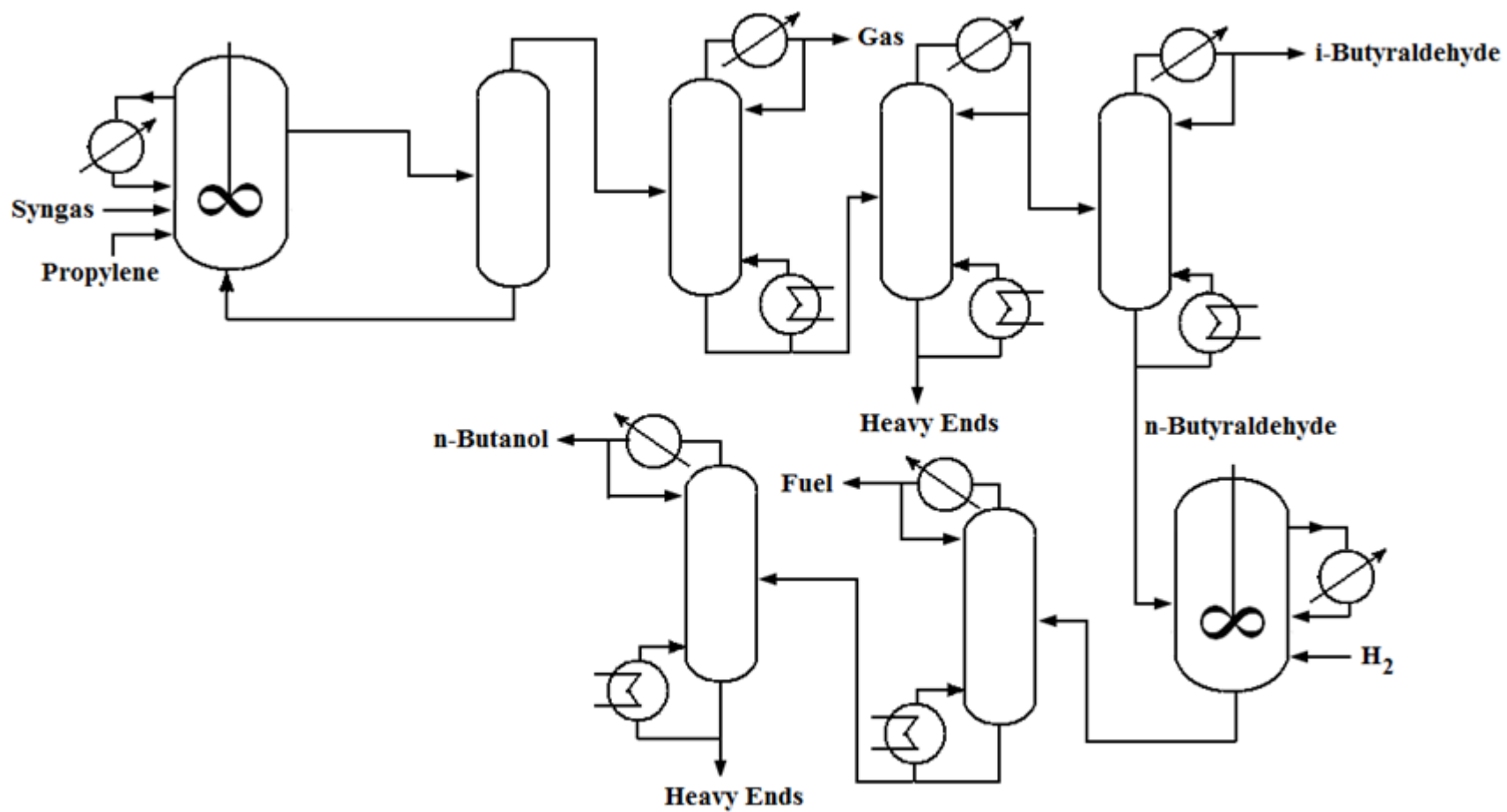
Improved catalyst like Wilkinson catalyst (Triphenyl phosphine and Rhodium chloride,  $\text{PPh}_3/\text{RhCl}_2$ ) has been developed which gives more normal isomer in the ratio of 10:1 under milder operating conditions (100 °C, 10-20 atm).

The normal aldehyde is separated and hydrogenated to the desired n-Butanol.



Industrial Low Pressure Hydroformylation: Forty-Five Years of Progress for the LP OxoSM Process, Johnson Matthey Technol. Rev., 2017, 61, (3), 246 –

256. <https://doi.org/10.1595/205651317X695875>



## Production of n-Butyraldehyde and *n*-Butanol from Propylene

## Overall Rate and Influence of Reaction Parameters to Selectivity and Reactivity

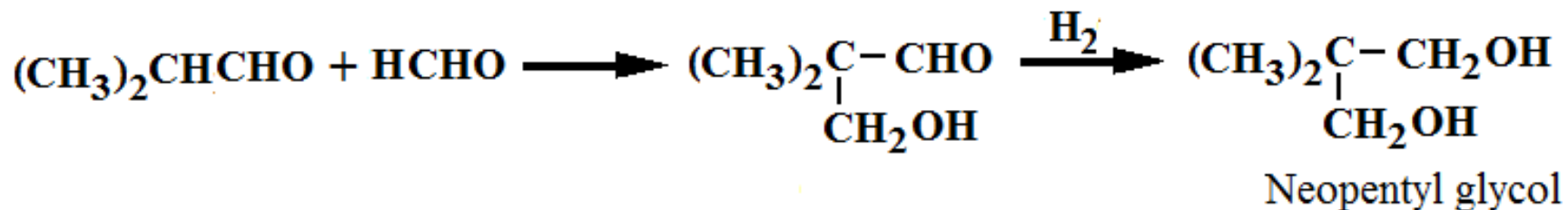
$$\frac{d[\text{aldehyde}]}{dt} = k_{\text{obs}}[\text{alkene}][\text{H}_2][\text{Co}][\text{CO}]^{-1}$$

If a 1:1 H<sub>2</sub>/CO ratio is maintained, the rate will be independent of total pressure, since the rate is proportional to pH<sub>2</sub> and inversely proportional to pCO. However, a certain minimum CO partial pressure is required to maintain the stability of [CoH(CO)<sub>4</sub>], which decomposes to cobalt metal at low pCO. Thus, reasonable reaction rates in the temperature range 110–180 °C require rather high CO partial pressures (pCO), and total H<sub>2</sub>/CO pressures of 200–300 bar.

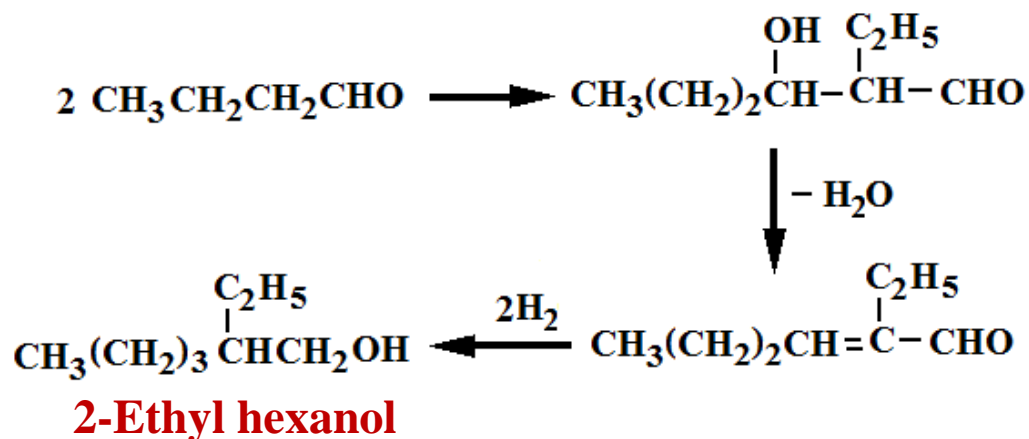
**Disadvantage:** high CO partial pressure decreases the hydroformylation reaction rate.

**Advantages:** high pCO increases linear:branched ratio, decreases alkene isomerization.

**Isobutyraldehyde is used to make neopentyl glycol, which is used largely in unsaturated polyester synthesis to enhance alkali resistance of the cured product.**



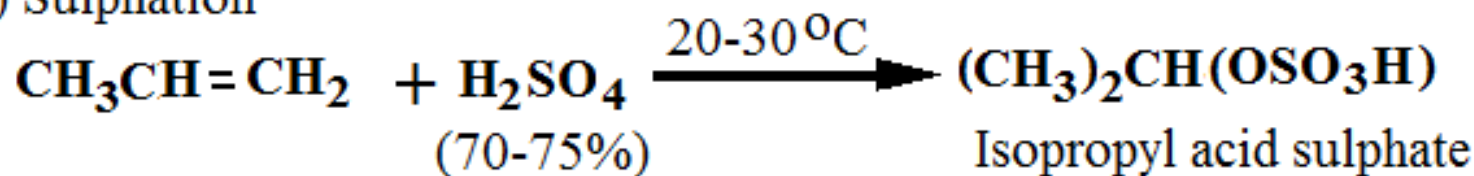
**2-Ethyl hexanol is produced by the aldol condensation of n-butyraldehyde. The reaction occurs in presence of aqueous caustic soda and produces 2-ethyl-3-hydroxyhexanal. The aldehyde is then dehydrated and hydrogenated to 2-ethyl hexanol.**



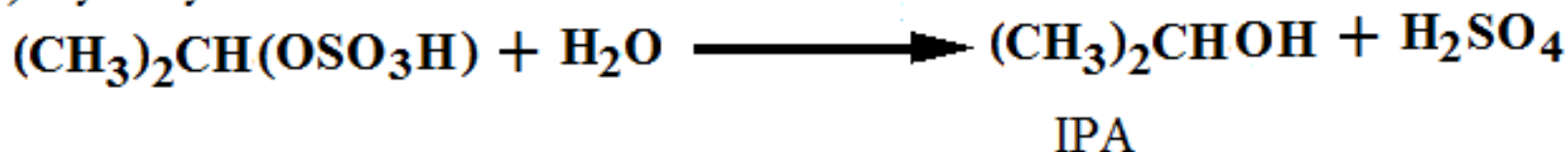
**2-Ethyl hexanol is one of the chemicals used for producing PVC plasticizers (by reacting with phthalic acid, the product is di-2-ethylhexyl phthalate).**

# Production of IPA by Indirect Hydration of Propylene

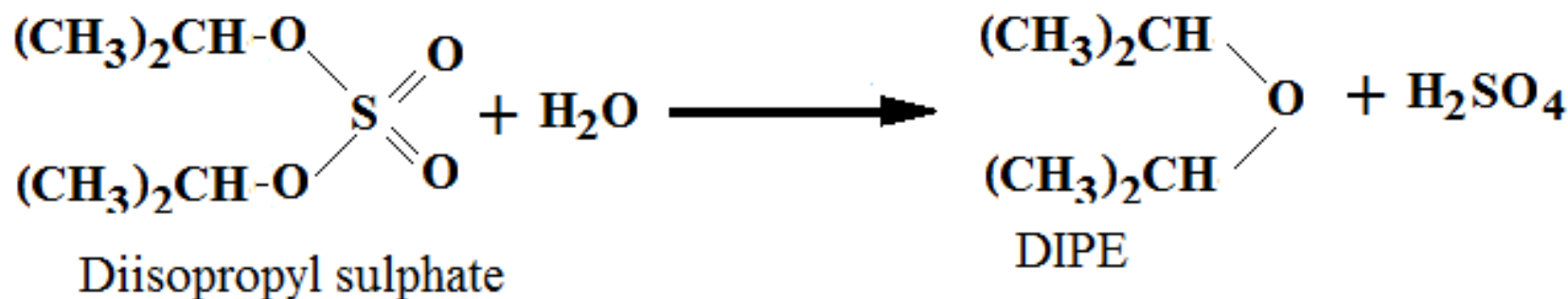
(a) Sulphation



(b) Hydrolysis

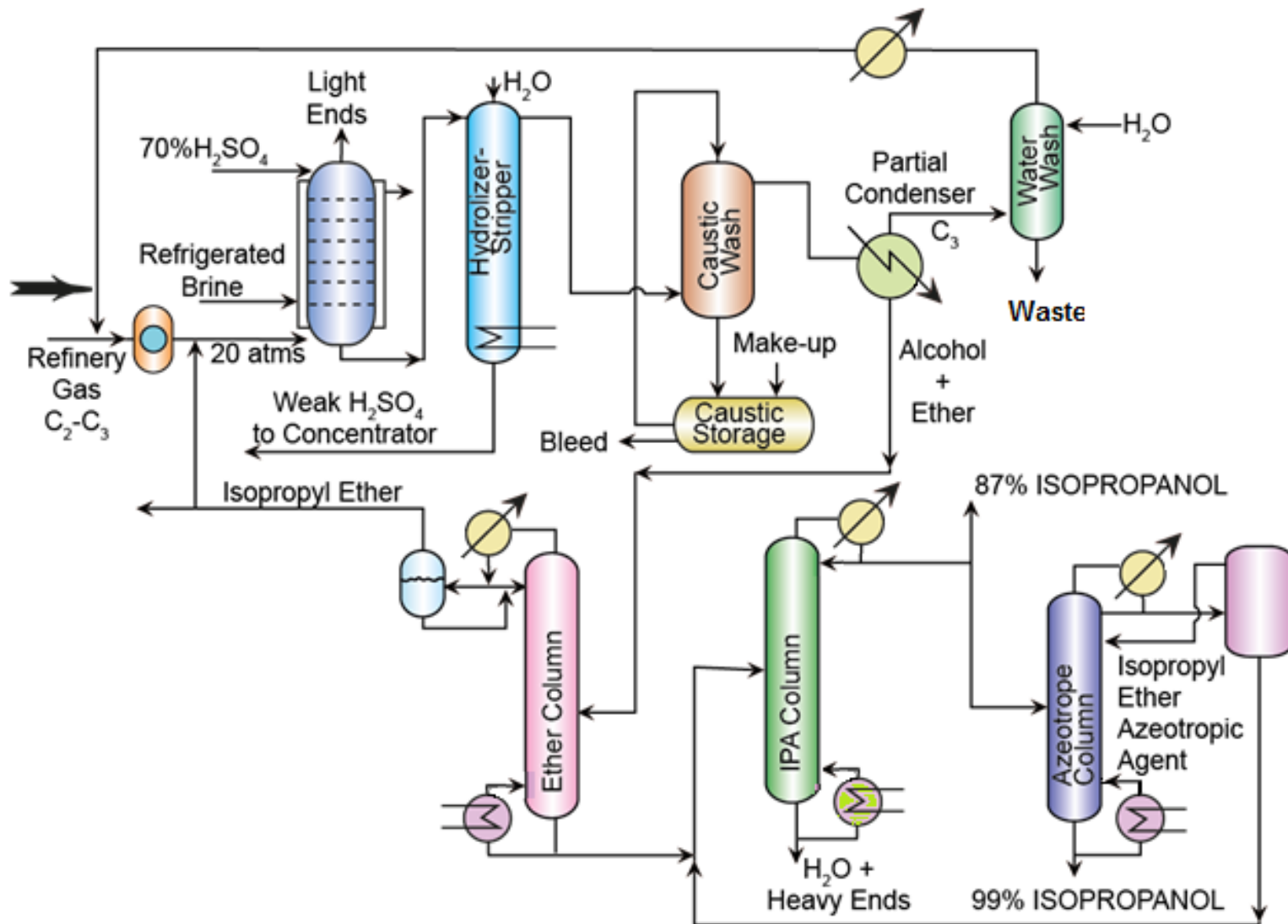


(c) Etherification side reaction



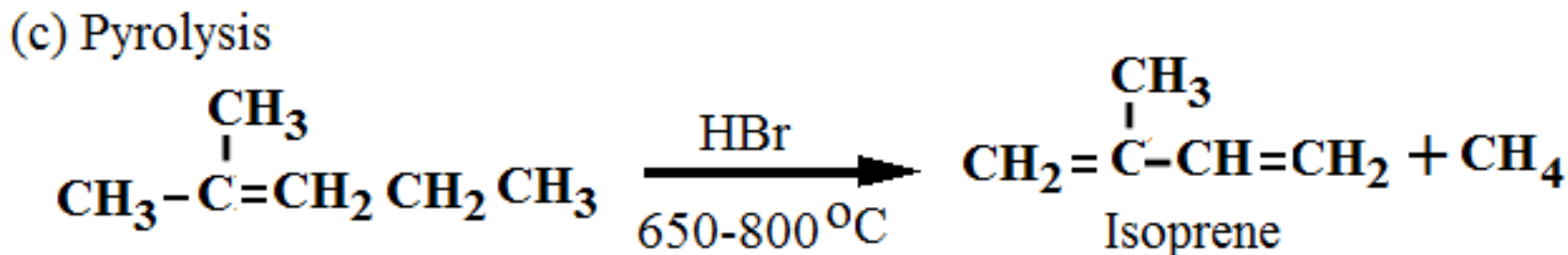
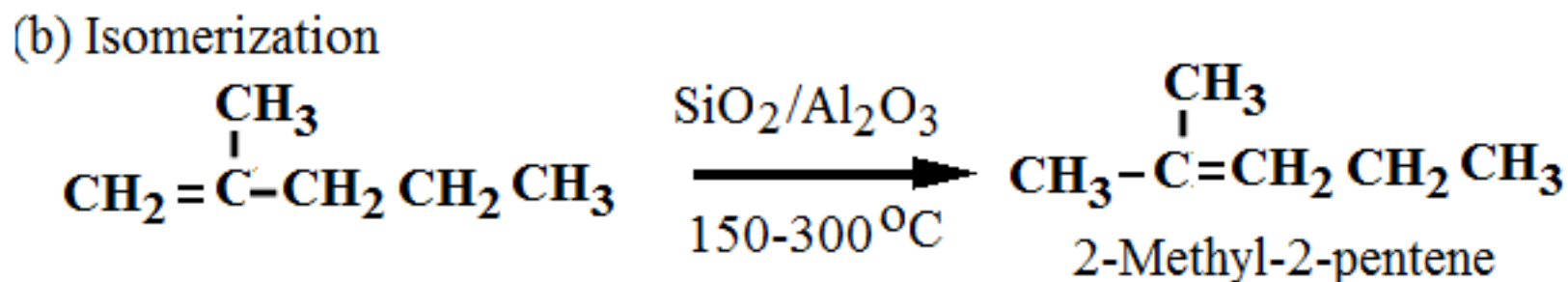
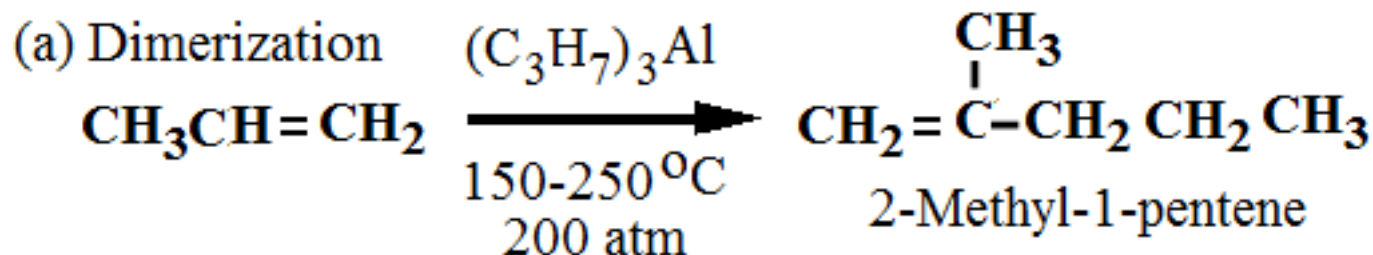
**Kinetic of acetone hydrogenation for synthesis of isopropyl alcohol over Cu-Al mixed oxide catalyst. *Catalysis Today*. 2020, 348, 118-126.**

DOI: <https://doi.org/10.1016/j.cattod.2019.07.051>



**Flowsheet for the Production of IPA from Propylene**

# Isoprene from Propylene : Goodyear Process





## 24



*Thank you!*