# Lecture 13: Petrochemicals: Overview

## *13.1 Introduction*

- In this lecture, we present a brief overview of petrochemical technologies and discuss upon the general topology of the petrochemical process technologies.
- Petrochemicals refers to all those compounds that can be derived from the petroleum refinery products
- Typical feedstocks to petrochemical processes include
    - C1 Compounds: Methane & Synthesis gas
    - C2 Compounds: Ethylene and Acetylene
    - C3 Compounds: Propylene
    - C4 Compounds: Butanes and Butenes
    - Aromatic Compounds: Benzene
- It can be seen that petrochemicals are produced from simple compounds such as methane, ethylene and acetylene but not multicomponent products such as naphtha, gas oil etc.
- **13.1.1 Definition :** These are the chemicals that are made from petroleum and natural gas. Petroleum and natural gas are made up of hydrocarbon molecules, which comprises of one or more carbon atoms, to which hydrogen atoms are attached.
- About 5 % of the oil and gas consumed each year is needed to make all the petrochemical products. Petrochemicals play an important role on our food, clothing, shelter and leisure. Because of low cost and easy availability, oil and natural gas are considered to be the main sources of raw materials for most petrochemicals.

**13.1.2 Classification**: Petrochemicals can be broadly classified into three categories-

**a. Light Petrochemicals:** These are mainly used as bottled fuel and raw materials for other organic chemicals. The lightest of these -- methane, ethane and ethylene -- are gaseous at room temperature.The next lightest fractions comprise petroleum ether and light naphtha with boiling points between 80 and 190 degrees Fahrenheit.

**b. Medium Petrochemicals:** Hydrocarbons with 6 – 12 carbon atoms are called "gasoline", which are mainly used as automobile fuels. Octane, with eight carbons, is a particularly good automobile fuel, and is considered to be of high quality. Kerosene contains 12 to 15 carbons and is used in aviation fuels, and also as solvents for heating and lighting.

**c. Heavy Petrochemicals:** These can be generally categorized as diesel oil, heating oil and lubricating oil for engines and machinery. They contain around 15 and 18 carbon atoms with boiling points between 570 and 750 degrees Fahrenheit. The heaviest fractions of all are called "bitumens" and are used to surface roads or for waterproofing.

Bitumens can also be broken down into lighter hydrocarbons using a process called "cracking."

## 13.2 Process Topology

- Reactors: Reactors are the most important units in petrochemical processes. Petrochemicals are manufactured by following simple reactions using relatively purer feedstocks. Therefore, reaction chemistry for petrochemicals manufacture is very well established from significant amount of research in this field. Essentially all petrochemical processes need to heavily depend upon chemical transformation to first product the purification.
- Separation: With distillation being the most important unit operation to separate the unreacted feed and generated petrochemical product, the separation processes also play a major role in the process flow sheet. Where multiple series parallel reactions are involved, the separation process assumes a distillation sequence to separate all products from the feed. A characteristic feed recycle will be also existent in the process topology. Apart from this, other separation technologies used in petrochemical processing units include phase separators, gravity settling units and absorption columns. Therefore, the underlying physical principle behind all these separation technologies is well exploited to achieve the desired separation.
- Dependence on Reaction pathway: A petrochemical can be produced in several ways from the same feedstock. This is based on the research conducted in the process chemistry. For instance, phenol can be produced using the following pathways
    - Peroxidation of Cumene followed by hydrolysis of the peroxide
    - Two stage oxidation of Toluene
    - Chlorination of Benzene and hydrolysis of chloro-benzene
    - Direct oxidation of Benzene
- We can observe that in the above reaction schemes, there are two reaction pathways for phenol from benzene i.e., either chlorination of benzene or oxidation of benzene. Therefore, choosing the most appropriate technology for production is a trivial task.
- Complexity in pathway: In the above Cumene example case, it is interesting to note that toluene hydrodealkylation produces benzene which can be used to produce phenol. Therefore, fundamentally toluene is required for the generation of various petrochemicals such as benzene and phenol. In other words, there is no hard and fast rule to say that a petrochemical is manufactured using a suggested route or a suggested intermediate petrochemical. Intermediate petrochemicals play a greater role in consolidating the manufacture of other downstream petrochemicals.

## 13.3 Summary of petrochemical processes presented in the course

We next present a summary of the petrochemical processes that would be presented in the course

- Lecture 13
    - Methanol from Synthesis gas route
- Lecture 14
    - Formaldehyde from Methanol
    - Chloromethanes from methane
- Lecture 15
    - Ethylene and acetylene production via steam cracking of hydrocarbons
- Lecture 16
    - Vinyl chloride from ethylene using two step process
- Lecture 17
    - Ethanolamine from ethylene
- Lecture 18
    - Isopropanol from Propylene
    - Cumene from propylene
- Lecture 19
    - Acrylonitrile from propylene
    - Oxo process for converting olefins and synthesis gas to aldehydes and alcohols
- Lecture 20
    - Butadiene from Butane
    - Hydrodealkylation of Toluene
- Lecture 21
    - Phenol from Cumene
    - Phenol from Toluene Oxidation
- Lecture 22
    - Styrene from Benzene
    - Pthalic anhydride from o-xylene
- Lecture 23
    - Maleic anhydride from Benzene
    - DDT manufacture from Benzene

## *13.4 Manufacture of Methanol from Synthesis Gas*

### 13.4.1 Introduction

- Synthesis gas is $H_2$ + CO
- When synthesis gas is subjected to high pressure and moderate temperature conditions, it converts to methanol.
- Followed by this, the methanol is separated using a series of phase separators and distillation columns.
- The process technology is relatively simple

### 13.4.2 Reactions

- Desired: $CO + 2H_2 \rightarrow CH_3OH$
- Side reactions: $CO + 3H_2 \rightarrow CH_4 + H_2O$
  $2CO + 2H_2 \rightarrow CH_4 + CO_2$
- All above reactions are exothermic
- Undesired reaction: $zCO + aH_2 \rightarrow$ alchohols + hydrocarbons
- Catalyst: Mixed catalyst made of oxides of Zn, Cr, Mn, Al.

### 13.4.3 Process Technology (Figure 13.1)

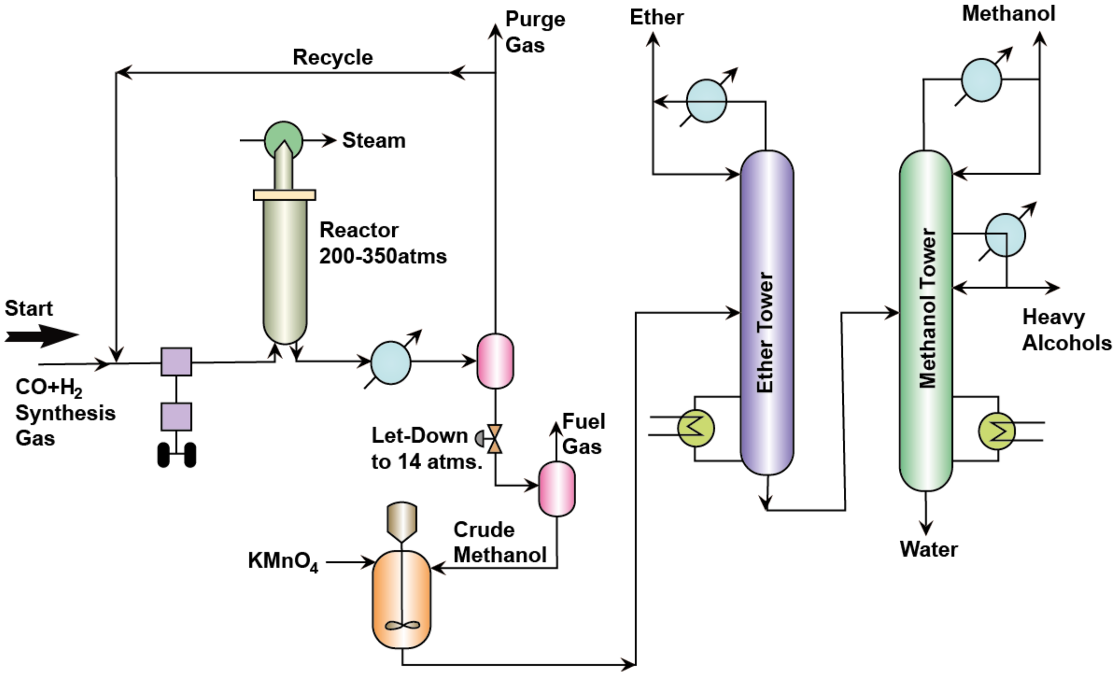


**Figure 13.1 Flow sheet of manufacture of Methanol from Synthesis Gas**

- $H_2$ and CO adjusted to molar ratio of 2.25
- The mixture is compressed to 200 – 350 atms
- Recycle gas (Unreacted feed) is also mixed and sent to the compressor
- Then eventually the mixture is fed to a reactor. Steam is circulated in the heating tubes to maintain a temperature of 300 – 375 $^{o}$C

- After reaction, the exit gases are cooled
- After cooling, phase separation is allowed. In this phase separation operation methanol and other high molecular weight compounds enter the liquid phase and unreacted feed is produced as the gas phase.
- The gas phase stream is purged to remove inert components and most of the gas stream is sent as a recycle to the reactor.
- The liquid stream is further depressurized to about 14 atms to enter a second phase separator that produces fuel gas as the gaseous product and the liquid stream bereft of the fuel gas components is rich of the methanol component.
- The liquid stream then enters a mixer fed with $KMNO_4$ so as to remove traces of impurities such as ketones, aldehydes etc.
- Eventually, the liquid stream enters a distillation column that separates dimethyl ether as a top product.
- The bottom product from the first distillation column enters a fractionator that produces methanol, other high molecular weight alcohols and water as three different products.

## 13.4.4 Technical questions

1. **Why pressure is not reduced for the first phase separator?**

Ans: Methanol is separated out in the liquid stream by just cooling the reactor product stream. Therefore, since the separation is achieved physically, there is no need to reduce the pressure of the stream. Also, if pressure is reduced, then again so much pressure needs to be provided using the compressor.

2. **Why the pressure is reduced to 14 atms for the phase separator?**

Ans: The second phase separator is required to remove dissolved fuel gas components in the liquid stream at higher pressure. If this is not done, then methane will remain in the liquid stream and fractionators will produce methane rich ethers which don’t have value. Fuel gas on the other hand has value or it can be used as a fuel to generate steam in a boiler or furnace.

3. **Why two compressors are used in the process flowsheet but not one?**

Ans: The main compressor is the feed compressor where feed is compressed to 3000 – 5000 psi. The second compressor is for the recycle stream which is brought to the reactor inlet pressure conditions by taking into account the pressure losses in the reactor, cooler and phase separator.

### 4. How multiple products are obtained from a single distillation column?

Ans: This is an important question. Any distillation column consists of liquid reflux stream. A careful simulation of a distillation column using process simulators such as ASPEN or HYSYS or PRO II will give the liquid compositions at each tray. Using this information, one can exploit whether the intermediate liquid stream is having composition of any specific product. In such case, the liquid stream from the column can be taken out (as a pump around stream in the crude distillation column) and the balance could be cooled and sent back to a section above the distillation unit. Alternatively, without pump around also we can operate the column, but the basis of keeping pump around or not is based on the desired liquid reflux flow rates on the particular tray.

### 5. Can heat integration be carried out in the flowsheet?

Ans: Yes, the reactor product is at higher temperature and can be energy integrated with the feed stream after compression. This is also due to the fact that compression usually increases the temperature and feed stream can be subjected to further heating after compression.

### 6. From engineering perspective, what is the most difficult part in the process flow sheet

Ans: The design and operation of the high pressure reactor is the most difficult. To withstand such high pressure, thick walled reactor needs to be designed. Other materials of construction need to be as well looked into for safeguarding the long term shelf life of the reactor.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984

# Lecture 14: Formaldehyde and Chloromethanes

## *14.1 Introduction*

- In this lecture, we present the production technology for formaldehyde and chloromethanes.
- Formaldehyde is produced from methanol
- Chloromethanes are produced from methane by chlorination route.

## *14.2 Formaldehyde production*

### 14.2.1 Reactions

a) Oxidation: $CH_3OH + 0.5\ O_2 \rightarrow HCHO + H_2O$
b) Pyrolysis: $CH_3OH \rightarrow HCHO + H_2$
c) Undesired reaction: $CH_3OH + 1.5\ O_2 \rightarrow 2H_2O + CO_2$

In the above reactions, the first and third are exothermic reactions but the second reaction is endothermic. The reactions are carried out in vapour phase.

Catalyst: Silver or zinc oxide catalysts on wire gauge are used.

Operating temperature and pressure: Near about atmospheric pressure and 500 – 600 $^oC$

### 14.2.2Process Technology ( Figure 14.1 ):

- Air is sent for pre-heating using reactor outlet product and heat integration concept.
- Eventually heated air and methanol are fed to a methanol evaporator unit which enables the evaporation of methanol as well as mixing with air. The reactor inlet temperature is 54 $^oC$.
- The feed ratio is about 30 – 50 % for $CH_3OH$: $O_2$
- After reaction, the product is a vapour mixture with temperature 450 – 900 $^oC$
- After reaction, the product gas is cooled with the heat integration concept and then eventually fed to the absorption tower.
- The absorbent in the absorption tower is water as well as formaldehyde rich water.
- Since formaldehyde rich water is produced in the absorption, a portion of the rich water absorbent solution from the absorber is partially recycled at a specific section of the absorber.
- From the absorber, HCHO + methanol rich water stream is obtained as the bottom product.
- The stream is sent to a light end stripper eventually to remove any light end compounds that got absorbed in the stream. The vapors from the light end unit consisting of light end compounds can be fed at the absorption unit at

specific location that matches with the composition of the vapors in the absorption column.

- Eventually, the light end stripper bottom product is fed to a distillation tower that produces methanol vapour as the top product and the bottom formaldehyde + water product (37 % formaldehyde concentration).

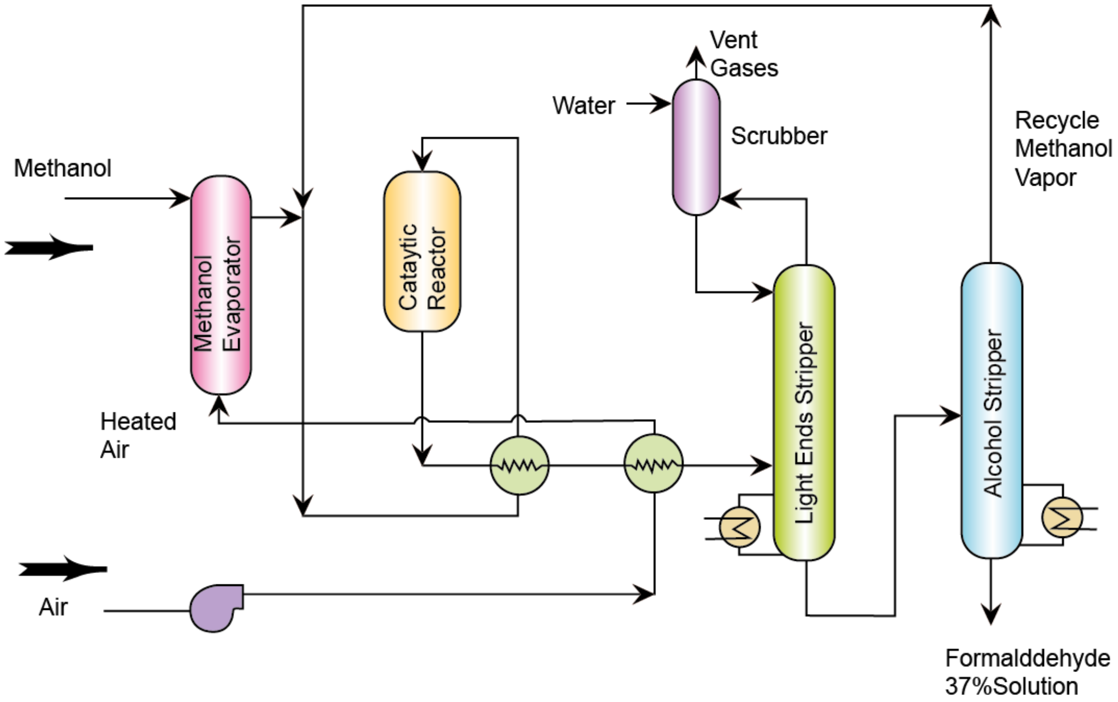


**Figure 14.1 Flow sheet of Formaldehyde production**

## *14.3Technical questions*

1. **Why water + HCHO + methanol stream is sent to a specific section of the absorber but not the top section of the absorber?**

Ans: This is to maximize the removal efficiency of both water and formaldehyde rich solution. If both are sent from the top, then formaldehyde rich solution will be dilute and not effective in extracting more HCHO + methanol from the gas phase stream.

2. **Explain Why light end stripper is used after absorber?**

Ans: Water + HCHO + Formaldehyde solution may absorb other light end compounds which are not desired for absorption. This is due to the basic feature of multicomponent absorption where absorption factors for various absorbing components is not biased sharply and other undesired components also get absorbed. Therefore, the light end stripper would take care of removing these unwanted components by gently heating the same.

3. **Suggest why pure formaldehyde is not produced in the process?**

Ans: Pure formaldehyde is not stable and tends to produce a trimer or polymer. Formaldehyde is stable in only water and therefore, 37% formaldehyde solution with 3 – 15 % methanol (stabilizer) is produced as formalin and sold.

4. **What type of process design is expected for the air preheater?**

Ans: Since we have a problem of vapour and air, we should use extended surface area heat exchanger or finned heat exchanger.

## *14.4Chloromethanes*

Chloromethanes namely methyl chloride ($CH_3Cl$), methylene chloride ($CH_3Cl_2$), Chloroform ($CHCl_3$) and Carbon Tetrachloride ($CCl_4$) are produced by direct chlorination of $Cl_2$ in a gas phase reaction without any catalyst.

### 14.4.1 Reactions

$CH_4 + Cl_2 \rightarrow CH_3Cl + H_2$

$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + H_2$

$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + H_2$

$CHCl_3 + H_2 \rightarrow CCl_4 + H_2$

- The reactions are very exothermic.
- The feed molar ratio affects the product distribution. When $CH_4/Cl_2$ is about 1.8, then more $CH_3Cl$ is produced. On the other hand, when $CH_4$ is chosen as a limiting reactant, more of $CCl_4$ is produced. Therefore, depending upon the product demand, the feed ratio is adjusted.

### 14.4.2Process Technology

- Methane and $Cl_2$ are mixed and sent to a furnace
- The furnace has a jacket or shell and tube system to accommodate feed pre-heating to desired furnace inlet temperature (about 280 – 300 $^{o}$C).
- To control temperature, $N_2$ is used as a diluent at times.
- Depending on the product distribution desired, the $CH_4/Cl_2$ ratio is chosen.
- The product gases enter an integrated heat exchanger that receives separated $CH_4$ (or a mixture of $CH_4 + N_2$) and gets cooled from the furnace exit temperature (about 400 $^{o}$C).
- Eventually, the mixture enters an absorber where water is used as an absorbent and water absorbs the HCl to produce 32 % HCl.
- The trace amounts of HCl in the vapour phase are removed in a neutralizer fed with NaOH

- The gas eventually is compressed and sent to a partial condenser followed with a phase separator. The phase separator produces two streams namely a liquid stream consisting of the chlorides and the unreacted $CH_4/N_2$.
- The gaseous product enters a dryer to remove $H_2O$ from the vapour stream using 98% $H_2SO_4$ as the absorbent for water from the vapour.
- The chloromethanes enter a distillation sequence. The distillation sequence consists of columns that sequentially separate $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$ and $CCl_4$.

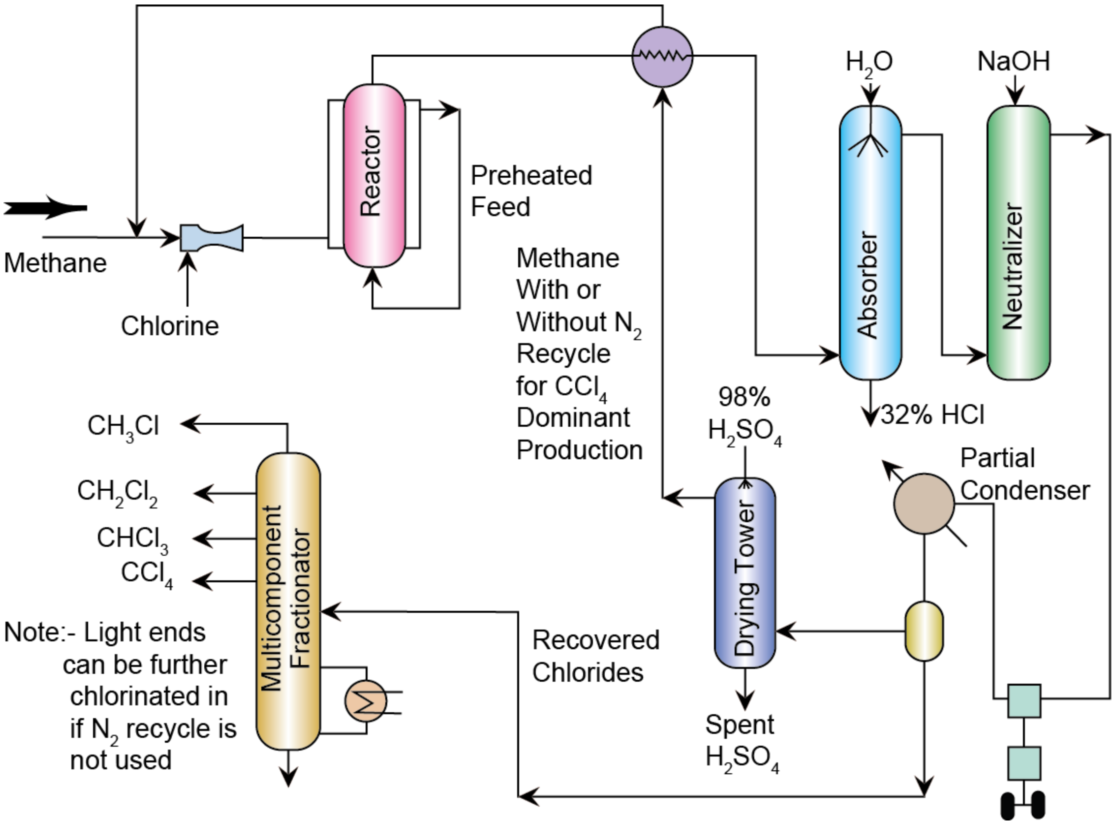


**Figure 14.2 Flowsheet of Chloromethane production**

## 14.4.3Technical questions

1. **Why compressor is used before partial condenser?**

Ans: The compressor increases the pressure of the system which is beneficial to increase the boiling points of the mixtures. Note that the boiling points of chloromethanes are -97.7, -97.6, -63.5 and -22.6 $^{o}$C for $CH_3Cl$, $CH_2Cl_2$, $CHCl_3$ and $CCl_4$ respectively. On the other hand, the boiling point is -161.6 $^{o}$C. For these boiling point mixtures, when the system pressure is increased substantially, the boiling points of the compounds increase and could reach close to those of the cooling water (20 – 30 $^{o}$C). Cooling water is required in the partial condenser and if it is not used, a refrigerant needs to be used which requires an additional refrigeration plant. Therefore, the system pressure is increased.

2. **Why water is removed using the dryer?**

Ans: Water enters the vapour system due in the absorption column where solvent loss to the vapour will be a common feature. Water molecule can react with the highly active intermediate chloromethanes to form oxychlorides, which are highly undesired.

3. **Will there be any difficulty in separation by increasing boiling points of the chloromethanes in the distillation sequences?**

Ans: Definitely yes. This is because the relative volatility of compounds atleast slightly increases with reducing pressure and viceversa. But due to cooling water criteria in the distillation sequences also, there is no other way economical than doing distillation at higher pressure.

4. **Since the boiling point of $CH_3Cl$ and $CH_2Cl_2$ are very close, what do you expect for the production of $CH_3Cl$ from the first column?**

Ans: It is indeed difficult to separate $CH_3Cl$ and $CH_2Cl_2$ and therefore, good number of separation trays be used. Or structured packing be used to reduce the height of the first column.

5. **When the reactions are highly exothermic, why is the feed pre-heated?**

Ans: Irrespective of the reactions being exothermic or endothermic, the reaction rate always increases with temperature for non-equilibrium reactions. Therefore, feed is pre-heated to the desired temperature so as to fastly convert the reactants to products.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984

# Lecture 15: Hydrocarbon Steam Cracking for Petrochemicals

## 15.1 Introduction

In industrial processes, hydrocarbons are contacted with $H_2O$, depending upon the desired effect. When hydrocarbon vapors at very high pressures are contacted with water, water which has a very high latent heat of vaporization quenches the hydrocarbon vapors and transforms into steam. In such an operation, chemical transformations would not be dominant and energy lost from the hydrocarbons would be gained by water to generate steam. The quenching process refers to direct contact heat transfer operations and therefore has maximum energy transfer effeiciency. This is due to the fact that no heat transfer medium is used that would accompany heat losses. The steam cracking of hydrocarbons is an anti-quenching operation, and will involve the participation of water molecule in reactions in addition to teh cracking of the bnydriocarbond on their own. Since steam and the hydrocarbons react in the vapour phase the reaction products can be formed very fast. Therefore cracking of the hydrocarbons on their own as well as by steam in principle is very effective.

When steam cracking is carried out, in addition to the energy supplied by the direct contact of steam with the hydrocarbons, steam also takes part in the reaction to produce wider choices of hydrocarbon distribution along with the generation of $H_2$ and CO.

- Hydrocarbons such as Naphtha and LPG have lighter compounds.
- When they are subjected to steam pyrolysis, then good number of petrochemicals can be produced.
- These include primarily ethyelene and acetylene along with other compounds such as propylene, butadiene, aromatics (benzene, toluene and xylene) and heavy oil residues.
- The reaction is of paramount importance to India as India petrochemical market is dominated by this single process.

## 15.2 Reaction

$C_xH_y + H_2O + O_2 \rightarrow C_2H_4 + C_2H_6 + C_2H_2 + H_2 + CO + CO_2 + CH_4 + C_3H_6 + C_3H_8 + C_4H_{10} + C_4H_8 + C_6H_6 + C +$ Heavy oils

- The reaction is pretty complex as we produce about 10 to 12 compounds in one go
- The flowsheet will be reaction-separation-recycle system only in its topology. But the separation system will be pretty complex.
- Almost all basic principles of separation appears to be accommodated from a preliminary look.
- Important separation tasks: Elimination of CO and $CO_2$, Purification of all products such as ethylene, acetylene etc.

- The process can be easily understood if we follow the basic fundamental principles of process technology
- Typical feed stocks are Naphtha & LPG
- Reaction temperature is about 700 – 800 °C (Vapor phase reaction).

## *15.3 Process technology (Figure 15.1)*

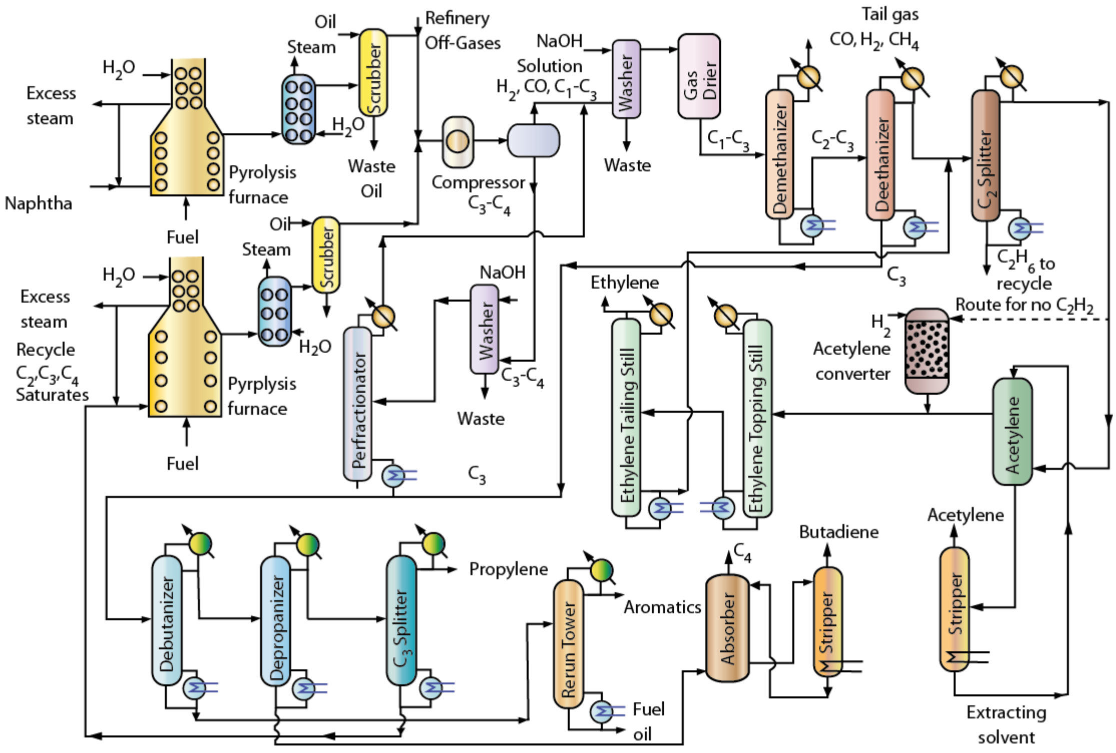


**Figure 15.1 Flow sheet of Hydrocarbon Steam Cracking for Petrochemicals**

- Naphtha/LPG saturates is mixed with superheated steam and fed to a furnace fuel gas + fuel oil as fuels to generate heat. The superheated steam is generated from the furnace itself using heat recovery boiler concept.
- The $C_2$-$C_4$ saturates are fed to a separate furnace fed with fuel gas + fuel oil as fuels to generate heat.
- In the furnace, apart from the steam cracking, steam is also generated. This is by using waste heat recovery concept where the combustion gases in the furnace.
- After pyrolysis reaction, the products from the furnace are sent to another heat recovery steam boiler to cool the product streams (from about 700 – 800 °C) and generate steam from water.
- After this operation, the product vapours enter a scrubber that is fed with gas oil as absorbent. The gas oil removes solids and heavy hydrocarbons.
- Separate set of waste heat recovery boiler and scrubbers are used for the LPG furnace and Naphtha steam cracking furnaces
- After scrubbing, both product gases from the scrubbers are mixed and fed to a compressor. The compressor increases the system pressure to 35 atms.

- The compressed vapour is fed to a phase separation that separates the feed into two stream namely the vapour phase stream and liquid phase stream. The vapour phase stream consists of $H_2$, CO, $CO_2$ $C_1$-$C_3$+ components in excess. The liquid phase stream consists of $C_3$ and $C_4$ compounds in excess.
- Subsequently, the vapour phase and liquid phase streams are subjected to separate processing.

  Gas stream processing:
    - $CO_2$ in the vapour phase stream is removed using NaOH scrubber. Subsequently gas is dried to consist of only $H_2$, CO, $C_1$-$C_3$ components only. This stream is then sent to a demethanizer which separates tail gas ($CO + H_2 + CH_4$) from a mixture of $C_1$-$C_3$ components. The $C_2$-$C_3$+ components enter a dethanizerwhich separates $C_2$ from $C_3$ components.
    - Here $C_2$ components refer to all kinds of $C_2$s namely ethylene, acetylene etc. Similarly, $C_3$ the excess of propylene, and propane.
    - The C2 components then enter a C2 splitter which separates ethane from ethylene and acetylene.
    - The ethylene and acetylene gas mixture is fed to absorption unit which is fed with an extracting solvent (such as N-methylpyrrolidinone) to extract Acetylene from a mixture of acetylene and ethylene.
    - The extractant then goes to a stripper that generates acetylene by stripping. The regenerated solvent is fed back to the absorber.
    - The ethylene stream is fed to a topping and tailing still to obtain high purity ethylene and a mixture of ethylene and acetylene as the top and bottom products. The mixture of ethylene and acetylene is sent back to the C2 splitter unit as its composition matches to that of the C2 splitter feed.
- Liquid stream processing
    - The liqiuid stream consists of C3,C4, aromatics and other heavy oil components is fed to a NaOH scrubber to remove $CO_2$
    - Eventually it is fed to a pre-fractionator. The pre-fractionator separates lighter components from the heavy components. The lighter components are mixed with the vapour phase stream and sent to the NaOH vapour phase scrubber unit.
    - The pre-fractionator bottom product is mixed with the deethanizer bottom product.
    - Eventually the liquid mixture enters a debutanizer that separates C3, C4 components from aromatics and fuel oil mixture. The bottom product eventually enters a distillation tower that separates aromatics and fuel oil as top and bottom products respectively.
    - The top product then enters a depropanizer that separates C3s from C4 components.
    - The C4 components then enter an extractive distillation unit that separates butane + butylenes from butadiene. The extractive

distillation unit consists of a distillation column coupled to a solvent stripper. The solvent stripper produces butadiene and pure solvent which is sent to the distillation column.

- The C3 components enter a C3 splitter that separates propylene from propane + butane mixture. Thesaturates mixture is recycled to the saturates cracking furnace as a feed stream.

## 15.4 Technical questions

1. **Why two separate furnaces are used for C2-C4 saturates and Naphtha feed stocks?**

Ans: The purpose of steam cracking is to maximize ethylene and acetylene production. For this purpose if we mix C2-C4 saturates and naphtha and feed them to the same furnace, then we cannot maximize ethylene and acetylene production. The napntha steam cracker has its own operating conditions for maximizing ethylene and acetylene and so is the case for C2-C4 saturates.

2. **Why the product gases from naphtha and C2-C4 saturates steam cracker processed separately before mixing them and sending them to the compressor?**

Ans: Both crackers produce products with diverse compositions. Both cannot be fed to a single scrubber and remove the heavy hydrocarbons and oil components. While the scrubber associated to naphtha steam cracking needs to be remove significantly the oil and heavy hydrocarbons, this is not the case for steam cracker product vapour processing.

An alternate way of designing a single scrubber is to design a complex scrubber that has multiple feed entry points correspond to both product gases entering from various units. This refers to process intensification and would be encouraging.

3. **Why specifically the gases are compressed to 35 atm?**

Ans: The distribution of light and heavy components in vapour and liquid streams is critically dependent on the pressure. Therefore, the pressure of the system plays a critical role in the distribution of these key components.

4. **Why is it not possible to sharply split C3 components in the phase separator?**

Ans: This is the basic problem of the phase equilibrium factors associated to the intermediate components. Usually, phase equilibrium factors are highest for lighter components and lowest for the heavier components. But intermediate components such as C3s have phase equilibrium factors in between. Therefore, C3s get distributed between both vapour and liquid equally. This will be the case even with higher pressure and going for higher pressure is not economical as the pressurizing costs will be significantly.

5. **Why a tailing and topping still is required for ethylene production?**

Ans: The distillation column for separating ethylene from ethylene from C2 components needs to carry out a difficult separation. This is also due to the fact that the boiling points of C2 components is very close. Therefore, there needs to be two columns (indicating good number of trays).

6. **Explain how extractive distillation enables the separation of butadiene?**

Ans: Dimethyl formamide (solvent) is fed to the distillation column fed with butadiene, butane and butylenes. The solvent interacts differently with the components and therefore adjusts the relative volatility of the mixture which was close to 1 previously. Thereby, the solvent forms a high boiling mixture at the bottom with butadiene and thereby enables the difficult separation of butadiene from the C4 compounds. Thereby, the solvent + butadiene is fed to a stripper which removes butadiene from the DMF. One important issue here is that the solvent does not form an azeotrope with the butadiene and is therefore, easy to separate.

7. **When acetylene is not required, what process modifications will exist to the technology?**

Ans: When acetylene is not required, then the top product from C2 splitter (which is a mixture of acetylene and ethylene) is fed to a packed bed column and $H_2$ to convert the acetylene to ethylene. Eventually, one does not require the absorber-stripper technology for acetylene purification.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Shreve R. N., Austin G. T., Shreve's Chemical process industries, McGraw – Hill, 1984

# Lecture 16: Vinyl Chloride from Ethylene

## Introduction

- In this lecture we study the process technology involved in the production of Vinyl Chloride from Ethylene
- Vinyl chloride is produced in a two step process from ethylene
    - Ethylene first reacts with Chlorine to produce Ethylene dichloride
    - The purified Ethylene dichloride undergoes selective cracking to form vinyl chloride
- We first present the process technology associated to Ethylene Chloride

## *16.1 Ethylene dichloride*

### 16.1.1 Reactions

- $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$
- Undesired products: Propylene dichloride and Polychloroethanes
- Reaction occurs in a  liquid phase reactor with ethylene dichloride serving as the liquid medium and reactants reacting the liquid phase
- Catalyst is $FeCl_3$ or Ethylene dibromide

### 16.1.2 Process Technology (Figure 16.1)

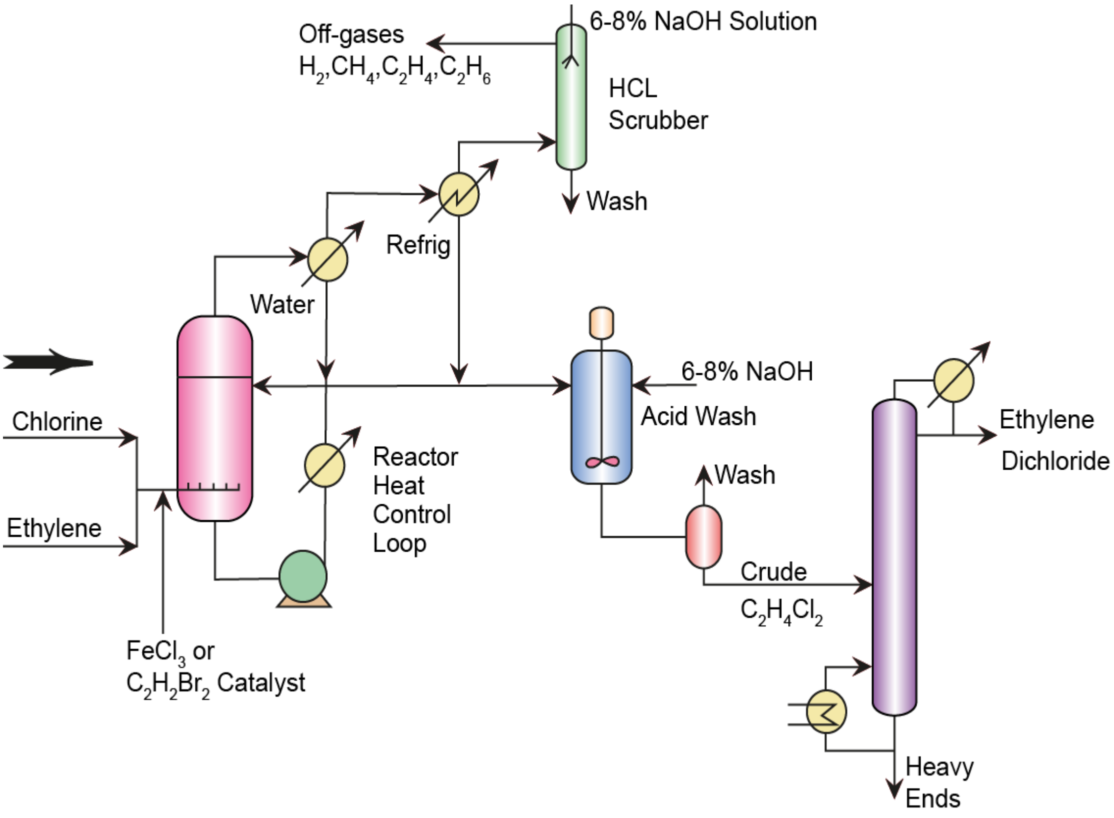


**Figure 16.1 Flow sheet of production of ethylene dichloride**

- $C_2H_4$ and $Cl_2$ are mixed and sent to the liquid phase reactor.
- Here, the feed mixture bubbles through the ethylene dichloride product medium
- Reactor operating conditions are 50 °C and 1.5 – 2 atms.
- The reaction is exothermic. Therefore, energy is removed using either cooling jacket or external heat exchanger
- To facilitate better conversion, circulating reactor designs are used.
- $FeCl_3$ traces are also added to serve as catalyst
- The vapour products are cooled to produce two products namely a vapour product and a liquid product. The liquid product is partially recycled back to the reactor to maintain the liquid medium concentration.
- The vapour product is sent to a refrigeration unit for further cooling which will further extract ethylene dichloride to liquid phase and makes the vapour phase bereft of the product.
- The liquid product is crude ethylene dichloride with traces of HCl. Therefore, acid wash is carried out first with dilute NaOH to obtain crude ethylene dichloride. A settling tank is allowed to separate the spent NaOH solution and crude $C_2H_4Cl_2$ (as well liquid).
- The crude ethylene dichloride eventually enters a distillation column that separates the ethylene dichloride from the other heavy end products.
- The vapour phase stream is sent to a dilute NaOH solution to remove HCl and produce the spent NaOH solution. The off gases consist of $H_2$, $CH_4$, $C_2H_4$ and $C_2H_6$.

## 16.1.3Technical questions

1. **Provide an insight into the liquid phase guided gas phase reaction?**

Ans: The liquid phase acts as a resistance phase for the movement of various gases. The recirculator enables greater turbulence of the liquid phase stream. Thereby, using these mechanisms, the gases are allowed to react with one another and produce ethylene dichloride which gets dissolved in the liquid.

2. **Why a water condenser followed by refrigeration is used when the single refrigeration can serve the purpose of cooling?**

Ans: This is an important question. Allowing only refrigeration enhances process costs drastically. Therefore, water is used to carry out partial condensation and then refrigeration, even though in principle, water condensation can be bypassed and reactor operation and stream contacting can be further optimized.

3. **Why do we need a settling tank after the acid wash unit associated to the crude ethylene dichloride?**

Ans: Typically, we observe HCL removal from vapour streams. In such case, the unit used is a scrubber or absorber. The gas/vapour is fed to the absorption column and is obtained as a gas. When a liquid is allowed for scrubbing, it is possible to obtain emulsions of the organic phase in the aqueous phase. Therefore, provide gravity settling mechanism should exist so as to separate the crude ethylene dichloride from the mixture emanating from the acid wash tank.

## *16.2 Vinyl chloride production*

### 16.2.1 Reaction

- $C_2H_4Cl_2 \rightarrow CH_2CHCl + HCl$
- Charcoal is used as the catalyst
- The reaction is a reversible gas phase reaction

### 16.2.2Process Technology (Figure 16.2)

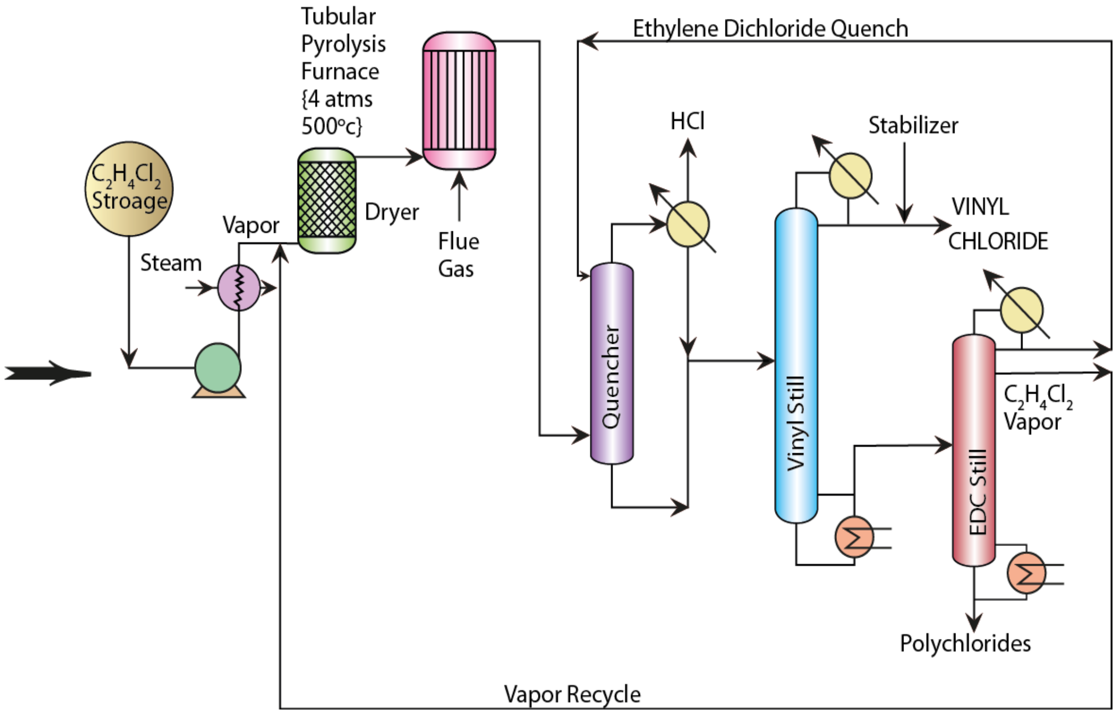


**Figure 16.2 Flow sheet of production of vinyl chloride**

- Ethylene dichloride is initially vaporized using a heat exchanger fed with process steam
- Ethylene vapors then enter a dryer that removes traces of water molecules
- After drying, the vapors enter a pyrolysis furnace operated at 4 atm and 500 $^oC$. The furnace is similar to a shell and tube arrangement with the gases entering the tube side and hot flue gas goes past the tubes in the shell side.
- The product vapors eventually enter a quenching tower in which cold ethylene dichloride is used to quench the product gases and cool them.

- The gases from the quench tower then enter a partial condenser which produces HCl as a gas and the liquid stream consisting of vinyl chloride, unreacted ethylene dichloride and polychlorides.
- The liquid stream from the quench tower as well as the condenser is fed to the vinyl still which produces the vinyl chloride product. The product is stabilized using a stabilizer as vinyl chloride is highly reactive without stabilizer.
- The bottom product from the vinyl still is fed to a distillation column which separates the ethylene dichloride from the polychlorides. The ethylene dichloride vapors are recycled back to the cracking furnace and the ethylene dichloride liquid is sent to the quenching tower to serve as the quenching liquid.

## 16.2.3 Technical questions

1. **Why ethylene dichloride is dried before entering the cracking furnace?**

Ans: To avoid the formation of other compounds during cracking. Vinyl chloride cracking is a very selective cracking that we wish to happen. The selective cracking needs very clean feed stock.

2. **Why quenching is carried out?**

Ans: The selective cracking reaction is a reversible reaction. Therefore, by doing cold ethylene dichloride quenching, we are suppressing the backward reaction and ensuring that only vinyl chloride gets formed in good quantities.

3. **Can heat integration be carried out in the process?**

Ans: IN principle it can be done but in reality no. The reason is that if quenching is not done immediately, then vinyl chloride can get converted back to the ethylene dichloride. Therefore, though there is a hot stream available, heat integration cannot be done due to prevalent process conditions.

4. **Can a partial condenser be used in the last distillation column to serve for both quenching, distillation reflux and produce vapour for the ethylene dichloride?**

Ans: Yes, this arrangement will be excellent as all requirements in the process will be met by going for a partial condenser. But it all depends on the quenching tower requirements and hence if ethylene dichloride needs to be cooled more than its boiling point, then partial condenser will not serve the purpose.

5. **What is the effect of pressure on quenching. This question is interesting as the reaction occurs at 4 atm and quenching occurs at higher pressure?**

Ans: Quenching is an operation used for minimizing temperature. As such its not absorption where pressure plays an important role. As such, the effect of pressure will not be significant in the quenching operation.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 17: Ethylene oxide and Ethanolamines

## *17.1 Introduction*

- In this lecture, we discuss upon the process technology for ethylene oxide and ethanolamines.
- Ethylene oxide is produced by the oxidation of ethylene using air
- Ethanolamines are produced using the series reaction scheme of ethylene oxide with ammonia.
- Ethanolamines are significantly used as absorbents to remove $CO_2$ and $H_2S$ from process gas streams.

## *17.2 Ethylene Oxide*

### 17.2.1 Reactions

- $C_2H_4 + 0.5\ O_2 \rightarrow CH_2O.CH_2O$
- Ethylene to air ratio: 3 – 10 %
- Side reaction products: $CO_2$, $H_2O$
- Catalyst: Silver oxide on alumina
- Operating temperature and pressure: 250 – 300 $^{o}$C and 120 – 300 psi
- Supressing agent for side reactions: Ethylene dichloride
- Reaction is exothermic

### 17.2.2 Process technology (Figure 17.1)

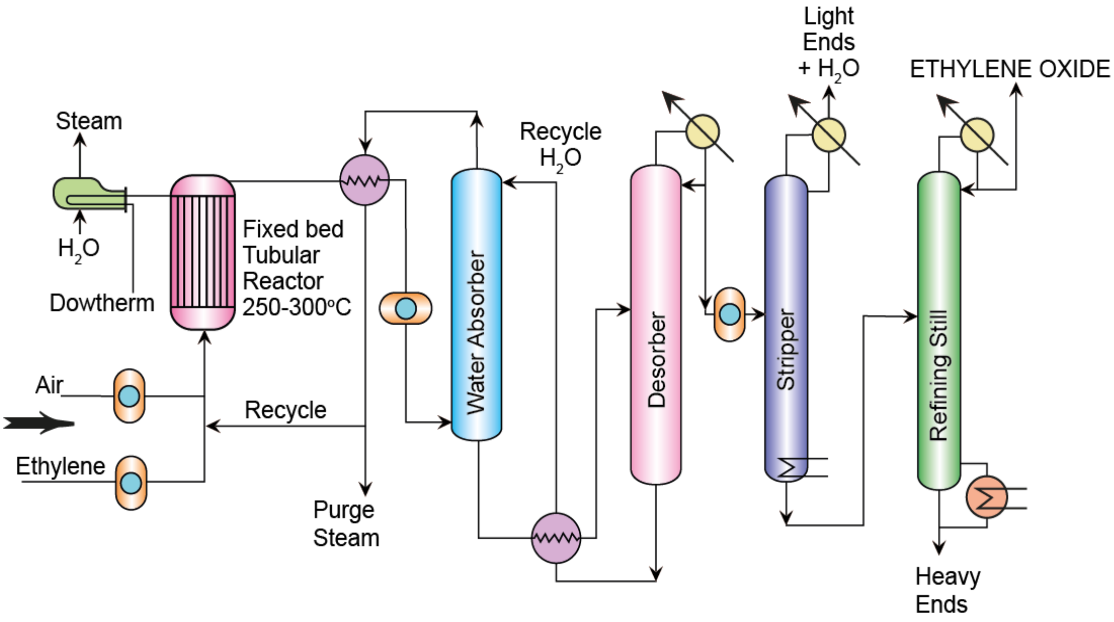


**Figure 17.1 Flow sheet of production of ethylene oxide**

- Air and ethylene are separate compressed and along with recycle stream are sent to the shell and tube reactor

- The reactor is fed on the shell side with Dowtherm fluid that serves to maintain the reaction temperature. A dowtherm fluid is a heat transfer fluid , which is a mixture of two very stable compounds, biphenyl and diphenyl oxide. The fluid is dyed clear to light yellow to aid in leak detection.
- The hot dowtherm fluid from the reactor is sent to a waste heat recovery boiler to generate steam
- The vapour stream is cooled using a integrated heat exchanger using the unreacted vapour stream generated from an absorber.
- The vapour stream is then sent to the heat integrated exchanger and is then sent back to the reactor and a fraction of that is purged to eliminate the accumulation of inerts such as Nitrogen and Argon.
- The product vapors are compressed and sent to a water absorber which absorbs ethylene oxide from the feed vapors. Eventually, the ethylene oxide rich water stream is sent to a stripper which desorbs the ethylene oxide + water as vapour and generates the regenerated water as bottom product. The regenerated water reaches the absorber through a heat integrated exchanger.
- The ethylene oxide + water vapour mixture is compressed (to about 4 - 5 atms) and then sent to a stripper to generate light ends + $H_2O$ as a top product and the bottom product is then sent to another fractionators to produce ethylene oxide as top product. The heavy ends are obtained as bottom product.

## 17.2.3 Technical questions

1. **What is Dowtherm?**

Ans: Dowtherm is an organic liquid that can attain to temperatures upto 300 $^oC$. These are special fluids used instead of steam/water. In this example, the operating temperature is about 250 - 300 $^oC$ and therefore usage of Dowtherm fluid is perfect.

2. **In what way compression is beneficial to the absorption?**

Ans: It is a known fact that absorption is most favoured at low temperature and high pressure. Therefore, compression of the cooled product gases will be very beneficial to maximize the dissolution of ethylene oxide in the water. Of course, along with ethylene oxide other light ends and heavy ends also dissolve in water and we have no control over that.

3. **Why again another compressor is used before the stripper?**

Ans: The second compressor aids to enhance the boiling points of the mixtures. Thereby, water can be used as a cooling fluid in the distillation columns, as the boiling point of the products is enhanced by compression. In this regard, it should be noted that ethylene oxide has a boiling point of 10.7 $^oC$ which can be drastically enhanced by compression to 4 – 5 atms.

4. **Why ethylene and air are separately compressed?**

Ans: This is due to the danger of generating an explosive mixture during compression step of the mixture.

5. **What process modifications are possible for the flowsheet?**

- Using a fluidized bed instead of packed bed reactor
- Using oxygen instead of air

6. **Discuss the energy integration capacity of the process?**

Ans: In this process, the heat integration drastically reduced process steam requirements. Steam is only required in the strippers and fractionators. This steam can be generated using waste heat recovery units using dowtherm fluid as the hot fluid to generate the steam. Thus in this process, it is observed that for 1 ton of ethylene oxide produced, only 0.1 ton of steam is required. This is all possible due to significant heat integration in the process.

## *17.3 Ethanolamines*

### 17.3.1 Reactions

- Ethylene Oxide + Ammonia → Monoethanolamine
- Monoethanolamine + Ammonia → Diethanolamine
- DIethanolamine + Ammonia → Triethanolamine
- The above reactions are series reaction scheme
- Reaction is exothermic
- Ammonia is in aqueous phase and ethylene oxide is in vapour state. Therefore, the reaction will be gas-liquid reaction
- Ethylene oxide is the limiting reactant

### 17.3.2 Process technology (Figure 17.2)

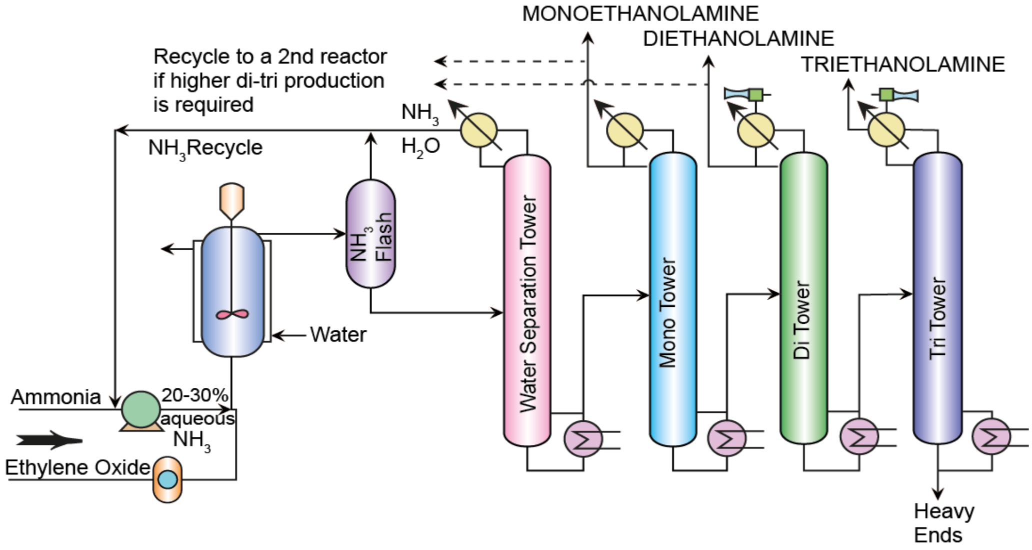


**Figure 17.2 Flow sheet of production of ethanolamines**

- Ammonia is mixed with ammonia recycle stream from the process and pumped to the CSTR where liquid phase ammonolysis takes place.
- Ethylene oxide is compressed and fed to the CSTR.
- The CSTR operating pressure will be such that the feed (and product) mixtures do not vaporize and good liquid phase reaction can occur.
- The reactor is cooled using water in the cooling jacket as the reactions are mildly exothermic
- The product stream is then sent to a flash unit that separates $NH_3$ + $H_2O$ as a vapour stream and water + ethanolamines as a liquid stream.
- The ammonia + water stream is recycled to mix with the fresh ammonia and enter the reactor.
- The bottom product from ammonia flash unit is sent to a water separation tower that again removes dissolved ammonia in the ethanolamine rich solution. Once again ammonia + water are generated and this stream is also recycled to mix with fresh ammonia feed.
- The bottom product consisting of crude mixture of ethanolamines and heavy ends.
- This mixture is fed to a monoethanolamine tower first to separate the monoethanol amine from the other two and heavy ends
- The bottom product from the first distillation tower then enters the second and third distillation towers which are operated under vacuum to produce diethanolamine and triethanolamine as top products. The bottom product from the last distillation tower is the heavy ends product.

## 17.3.3 Technical questions

1. **In what way operating the CSTR In liquid phase is beneficial?**

Ans: Liquids have higher mass transfer coefficients than solids. Therefore, if the reaction needs be facilitated with two components, if they are in liquid phases, then reactions could be faster. Therefore, pressure can play an important role in both altering the selectivity as well as conversion of the series reactions scheme.

2. **Why ammonia + water needs to be separated from the second tower i.e., water separation tower?**

Ans: Ammonia dissolves instantaneously in water to form ammonia solution. This chemical affinity of ammonia is very difficult to get it through. On the other hand, despite using flash unit, some ammonia will remain the water consisting of ethanolamines and heavy ends. Therefore, the second water separation tower is required to remove once again ammonia + water from the solution.

3. **Why vacuum is used in the second and third distillation towers?**

Ans: The diethanol and triethanolamines dissociate at high operating temperatures. Therefore, vacuum is used to reduce the operating temperature of the distillation columns (second and third).

4. **What process modifications you can suggest for better operation?**

Ans: When higher quantitites of di or triethanolamine is desired, then the monoethanolamine can be sent to another reactor in which ethylene oxide is added. It's not advisable to recycle it the CSTR shown in the process flow sheet as it can form amino-ethers but not diethanolamine.

5. **Can solvents (extraction) be used instead of vacuum distillation for the separation of di and triethanolamines?**

Ans: No, this is due to the reason that solvents tend to have similar solubility factors for both di and triethanolamines.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 18: Isopropanol and Acetone from Propylene

## *18.1 Introduction*

- In this lecture we study the process technology associated to the manufacture of isopropanol and acetone.
- Isoprpanol is manufactured from hydration of propylene
- Acetone is produced using the dehydrogenation route of isopropanol
- We first present the isopropanol process technology

## *18.2 Isopropanol manufacture*

### 18.2.1 Reaction

- Sulfation: $CH_3CHCH_2 + H_2SO_4 \rightarrow (CH_3)_2CH(OSO_3H)$ (Isopropyl acid sulphate)
- Hydrolysis: Isopropyl sulphate + $H_2O \rightarrow$ Isopropanol + Sulfuric acid
- Thus sulphuric acid is regenerated in the process
- Side reaction: Disiopropyl sulphate + $H_2O \rightarrow$ Diisopropyl ether + Sulfuric acid
- Therefore, the primary reaction is a gas liquid reaction in which propylene is absorbed into a tray tower fed with sulphuric acid.
- Operating conditions: Room temperature but 20 – 25 atms pressure
- Reaction is highly exothermic

### 18.2.2 Process technology (Figure 18.1)

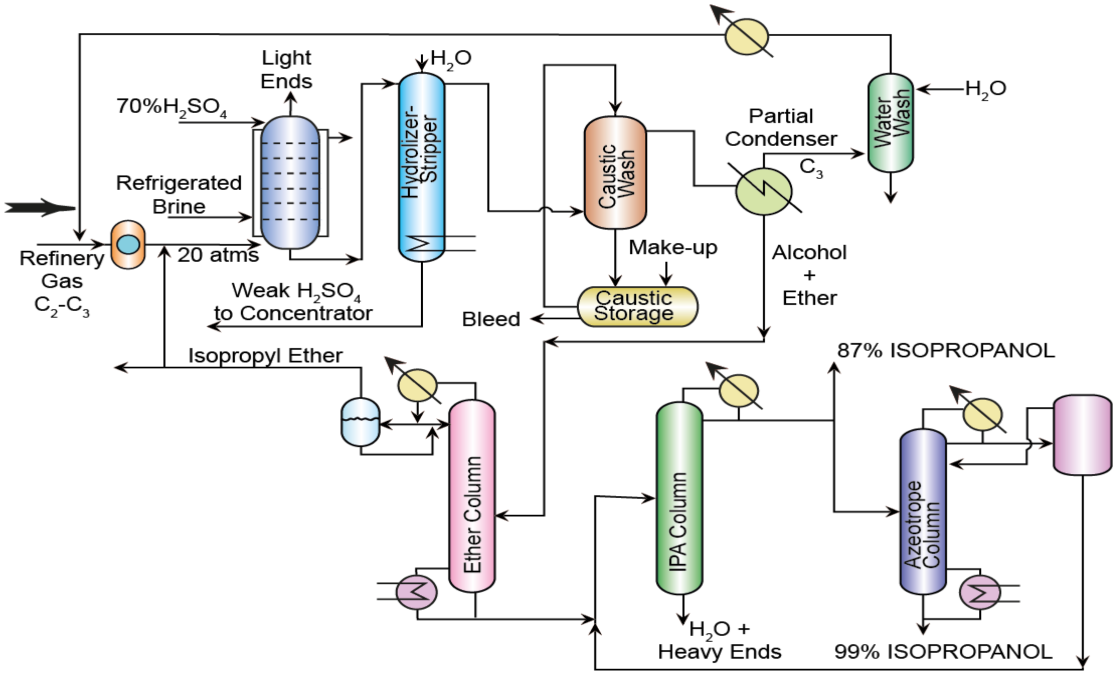


**Figure 18.1 Flow sheet of Isopropanol manufacture**

- Either pure propylene or a mixture of Propylene and other $C_2$, $C_3$ components can be fed to a reactor.
- The hydrocarbon feed is compressed and fed to the reactor at about 20 – 25 atms pressure.
- Sulphuric acid of about 70% acid strength is fed in a countercurrent mode to the tray column where reactive absorption takes place. Here, sulfonation reaction takes place.
- The reaction is highly exothermic and therefore, refrigerated brine is used to control the temperature in the absorber. Jacketed arrangement will be preferred for the tray absorption column to circulate the refrigerated brine in the cooling jacket.
- After reaction, the unreacted light ends such as saturated components will leave the unit as the gas stream.
- The sulfonated product rich stream is then sent to a hydrolyzer cum stripper where isopropanol is produced and is vaporized due to existing stripper temperatures.
- The hydrolyzer is fed with water to facilitate the conversion of the sulfonate product.
- The isopropanol rich vapors then enter a caustic wash unit to remove the acidic impurities.
- The isopropanol rich vapors then enter a partial condenser which separates the unreacted propylene from the alcohol + ether mixture. Here, propylene is separated as the vapour and alcohol + ether is separated as the liquid stream.
- The separated propylene gas is once again subjected to water wash to remove soluble impurities (such as ethers and alcohols). Subsequently, pure propylene is sent to mix with the fresh feed stream. Before sending to the unit, the propylene is cooled to room temperature so as to have identification conditions as the fresh feed stock.
- The alcohol and ether enter a ether column that separates isopropyl ether which is returned to the reactor.
- The bottom product consisting of isopropyl alcohol and water is sent to a isopropyl alcohol column that produces water + heavy ends as the bottom product and 87 % isoprpanol-water azeotrope mixture as the top product.
- The azeotrope is sent to an azeotropic distillation column that uses isopropyl ether as a azeotropic agent to obtain 99 % isopropanol as the bottom product. The top product is a mixture of isopropyl ether and water. The top product is a low boiling azeotrope. This stream upon gravity settling will produce the isopropyl ether as the top product which is sent as a reflux stream to the azeotropic column. The bottom product is a mixture of isopropanol and water is recycled back to the isopropyl alcohol column along with the bottom product generated from the ether separating column.

## 18.2.3 Uses of Isopropanol :

There may be many uses of iso-propanol, industrial as well as common uses. It finds use in pharmaceutical applications because of the low toxicity of any residues. Isopropanol is also used as a chemical intermediate in some industrial processes. It is also used as a gasoline additive.

## 18.2.4 Technical questions

1. **Why refrigerated brine is used in the sulfonation reactor?**

Ans: The reaction temperature is room temperature (25 – 30 $^{o}$C). Therefore, refrigerated fluid is used. Brine is used here, as refrigerated is antifreeze and can allow solution to reach lower temperatures without freezing problem.

2. **Why a partial condenser but not total condenser is used to separate $C_3$ from alcohol + ether?**

Ans: Apart from costs, the total condenser produces a single stream and this is of no use as propylene must be separated and sent as a gas back to the sulfonation reactor. All this is achieved in a single process unit by using partial condensation principle.

3. **Why is isopropyl ether circulated back to the sulfonation reactor?**

Ans: To suppress the side reaction and hence decomposition of sulfonation to less valued product.

4. **Present the working principle of an azeotropic distillation column?**

Ans: The azeotropic distillation column is fed with the azeotrope mixture and another component which forms a low boiling heterogenous azeotrope with the feed (azetropic mixture) components as one of the products and a purer compound as the other product. The low boiling azeotrope is then sent to a gravity settler that separates the heterogeneous phases into two products namely the azeotropic agent and an impure mixture of the original components. The impure mixture is actually fed to one of the distillation columns in the process flow sheet at a location that matches with the purity of the stream.

5. **What happens to the water in which acid gets dissolved in the hydrolyzer cum stripper column?**

Ans: Here, the stream is a weak acid stream that is fed to a multiple effect evaporator to concentrate the weak acid solution to a strong acid solution. The strong acid solution then can be used as one of the raw materials in the process.

6. **Can you do heat integration for the partial condenser with the sulfonation reactor?**

Ans: No, the reason is that sulfonation reaction is highly exotermic and heat needs to be quickly removed. This is not possible when vapors are used as the cooling stream as gas phase heat transfer coefficients are significantly lower than the liquid phase heat transfer coefficients.

7. **Can a partial condenser be used for the ether column?**

Ans: Yes, the reason is that there is no hard and fast rule that isopropyl ether be added in the liquid phase to the sulfonation reactor. In fact, it should be added as a vapour phase only and therefore, partial condenser should be used in place of total condenser to save costs as well as meet the process specifications.

## *18.3 Acetone manufacture from isopropanol*

### 18.3.1 Reactions

- Dehydrogenation of Isopropanol
- Isopropanol → Acetone + $H_2$
- Reaction pressure: 3 – 4 atms
- Reaction temperature: 400 – 500 $^{o}$C
- Copper catalyst on porous carrier is used
- Vapor phase reaction

### 18.3.2 Process Technology (Figure 18.2)

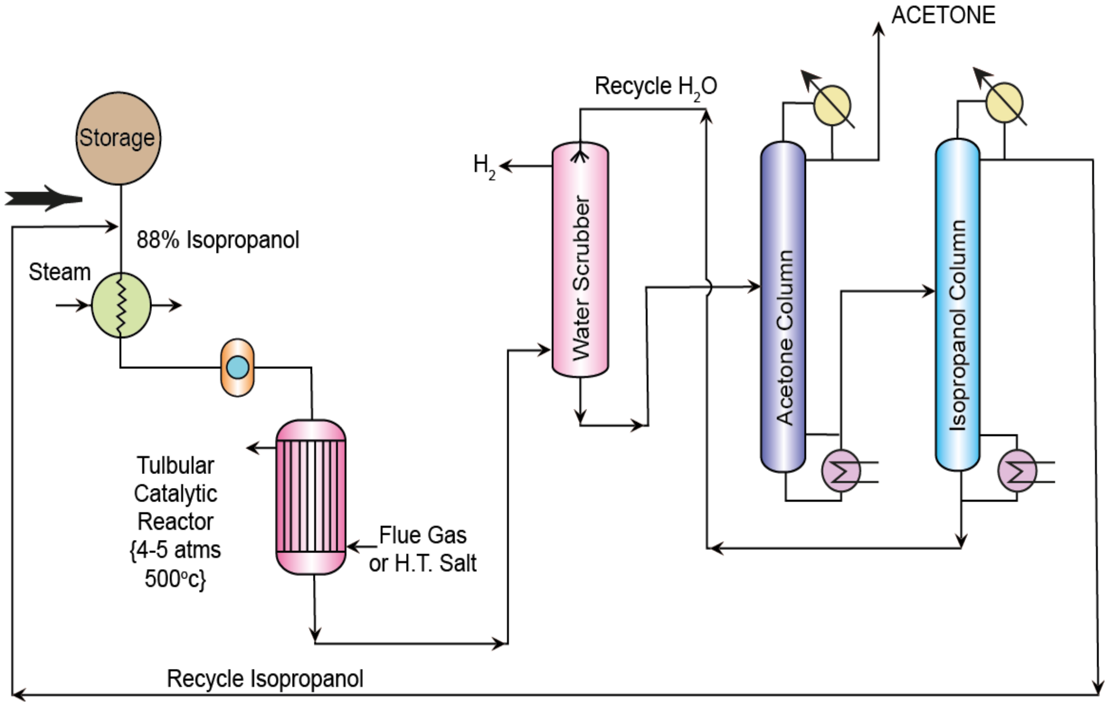


**Figure 18.2 Flow sheet of acetone manufacture from isopropanol**

- First, Isopropanol is heated using steam to vaporize the same
- Then, Isopropanol is compressed to desired reactor pressure i.e., 4 – 5 atms
- The compressed Isopropanol then enters a catalytic shell and tube reactor in the tube side. The tube is packed with the porous copper catalyst
- The reactor is operated at 400 – 500 $^oC$ using flue gas for heating. The flue gas is passed in the shell side of the shell and tube reactor.
- After reaction, the gases are condensed using cooling water condenser. The condensed isopropanol and acetone are sent for fractionation.
- The gases consisting of the remaining quantities of isopropanol and acetone are absorbed into water using a water scrubber.
- The acetone + isopropanol obtained from the condenser and water + isopropanol +acetone are sent to an acetone fractionator that separates acetone as the top product and isopropanol + water as bottom product.
- The bottom product isopropanol + water from the acetone fractionators is sent to a isoprpopanol column.
- This column produces water as the bottom product and isopropanol as the top product.
- The water is cooled using a water condenser and sent to the water scrubber as fresh water solvent.

## 18.3.3 Uses of Acetone :

Aceone is used as a polar, aprotic solvent in a variety of organic reactions. One important property for which it is used as laboratory solvent is because does not form an azeotrope with water.

Acetone is also used in various medical and cosmetic applications. It also forms an important component in food additives and food packaging.

## 18.3.4 Technical questions

1. **Is pure isopropanol required as feedstock in the reactor?**

Ans: This question is asked due to the fact that isopropanol production process involves the formation of an azeotrope with 87 % Isopropanol and 13 % water. Therefore, if the azeotrope itself can be used as feedstock, then one can save azeotropic column costs if an acetone plant is constructed next to the isopropanol.

Yes, isopropanol azeotrope can be used as a feed stock. In this case, the water will not react and will condense in the condenser after the reactor.

2. **Can't we feed the product gases directly to the water absorber eliminating the condenser?**

Ans: The condenser removes the condensable components from the product vapors. If condenser is not used, then the hot vapors move to the absorber and absorber load and degree of separation should be pretty high and hence higher cost. Therefore, it's better to use the water cooling condenser.

3. **Apply lechartlier principle and suggest what pressures be operated in the reactor. Eventually comment on the existing pressures?**

Ans: If we apply Lechartlier principle, dehydrogenation reaction is favoured by lower pressures. However, higher pressures are used in this case. If the pressure of the system does not play a critical role in the conversion, then higher pressures are favoured as they reduce the size of the reactor significantly for the throughput available. Also, higher pressures are favourable for absorption and reduce the water load in the absorption column.

4. **Why is water from the isopropanol fractionators cooled and sent to the water absorber unit?**

Ans: This is due to the fact that absorption is favoured at lower temperature and higher pressure.

5. **Why is isopropanol again sent to the compressor along with the feed?**

Ans: The operating pressures of the absorber, acetone fractionator and isopropanol fractionators reduce sequentially as the stream progresses to the right side. Therefore, the last column produces the product with about atmospheric pressure only. Therefore, to bring it back to 5 atm as in the reactor conditions, the stream has to be compressed along with the feed stream.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 19: Cumene and Acrylonitrile from Propylene

## 19.1 Introduction

- In this lecture, we study the process technology associated to the production of cumene and acrylonitrile from propylene
- Both Cumene and Acrylonitrile are very important compounds that are required for the manufacture of other downstream petrochemicals
- We first present the process technology associated to the Cumene

## 19.2 Cumene

### 19.2.1Reactions

- C6H6+
- The reaction is exothermic
- Side reaction:
- $C_6H_6 + C_3H_6 \longrightarrow nC_9H_{12}$
- Catalyst: $H_3PO_4$ impregnated catalyst on porous carrier
- Operating conditions: 25 atms pressure and 250 $^oC$ temperature.

### 19.2.2Process technology (Figure 19.1)

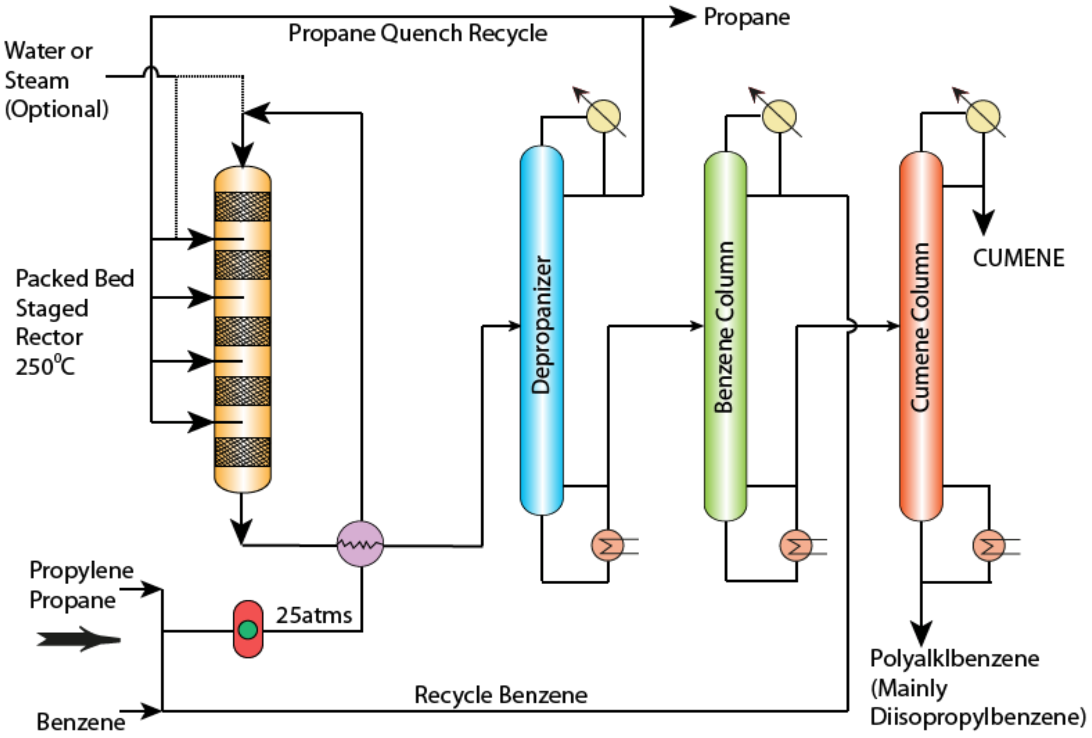


Figure 19.1 Flow sheet of Cumene production

- Propylene obtained from refinery processes as a mixture of propylene and propane
- The mixture along with benzene is compressed to 25 atms
- Eventually the mixture enters a heat integrated exchanger to heat the pre-heat the feed mixture.
- The feed mixture enters a packed bed reactor.
- The stream distribution in the packed bed reactor corresponds to cold shot arrangement i.e., cold propane from the distillation column in the process is added after every reactor with the product stream so that the temperature of the stream is controlled.
- Here, propylene is the limiting reactant and therefore, presumably all propylene undergoes conversion.
- Here, propane does not react but is a diluents or inert in the system. In that way it controls the reaction temperature.
- The reactor units are maintained at about 250$^{o}$C
- The product vapors are cooled using the heat integrated exchanger
- The vapors then pass to a depropanizer which separates propane from the product mixture.
- The bottom product consisting of benzene, cumene and polyalkyl benzenes enters another distillation column which separates benzene from the mixture of cumene and polyalkyl benzene. The benzene stream is recycled to enter the compressor.
- The bottom product from the benzene column is sent to a cumene column which produces cumene as top product and poly alkyl benzene as bottom product.
- Therefore, the entire process technology is nothing but a simple reactor separator recycle arrangement.

### 19.2.3Technical questions

1. **What alternative reactor arrangement is possible if pure propylene feed is used?**

Ans: When pure propylene is used, then there is no propane for quenching. Therefore, the packed bed reactor shall be provided a cooling jacket which can control the temperature of the reactor.

2. **Comment on the sequence of distillation columns separating propane, benzene and cumene in series?**

Ans: The distillation columns are so arranged so that lighter components are separated first followed by heavier components. Since no component is present which will decompose on long time heating, this arrangement is followed. If not, the component which can decompose upon long time heating will be separated first following by the lighter to heavier component sequence in the remaining components.

3. **In what way propane quenching plays a role in the reactions?**

Ans: Propane quenching reduces polymerization of cumene and formation of polyalkyl benzenes.

4. **How can one suppress polyalkylbenzene formation?**

Ans: By using high feed ratio of benzene to propylene and using propane as a diluent

5. **Is further heat integration not possible?**

Ans: A further heat integration can be carried out using hot vapors in the distillation column to be as hot streams in the reboilers of various distillation columns.

6. **In what way higher pressure in the product vapors from the reactor are beneficial for the deprpopanizer unit?**

Ans: The depropanizer unit requires condensation of propane vapors in the condenser. Propane's boiling point is less than 0°C at 1 atm pressure. Therefore, higher pressures to the extent of 25 atms will enhance propane boiling point to about 25 – 30°C for which cooling water can be used as the cooling media in the condenser. If not, refrigerant needs to be used and the refrigerant will require a refrigerating unit along with the process. This is much much expensive than using cooling water as the cooling media.

## *19.3 Acrylonitrile*

### 19.3.1Reactions

- $C_3H_6 + NH_3 + O_2 \longrightarrow C_3H_3N + H_2O$
- 
- The reaction is exothermic
- Stoichiometric ratio: $C_3H_6 : NH_3 : O_2 = 1:1:1.5$
- Operating conditions: 1.5 – 3 atms pressure and 400 – 500°C
- By products: Acetonitrile and Hydrogen cyanide from side reactions
- Catalyst: Mo-Bi catalyst

### 19.3.2Process Technology (Figure 19.2)

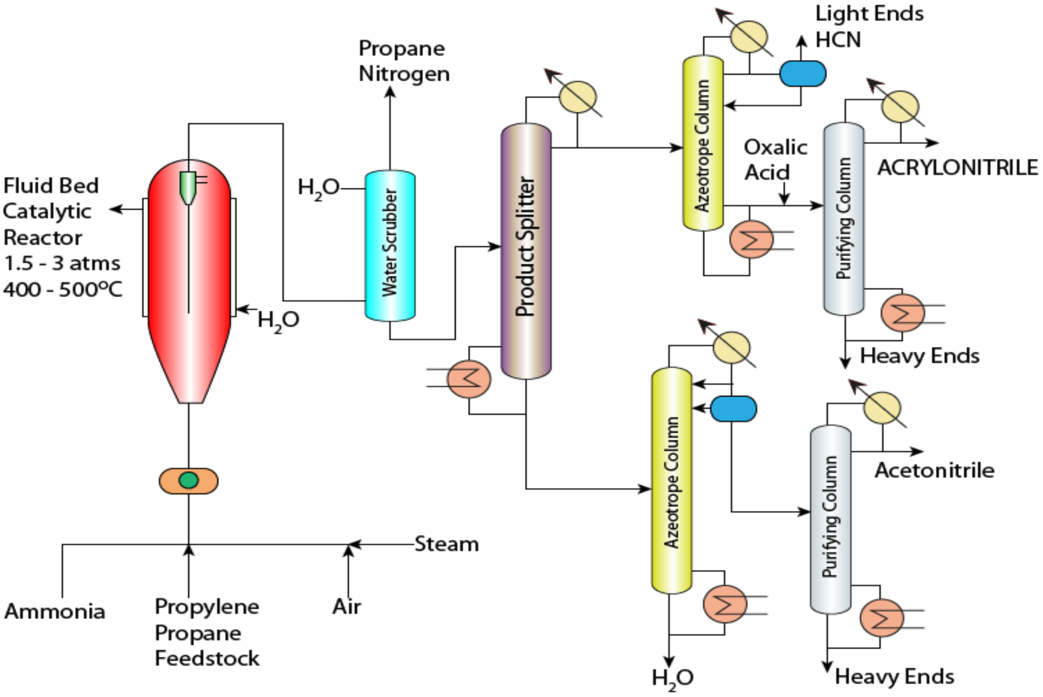


Figure 19.2 Flow sheet of Acrylonitrile production

- Propylene + Propane, Air and Ammonia, Steamare compressed to required pressure and are sent to the fluidized catalytic reactor consisting of the Mo-Bi spherical catalyst. The reactor is maintained at 400 – 500°C.
- Cyclone separator is also kept in the fluidized bed reactor in which catalyst and product gases are separated after fludization. The contact time for fluidization is in the order of seconds.
- The product vapors then enter a water scrubber that does not absorb propane and nitrogen from the products. The products absorbed in the water include acrylonitrile, acetonitrile and other heavy ends.
- The very dilute acryolonitrile (about 3 %) solution in water is sent to a fractionator. The fractionators separates acrylonitrile + heavy ends + HCN + light ends as a top product stream and acetonitrile + water + heavy ends as a bottom product.
- The top product then enters an extractive distillation column with water as extractant. The azeotropic distillation column vapour is partially condensed to obtain a vapour, aqueous and organic layer. The vapour consists of Light ends and HCN and is let out. The organic layer consists of acrylonitrile and heavy ends is sent for further purification. The aqueous layer is sent as a reflux to the azeotropic column. In other words, addition of water enabled the formation of a heterogenousazeotropic mixture at the top.
- The bottom product from the azeotropic distillation column enters a product purification unit along with oxalic acid where acrylonitrile is further purified from heavy ends (+ oxalic acid) and is obtained as a 99.5 % pure product.

- In similarity to this, the bottom product from the product splitter enters an azeotropic column which produces water as a bottom product. The total condenser in this column generates both aqueous and organic layers. The organic layer is rich in acetonitrile and heavy ends where as the aqueous layer is sent back as a reflux to the azeotropic column.
- The bottom product from the acetonitrile azeotropic column enters a purification unit where distillation principle enables the separation of acetonitrile from the heavy ends.

## 19.3.3Technical questions

1. **Why is oxalic acid added in the acrylonitrile purification column?**

Ans: One of the byproducts of the ammonoxidation of propylene are cyanohydrins.These organic compounds readily dissociate to form volatile compounds. These volatile compounds are severely polluting compounds. Therefore, to avoid this, oxalic acid is added to the purification column in order to form complex compounds with these cyanohydrins and these compounds eventually enter the heavy end products.

2. **A careful analysis of the process flowsheet shown indicates that while absorption is favoured at lower temperatures and higher pressures, exactly opposite conditions exist for the reactor outlet stream (at about 1 atm pressure and 400 – 500$^o$C). What additional process modifications are suggested?**

Ans: Cooling the vapour product stream from 400$^o$C to about 50$^o$C in a series of heat exchangers. Since vapour is involved, extended area exchangers will be beneficial. Heat integration with the reboilers of any of the distillation columns is also beneficial.

Pressurizing the vapour pressure to higher pressure and allowing it to enter the scrubber at the same temperature. This is beneficial but compressor costs will be enormous.

Therefore, in the light of the process costs, cooling the vapour stream is beneficial than compression to favour good absorption.

3. **In certain processes for acrylonitrile production, cyanohydrins removal is desired. If so, what process modifications are suggested?**

Ans: Cyanohydrins are in the bottom product obtained in the product splitter. Therefore, the bottom product can be sent to a reactor where cyanohydrins can be converted to acrolein and these acroleins can be separated and sent back to the ammonoxidation reactor (fluidized beds). In that case, oxalic acids are not used and the heavy ends will not also get produced significantly and therefore process topology will be somewhat different from what is being shown here. For further details upon how the process flowsheet changes please refer to Chemical Engineering Design

(Book) by Sinnott where in Appendix these modifications have been explained thoroughly in the process description.

4. **Is a partial condenser required in the acetonitrile azeotropic column?**

Ans: No, the reason is that the bottom product from the product splitter consists of heavy ends, acetonitrile and water and does not consist of lighter ends and HCN. Therefore, a partial condenser is not required and a total condenser producing two separate liquid phase streams that separate upon gravity is required.

5. **A feed stock heater is not shown in the process. However, reactor operating conditions are indicate high temperature operation. How is the feed stock heated?**

Ans: The heat for achieving the feed to desired temperature is provided by superheated steam that is mixed along with the feedstock. Typical feed molar composition is propylene 7, ammonia 8, steam 20 and air 65. Additional heat for the reaction is obtained from the highly exothermic reaction in the fluidized bed catalytic reactor.

6. **What are the advantages of the fluidized catalytic reactor when compared to a packed bed reactor?**

Ans: It is well known that the heat and mass transfer coefficients of gases are predominantly lower than those of the liquids. Therefore, fluidization principle effectively enhances bulk phase mass and heat transfer coefficients of the gas solid catalytic reaction. In other words, due to fluidization, less contact time that is required in the process, higher conversions can be achieved.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 20: Isoprene and Oxoprocessing

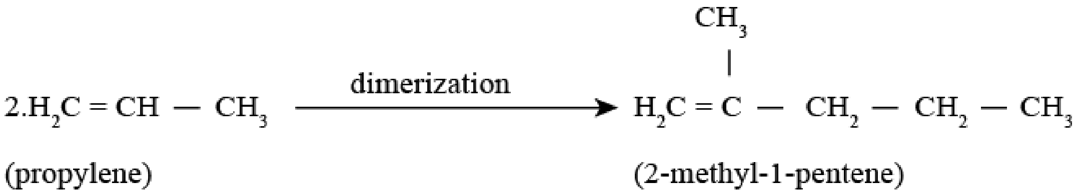
## *20.1 Introduction*

- In this lecture, we discuss the process technology for isoprene and oxoprocessing.
- Isoprene is prepared using propylene and is an important commodity for polymerization reactions and products.
- Oxoprocessing involves reaction between olefins and synthesis gas at high pressure to yield aldehydes. The aldehydes can be subsequently subjected to hydrolysis to obtain short as well as long chain alcohols.
- We first present the process technology associated to isoprene manufacture

## *20.2 Isoprene*

### 20.2.1Reactions

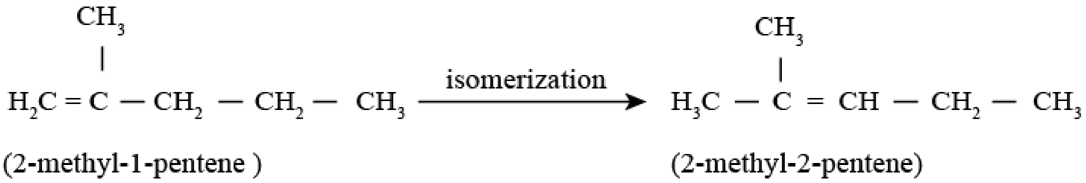
- Isoprene is manufacture from propylene using three consecutive reactions. These are
    - Dimerization of propylene to obtain 2-methyl-1-pentene



$$2.H_2C=CH-CH_3 \xrightarrow{\text{dimerization}} H_2C=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-CH_3$$

(propylene) (2-methyl-1-pentene)

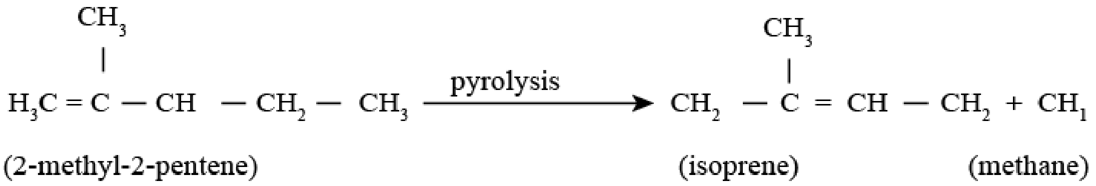
- 
    - Isomerization of 2-methyl-1-pentene to obtain 2-methyl-2-pentene



$$H_2C=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_2-CH_3 \xrightarrow{\text{isomerization}} H_3C-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3$$

(2-methyl-1-pentene ) (2-methyl-2-pentene)

- 
    - Pyrolysis of 2-methyl-2-pentene to obtain isoprene along with methane as a side – product.



$$H_3C=\overset{\overset{CH_3}{|}}{C}-CH-CH_2-CH_3 \xrightarrow{\text{pyrolysis}} CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2+CH_1$$

(2-methyl-2-pentene) (isoprene) (methane)

- Since three reactions are involved that have distinct operating conditions as well as catalyst requirements, the process involves a series of reactor-separator-recycle networks.
- We therefore, consider presenting all these cases separately so that the process can be well understood.

### 20.2.2Dimerization reaction

- Catalyst is tripropyl aluminium
- A solvent carrier is used that enables the recovery of the catalyst from the product stream.
- Operating conditions are 150 – 200$^o$C and 200 atms.

### 20.2.3Isomerization reaction

- The reaction requires an acid catalyst on porous carrier
- Operating conditions are 150 – 300 $^o$C and normal pressure conditions

### 20.2.4Pyrolysis reaction

- HBr catalyst is used
- Operating conditions are 650 – 800 $^o$C and normal pressure.

## 20.2.5Process technology (Figure 20.1)

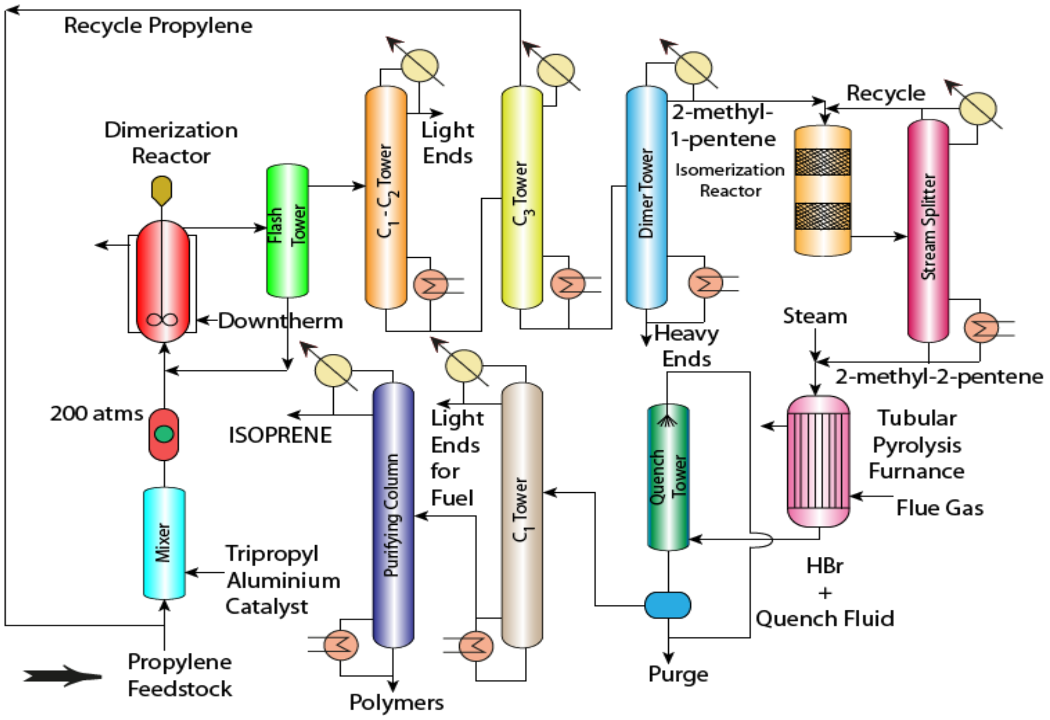


Figure 20.1 Flow sheet of isoprene production

- The process technology consists of three major blocks namely
  - Dimerization-separator-recycle network (DSR)
  - Isomerization-separator-recycle network (ISR)
  - Pyrolysis-separator-recycle network (PSR)

### 20.2.6DSR network

- Propylene feed is mixed along with unreacted propylene (recovered in a distillation column in the DSR) to enter a mixer.
- The mixer is fed with tripropyl aluminium catalyst (this catalyst is in liquid phase)
- The mixture is compressed to about 200 atms. At these conditions, the mixture is in the liquid phase.
- The liquid phase dimerization feed enters the dimerizatoin reactor
- The dimerization reactor is a CSTR with dowtherm fluid circulated in the cooling jacket to remove the heat generated from the exothermic reaction
- After the reaction, the liquid stream is subjected to flash operation. From the flash tower a vapour and liquid stream are produced. The liquid stream consists of the catalyst + solvent where as the vapour stream consists of the unreacted propylene, light ends and the product formed.
- The liquid stream from the flash tower is recycled back to the dimerization CSTR.
- The vapour stream enters a fractionation tower that produces light ends such as $C_1$-$C_2$ as the top product. The bottom product consists of propylene and dimerized product i.e., 2-methyl-1-pentene
- This product is subjected to again fractionator in a separate tower to obtain 2-methyl-1-pentene as the bottom product and propylene as the top product. The top propylene product is then recycled back to mix with the fresh propylene feed stock and enter the mixer unit.

### 20.2.7ISR network

- 2-methyl-1-pentene enters an isomerisation reactor which consists of acid catalyst (on porous carrier).
- The isomerisation reactor is a packed bed reactor operated at desired operating temperature.
- After the reaction, the products are sent to a fractionators that separates unreacted 2-methyl-1-pentene from the isomerized product i.e., 2-methyl-2-pentene.

## 20.2.8PSR network

- 2-methyl-2-pentene enters a pyrolysis furnace.
- Steam is also mixed with the organic vapors so as to quickly facilitate cracking in the pyrolysis furnace.
- The furnace is a shell and tube arrangement with the reactants entering the tubes and the hot flue gases enter the shell.
- HBr catalyst also enters the tubes of the pyrolysis furnace
- After reaction, the product gases (HBr+product+reactant) are taken out and are quenched with a solvent in a quench tower. The quenching then produces a gas liquid mixture which is sent to a phase separator unit. The liquid stream from the phase separator stream consists of HBr+solvent and this is sent for quenching.
- Fresh HBr can be generated from the HBr + solvent obtained from the phase separator
- The gas fraction from the phase separator enters a $C_1$ tower that separates fuel gas and other light ends as a top product.
- The bottom product from this tower consists of polymeric compounds and isoprene is fed to a purification tower to fractionate isoprene from the polymeric compounds

## 20.2.9Technical questions

1. **What solvent can be used in the quenching process?**

Ans: HBr can be readily absorbed into water. Therefore, water can be used as a solvent in the quenching process. There is a patent available where it says that acetone can be used to recover HBr. More details can be obtained of this patent by furthering the search on the patent data base using the internet.

2. **In the process flow sheet given the HBr recovery is not shown. Do you think the flow sheet is correct. Suggest any modifications to the flow sheet?**

Ans: Yes, the flowsheet has an error in that sense. The flowsheet should give a section for HBr recovery where HBr is recovered in the quenched solvent and the fresh HBr gas is allowed to enter the pyrolysis furnace along with the steam. In such case, one has to put an additional HBr stripper which can strip HBr from the HBr + solvent stream that is fed to this unit and the HBr can be sent to the pyrolysis unit. The fresh solvent can be then sent to a cooler and sent to the quench tower and the existing recycle stream to the quenching tower will not be there. Instead, this stream will go to the stripper as a feed stream.

3. **Can we not do heat integration partially for the pyrolysis furnace with the vapour products?**

Ans: HBr is very corrosive and therefore, if we go for heat integration using the vapour product, then the shelf life of the pyrolysis furnace will be minimized. Therefore, better we don't go for heat integration in this way.

4. **Is a purge stream required in the process flowsheet shown for the quench fluid + HBr mixture?**

Ans: Yes, and this is not shown in the process flow sheet. Some impurities such as some light ends that might dissolve with the solvent will have to be purged, if not these can cause coking problems and can cause unwanted organics in the pyrolysis furnace reactor.

5. **What sort of regeneration would you recommend for the isomerisation catalyst?**

Ans: Heating the catalyst in oxygen or air to remove coke would be beneficial to regain the activity of the isomerisation catalytic bed.

6. S**uggest what changes will be there in the process flow sheet if pure propylene instead of a mixture of propylene, propane and $C_1$-$C_2$ components is used?**

Ans: The $C_1$-$C_2$ tower and $C_3$ towers can be replaced with a single tower after flash unit. This new unit will separate all light ends in trace amounts in a single tower with middle product being 2-methyl-1-pentene and heavy ends as bottom product. Therefore, a complex distillation unit arrangement would be at the maximum required replacing three distillation columns in series.

## *20.3 Oxo processing of olefins*

### 20.3.1Introduction

- In an oxo process, we react an olefin with synthesis gas to obtain aldehyde i.e.,
- Olefin + CO + $H_2 \rightarrow$ Aldehyde
- This reaction is called as hydroformylation
- **Dimerization (Option):** Alternatively, if desired, the aldehyde dimerization reaction can be also carried out. In that case, two molecules of aldehydes react to obtain a higher order aldehyde.
- In short, the oxo processing can be targeted to generate both short chain and long chain aldehydes.
- **Hydrogenation (Option):** When short and long chain aldehydes are subjected to hydrogenation then one can produce alcohol or an acid.
- **Oxygenation (Option):** When short and long chain aldehydes are subjected to reaction with oxygen or air, then acids can be formed.
- Thus the oxo processing of olefins can generate

    - Short and long chain aldehydes
    - Short and long chain alcohols
    - Short and long chain acids
- Therefore, gases can be converted into these useful products. Various applications of these compounds include plasticizers for polymerization reactions, solvents, detergent raw materials etc.
- The process will be demonstrated for propylene but can be suitably extended to other alkenes such as butylenes or ethylene.

## 20.3.2Reactions and Operating conditions

- **Addition reaction**
    - Catalyst: Cobalt naphthanate
    - Operating conditions: Pressure of 100 – 400 atms and temperature of 100 – 200 $^{o}$C
    - The reaction is exothermic
    - Reaction occurs on a packed bed reactor where the packed bed acts as a surface to deposit the catalyst i.e., Cobalt.
    - In due course of reaction, the Cobalt enters the product stream and therefore needs to be recovered.
- **Dimerization reaction**
    - Catalyst: Zinc salt
    - Operating conditions: Higher pressure and moderate temperatures.
- **Hydrogenation reaction**
    - Catalyst: Nickel
    - Operating conditions: 100 atms and 150 $^{o}$C

## 20.3.3Process technology

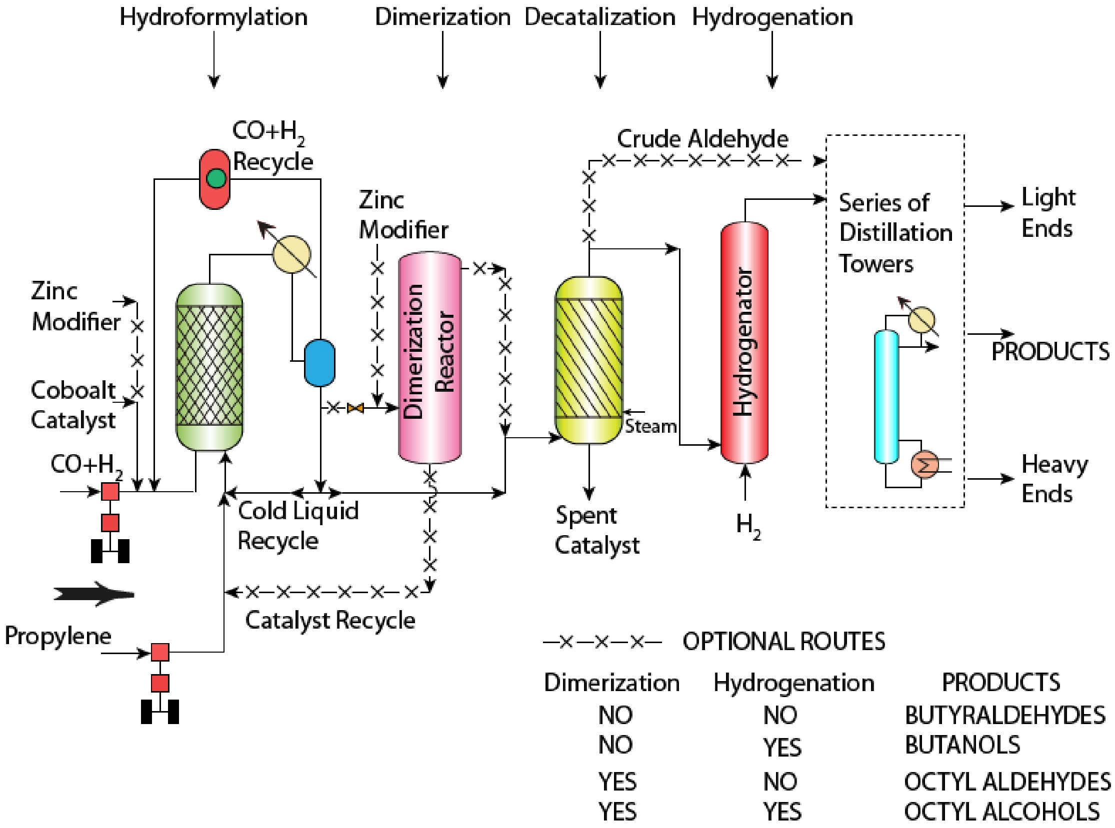


**Figure 20.2 Flow sheet of Oxo processing of olefins**

- To produce alcohols, the process consists of four basic steps namely hydroformylation, decatalization, hydrogenation and a separation network
- **Hydroformylation**
    - Propylene and synthesis gas are separately compressed and sent to the hydroformylation reactor along with the Cobalt catalyst (i.e., Cobalt napthanate).
    - The concentration of Cobalt Naphthenate is about 1 wt % Cobalt in the feed mixture.
    - During the reaction at the existing operating conditions some Cobalt gets deposited on the porous carrier.
    - Since the reaction is highly exothermic, there shall be cooling. To do so, cold liquid stream obtained after phase separation is recycled.
    - The product liquid from the reactor is sent to a partial condenser followed by phase separator. The phase separator separates the unreacted synthesis gas (by considering the propylene in the feed stock to be limiting) and the liquid product stream. The liquid product stream is partially recycled back to the reactor to serve as a diluent to control the temperatures in the packed bed reactor.
    - The liquid product stream consists of dissolved cobalt and hence it needs to be extracted back as the salt to enter the hydroformylation reactor.

  - Therefore, the product stream is partially sent to the Decatalization process so as to remove the catalyst from the stream
- **Decatalization**
  - The liquid product from the phase separator is sent to a packed bed unit where it is mixed along with steam at 180$^oC$ at a pressure of 20 atms.
  - At this condition, Cobalt salt in the hydrocarbon liquid gets transferred to the porous carrier as cobalt oxide.
  - For reuse, the cobalt oxide on the porous carrier is treated with acid to generate the cobalt naphthanate and this will be sent back to the hydroformylation reactor.
  - The vapors generated from decatalization unit consist of the aldehyde products
  - These are sent to the hydrogenation unit next to convert aldehydes to alcohols
- **Hydrogenation**
  - The aldehyde product vapors are fed to a nickel catalytic bed reactor
  - Hydrogen is also fed to the reactor at about 150 $^oC$ and 100 atms.
  - After reaction, butanols and other alcohols are sent to a separator network
- **Separator network**
  - The separator network consists of several fractionators in series
  - The fractionators in series produce light ends and heavy ends in addition to the desired product i.e., butanol

## 20.3.4Technical questions

1. **The flow sheet presented corresponds to production of butanol from propylene. If higher order alcohols are desired, how does the flow sheet get modified?**

Ans: An additional unit process entitled “Dimerization” will be part of the flow sheet. In such case, the cold liquid stream from the phase separator enters the dimerization reactor to convert lower order aldehydes to higher order aldehydes.

2. **Suppose we wish to produce both short chain and long chain aldehydes and do not wish to produce alcohols then how does the process topology change?**

Ans: When both short and long chain aldehydes are required, then we have to allow the cold liquid from the phase separator to enter the dimerization reactor partially only. Then the dimerization reactor product as well as the phase separator stream enter the decatalization unit to achieve catalyst recovery.

3. **Can the hydroformylation reactor be used as a dimerization reactor as well?**

Ans: Yes, in this way, we can produce all desired products in a single reactor and we can avoid dimerization reactor. But the balance between cobalt and zinc catalysts will dictate the product composition palette.

4. **Why high pressure is required in the hydroformylation reactor?**

Ans: Higher pressures enable the formation of a complex between Cobalt and the hydrocarbons participating in the reaction. If higher pressure is not existent, the cobalt complex can decompose and this does not favour higher conversions.

5. **Can the series of distillation columns in the separator network be replaced with a complex distillation column?**

Ans: Yes, this is possible and this is recommended as the light end and heavy end products are not significant in make and the aldehyde products are the actual products that are desired. A complex distillation reduces the number of columns required, enables complex interaction between both vapour and liquid streams and facilitates drastic reduction in the cost.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 21: Butadiene and Benzene Manufacture

## *21.1 Introduction*

- In this lecture, we present the process technologies associated to Butadiene and Toluene.
- Butadiene manufacture is considered using n-Butane as the feed stock.
- Benzene process technology refers to the famous hydrodealkylation process that uses toluene as the feed stock.
- We first present the process technology associated to Butadiene.

## *21.2Butadiene*

### 21.2.1 Reactions

- Main reaction: n-Butane → Butadiene + Hydrogen.
- Side reaction: n-Butane→ n-Butylene + Hydrogen.
- Catalyst: Chromium oxide on alumina.
- Coke deposition is a very important issue. Therefore, catalyst regeneration needs to be carried out very frequently.
- Reaction is exothermic .
- Operating conditions: 650$^{o}$C and 120-150 mm Hg (low pressure).
- Feed stock: n-Butane with some isopentane from refinery processes.

### 21.2.2 Process Technology (Figure 21.1)

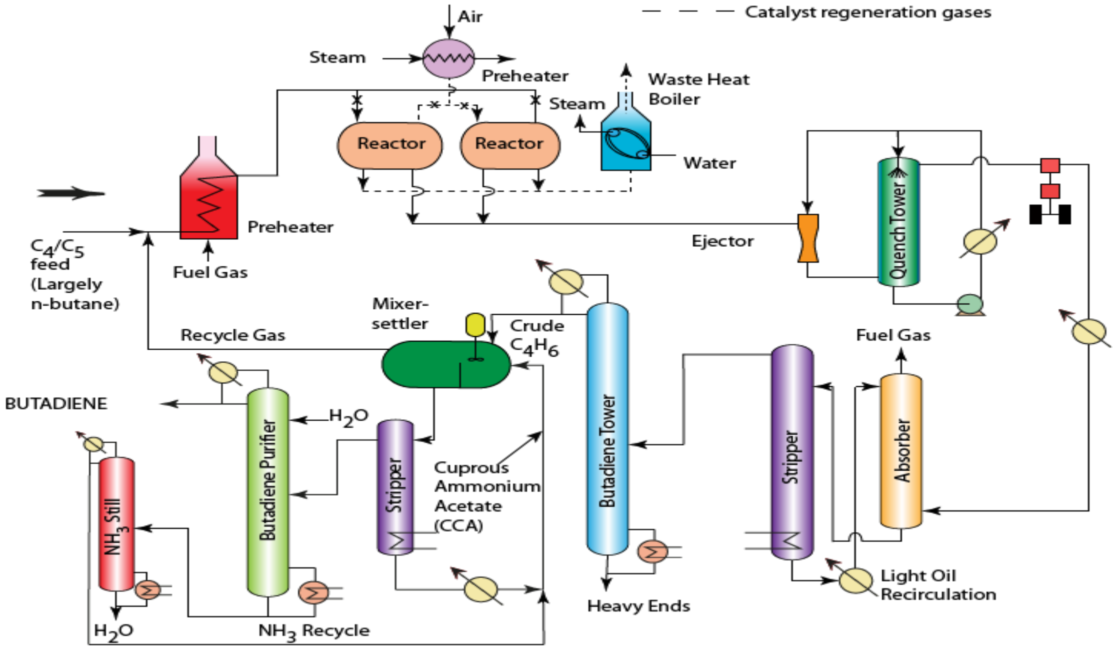


**Figure 21.1 Flow sheet of Butadiene manufacture**

- The process technology for Butadiene manufacture consists of a reactor-separator-recycle system.

- The separation network is extremely complex and involves quenching, absorption, distillation and extractive distillation process.
- First, the feed stock is pre-heated in a furnace along with unreacted gases that have been recovered in the process using the separator network.
- After pre-heating in a furnace to desired temperature, the gases enter the catalytic packed bed reactors loaded with the catalyst.
- After the specified residence time, the product is withdrawn and the feed to the unit is stopped. The product withdraw and stoppage of the feed flow to the reactor unit is carried out using valves.
- The coked catalyst is subjected to combustion using pre-heated air. Air pre-heating is done using steam in an extended area heat exchanger equipment. Therefore during regeneration, another set of valves operate to allow the pre-heated air in and enable the product withdrawal after the combustion.
- The pre-heated air not only removes the coke as $CO_2$ but increases the reactor temperature to 650 $^oC$.
- The flue gases are sent to a waste heat recovery boiler so as to generate steam from water.
- The entire operation of a feed entry, product withdrawal, pre-heated air entry and combustion gases withdrawal from the packed bed reactor corresponds to one single cycle.
- Since the above operation is a batch operation, to make the operation continuous in accordance to the separation network, two reactors are used and these reactors are operated in cyclic fashion i.e., when the first reactor is subjected to reaction, the second reactor is subjected to catalyst regeneration and vice-versa.
- The hot reactor outlet gases are sent to a quenching operation where light gas oil is used to quench the gases using a recirculating quenching tower.
- After product gases from the quenching tower are compressed and cooled to enter an absorber
- In this absorber, naphtha is used as an absorbent to absorb all hydrocarbons except fuel gas.
- The absorbent + hydrocarbons enter a stripper that produces fresh naphtha and hydrocarbon mixture. The hydrocarbon mixture consists of unreacted feed stock and butadiene and some heavy ends.
- This mixture now enters a fractionator to separate the crude butadiene and heavy ends.
- The crude butadiene consists of butadiene and unreacted feed stock i.e., n-butane and isopentane. The separation of n-butane, other hydrocarbons with butadiene is one of the difficult separations and they cannot be separated using ordinary distillation. Therefore, a complicated route of separation is followed next that involves azeotropic distillation using ammonia.

- The crude butadiene is mixed with ammoniated cuprous ammonium acetate solution in a mixer settler. This solution is generated by absorbing ammonia into fresh cuprous ammonium acetate solution.
- The ammoniated cuprous ammonium acetate is sent to a mixer settler unit where the butadiene dissolves in the ammoniated solution. The gas from the mixer settler unit is recycled to mix with the feed stock and enter the pre-heater.
- The ammoniated cuprous ammonium acetate solution is thereby stripped to separate butadiene + ammonia from the ammonium acetate solution. The regenerated fresh solvent is allowed to absorb $NH_3$ and thereby enter the mixer-settler unit.
- The ammonia + butadiene mixture enters a fractionator fed with water. Here, water interacts with ammonia and generates the ammonium hydroxide product as the bottom product and butadiene is obtained as the top product.
- The ammonia solution is subjected to stripping to separate water and ammonia. The water is recycled back to the butadiene purifier and ammonia is allowed to get absorbed into the fresh cuprous ammonium acetate solution.
  This process is not followed in India . In India, it is manufactured from ethanol by catalytic cracking at 400-450 $^oC$ over metal oxide catalyst.

## 21.2.3 Technical questions

1. **Can the steam generated in the waste heat recovery boiler be sufficient to pre-heat the air if a principle of steam reuse is adopted?**

Ans: From the basic principle of thermodynamics, somewhere heat needs to be added to the system. If we presume that the feed pre-heater heats the feed to 650$^oC$ (the desired temperature of the reactor) and the catalyst is regeneration energizes the catalyst by 100$^oC$ (from 550 to 650$^oC$), the flue gas should be able to generate some steam. However, it can be speculated that the steam generated will not be enough to meet the total air pre-heater requirements. Therefore, some make up steam will be always required.

2. **Why is ammonia allowed to get absorbed into cuprous ammonium acetate?**

Ans: Ammonia absorption into cuprous ammonium acetate facilitates maximum absorption of butadiene. This is because ammonia in many cases enhanced absorption factors by allowing chemical interaction between molecules which is better than just physical absorption.

3. **Why is the fluid recirculated in the quench tower?**

Ans: We are targeting gas quenching using a liquid in this process. Quenching a liquid with liquid is instantaneous but quenching a gas with a liquid needs considerable amount of time, and hold up time is very important. Therefore, fluid internal recirculation is required in the vapour quenching tower.

4. **Why a cooler is used in the quenching tower?**

Ans: The quenching operation increases the temperature of the fluid that is used for quenching. And we can see that the fluid is always circulated. Therefore, the purpose of quenching is to just cool the gas and don't absorb any of the components into itself. Therefore, to do so, the fluid shall be cooled in between.

5. **Why compressor and cooler are at all required after quenching process?**

Ans: The unit following quench tower is absorption. Absorption is favoured at higher pressure and lower temperature. Therefore both compressor and cooler are required to achieve these conditions of favourable absorption.

6. **Why cooler is followed after compression but not vice versa?**

Ans: In general, compression enables enhancement in the temperatures of the gas/vapour. This is because we don't usually follow adiabatic compression but we follow polytropic compression in reality. And polytropic compression will enable heating the gas/vapour. Therefore, cooling is used after compressor but not vice-versa. If cooler is used before compressor then the gas entering absorber will be at a higher temperature and this is not favourable for absorption.

7. **Explain in a more elaborate way what happens in the Butadiene purification fractionators?**

Ans: The butadiene purification fractionator is fed with ammonia + Butadiene stream in which somehow ammonia should be recovered. Therefore, this unit is part of the azeotropic distillation that separates butadiene + ammonia as one of the products and eventually butadiene and ammonia are separated using water, as water absorbs ammonia instantaneously to form ammonium hydroxide. Eventually, it is also easy to strip the ammonia gas from aqueous ammonia solution.

8. **Why we cannot separate butadiene-butane mixture using ordinary fractionation?**

Ans: Their boiling points are very close and distillation requires large differences between boiling points of the components to be separated.

## *21.3Benzene production using hydrodealkylation route*

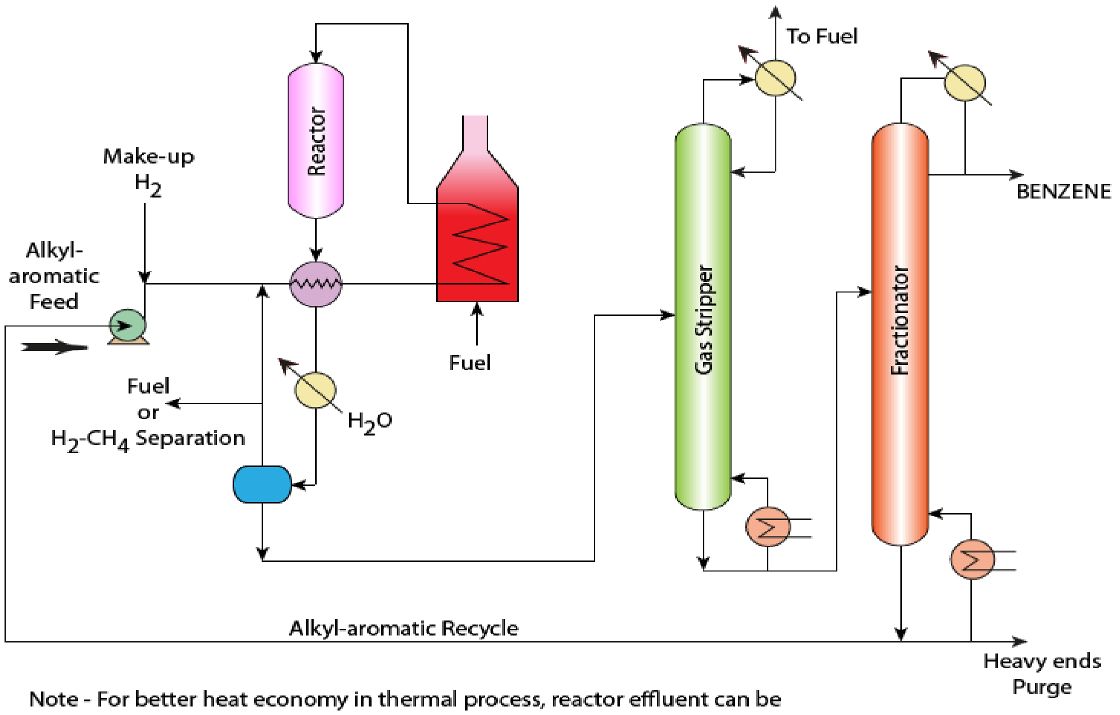
### 21.3.1Reactions

- Toluene does not have much market value.
- Therefore, Toluene is reacted with $H_2$ to produce Benzene and Methane
- Main reaction: Toluene + $H_2 \rightarrow$ Benzene + Methane
- Reactor operating conditions: 600 – 650 $^{o}$C and 35 – 40 atms
- Catalyst: Chromia on porous carrier.
- Other reactions: Alkyl aromatics + $H_2 \rightarrow$ Benzene + Alkanes

### 21.3.2Side reactions

- Toluene →Diphenyl + $H_2$
- Toluene + Benzene → Methyl diphenyl
- Toluene + $H_2$→ Alkanes (Cracking reaction)

### 21.3.3Process Technology (Figure 21.2)



Note - For better heat economy in thermal process, reactor effluent can be used for stripper and fractionator reboiler heat supply.

**Figure 21.2 Flow sheet of Benzene production using hydrodealkylation route**

- The process corresponds to a simple reactor-separator-recycle system facilitated with heat integration.
- Alkyl-aromatics (Toluenes and other higher order alkyl aromatics) along with makeup $H_2$ and recycle stream consisting of unreacted toluene is allowed to enter a feed pre-heater.
- The feed pre-heater increases the temperature of the reactants at the desired pressure.
- After the reaction, the reactor products are cooled using heat integration concept by exchanging heat with the cold feed stream. Further cooling of the stream is carried out using a water based cooler.
- The stream enters a phase separation unit where the fuel gas components such as $H_2$ and $CH_4$ are removed as vapour stream. The liquid stream consists of $H_2$, $CH_4$, Light ends, Benzene, Toluene, Diphenyl and other higher order aromatics.
- The vapour stream is partially purged and to a large extent recycled as the stream has good amount of $H_2$. The gas phase purge stream is for controlling the concentration of methane in the reactor.

- The liquid stream enters a gas stripper which removes the light ends as a gaseous product stream from the top tray. The bottom product is then sent to a fractionator.
- The fractionatorseparates benzene from all heavy ends. The heavy end product consisting of unreacted toluene, diphenyl etc. is largely sent back to the reactor by allowing mixing with the fresh feed.
- A purge stream is facilitated to purge components such as diphenyl in order to not allow their build up in the reactor.

## 21.3.4Technical questions

1. **Despite removing $H_2$ and $CH_4$ from the phase separator, why again we remove them from the gas stripper unit?**

Ans: This is due to the basic problem in the difficulty of sharp equilibrium factors which do not exist for these components. The equilibrium separation factors in a phase separator unit where the governing pressure and temperature dictate the distribution of components in the liquid and gas stream. Mostly methane and $H_2$ are removed as vapour stream in the unit. But still at the pertaining pressure and temperature of the phase separator, some lower order alkanes stay back in the liquid stream. Therefore, gas stripping is carried out to remove these.

2. **Comment upon fuel efficiency in the process and possibilities to enhance it?**

Ans: The process should indicate maximum fuel efficiency. This can be achieved by

a) Heat integration of feed and product streams to the reactor
b) Re use of fuel gas streams as a fuel in the pre-heating furnace.

If these two options are followed, then the process has maximum fuel efficiency and can be regarded to be very energy efficient.

3. **Do you suggest toput one more distillation column for the heavy end compounds. If so why?**

Ans: Yes, putting one more distillation column will separate toluene + diphenyl from other heavy end compounds. While diphenyl acts towards favouring forward reaction, the other heavy end compounds could tend to produce more coke during the reaction. Therefore, one more distillation unit to separate toluene+diphenyl from the heavy end compounds is recommendable.

4. **Do you suggest any other alternative to eliminate the water cooler and even enhance the energy efficiency of the process?**

Ans: Yes, it is possible, but existing temperatures of the gas stripper bottom sections need to be carefully analyzed. This is also due to the fact that phase separator operates at 450 psig and 100$^{o}$F. Therefore, heat integration with gas stripper or fractionator reboilers can be beneficial and this way the process can be made even more energy efficient.

5. **What is the basic problem of $H_2$ in the reactor?**

Ans: Hydrogen causes embrittlement due to severe adsorption on the metal surface at higher pressures. Therefore, chrome steel is used to avoid these embrittlement problems as material of construction for the reactor.

6. **Why is methane purged using the gas purge stream from the phase separator?**

Ans: The reaction kinetics dictate the maximum concentration of methane in the gas stream entering the reactor. Therefore, to achieve maximum conversion, methane is purged.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 22: Phenol from Cumene and Toluene

## *22.1 Introduction*

- Phenol is one of the most important petrochemicals. Ranging from solvents to polymers, phenol is required for several petrochemical processes as an important raw material.
- Phenol can be produced from many sources such as
  - Cumene
  - Toluene
  - Benzene
- Depending upon these raw materials, various chemical transformations and underlying physical principles apply.
- In this lecture, we discuss upon the process technology associated to Phenol production from Cumene and Toluene

## *22.2Phenol production from Cumene*

### 22.2.1 Reactions

- **Peroxidation:**Cumene + Air →CumeneHydroperoxide
- **Hydrolysis:**CumeneHydroperoxide + $H_2SO_4$→ Phenol + Acetone

### 22.2.2 For Peroxidation

  - Aqueous emulsion is prepared using emulsification agents
  - Operating conditions: Normal T & P
  - Emusification agent: NaOH (Alkali)

### 22.2.3For Hydrolysis

  - 10 – 25 % $H_2SO_4$ (Aqueous) is used
  - Operating conditions: 55 – 65$^{o}$C and atmospheric pressure conditions

## 22.2.4Process Technology (Figure 22.1)

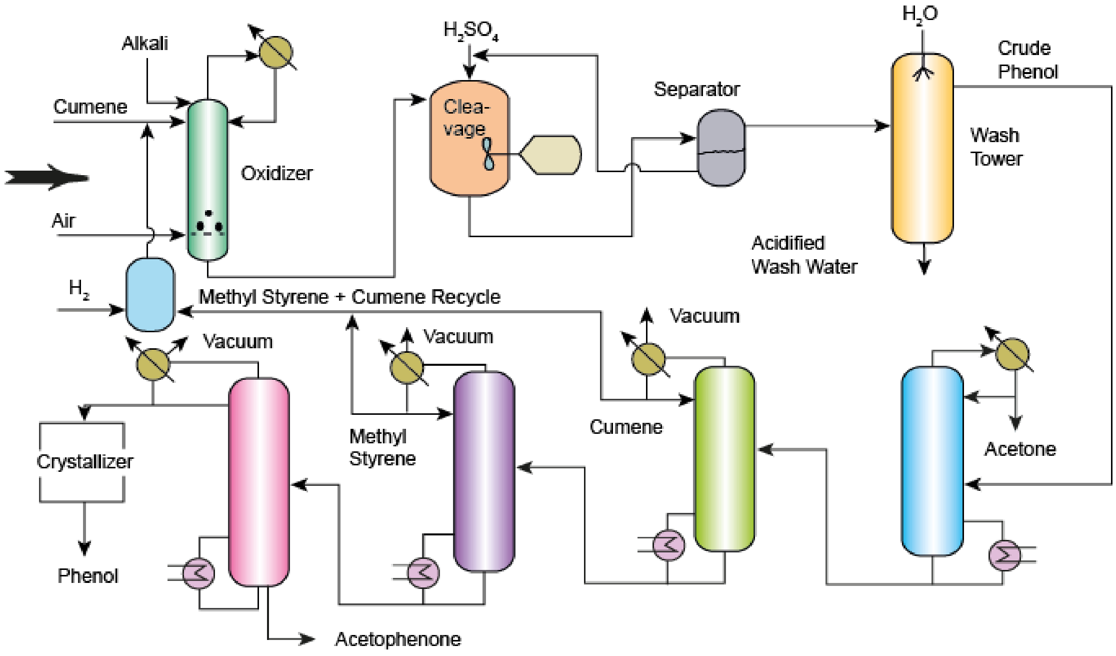


**Figure 22.1 Flow sheet of Phenol production from Cumene**

- Fresh cumene is mixed with hydrogenated unreacted cumene, cumene + alpha methyl styrene (recycle streams) .
- The pre-purification step involves converting unsaturates such as alpha methyl styrene and others to saturates. This is done by using nickel catalyst at 100 $^{o}$C and feeding hydrogen to the pre-purification reactor. The product from this unit then mixes with the fresh cumene.
- The fresh cumene and processed cumene and alpha methyl styrene are fed to the oxidation reactor. The oxidation reactor refers to a gas liquid reaction between air (Oxygen) and the cumene.
- An emulsion of cumene is prepared in the oxidation reactor by adding alkali to it.
- pH is maintained in the range of 8.5 – 10.5 to suit good emulsification conditions.
- After reaction, vent gases are condensed and recycled back and the product is sent to a cleavage unit.
- The cleavage unit consists of a stirrer and is fed with fresh and recycled $H_2SO_4$ aqueous solution to enable the hydrolysis of cumenehydroperoxide.
- The product streams from the cleavage unit enter a settler (phase separator) which upon gravity settling yields two streams namely the acid rich aqueous stream and the phenol rich organic stream.
- The aqueous stream consists of the sulphuric acid and is sent back to the cleavage unit as a recycle stream.
- The organic stream consists of cumene (unreacted), phenol (product), acetone (side product), alpha methyl styrene (side product) and acetophenone (side product).

- The organic stream from the gravity settler unit then enters a scrubber fed with water. In this operation, water extracts the remaining acids in the organic stream and produces crude phenol stream. Water leaving the unit consists of acidified wash water.
- The crude phenol then enters a distillation unit that separates acetone from the other components.
- The bottom product from this distillation column enters a vacuum distillation column that produces cumene as a top product.
- The bottom product from the distillation column enters another vacuum distillation unit to produce alpha methyl styrene.
- The bottom product of this distillation column enters the final vacuum distillation unit to produce phenol as top product and acetophenone as the bottom product.

## 22.2.5Technical questions

1. **Why unsaturates are saturated before entering the oxidization reactor?**

Ans: Unsaturated compounds will produce compounds other than cumenehydroperoxide. Since cumenehydroperoxide will only convert to phenol but not others, the product quality will drastically reduce if unsaturates are available in the feed stock.

2. **What is the basic advantage of emulsification?**

Ans: A gas liquid reaction requires maximum interfacial area to enhance reaction rates. Usually gas is sparged through liquid. But in this case, the liquid itself is emulsified so that the interfacial area can be even further enhanced.

3. **Are there any safety issues related to the oxidation reactor?**

Ans: Yes, cumenehydroperoxide is explosive after a certain minimum concentration. Therefore, all designs shall ensure that this component should not get accumulated beyond a specified concentration in any section of the units.

4. **Why are the vent gases recycled back?**

Ans: The vent gases in addition to $N_2$, unreacted $O_2$ will consist of hydrocarbons as the hydrocarbons could escape to the vapour phase due to their low boiling points even at room temperature. Therefore, these hydrocarbons including cumene are recycled back by using a condenser at the top.

5. **Suggest a technology for processing acidified wash water from environmental perspective?**

Ans: The acidified wash water can be neutralized using NaOH to obtain NaCl in these waters. Eventually, the NaCl rich solution can be concentrated using multiple effect evaporators to reduce the huge water problems. Near zero discharge is difficult for such cases.

6. **Why is alpha methyl styrene also recycled back to the reactor via hydrogenator?**

Ans: Alpha methyl styrene can be hydrogenated to convert to cumene. This is because alpha methyl styrene consists of a double bond in the alkyl group attached to the benzene ring. Therefore, by hydrogenation we convert unsaturated compound to cumene and this way it is recycled back to the reactor.

7. **Why there is sulphuric acid even after gravity settling in the organic phase?**

Ans: This is a basic problem of equilibrium separation factors for the sulphuric acid, as the acid has propensity to remain maximum in the aqueous phase but also to a little extent in the organic phase.

8. **Why vacuum distillation is required for all three distillation columns?**

Ans: To the best of the instructors knowledge, all organic compounds form azeotropes with others at atmospheric pressure when fractionated. Therefore, to bypass the formation of azeotrope, the pressure of the system is reduced which enhanced the relative volatility and eliminates the formation of the azeotrope. Further justification of this is available in the following azeotrope data bank:

a) Phenol-acetophenone forms an azeotrope with 7.8 wt % of phenol at 202 $^{o}$C and 1 atm pressure.
b) Alpha methyl styrene-phenol forms an azeotrope with 93 % of alpha methyl styrene at 162 $^{o}$C and 1 atm.

When vacuum distillation is considered, relative volatility of the mixture is improved and this improvement bypasses the azeotrope formation. Hence, purer products can be obtained.

9. **Don’t you think water will also enter crude phenol?**

Ans: Yes, water also enters crude phenol as solvent loss in the wash tower will provide some water into the crude phenol stream. But its concentration is not significant when compared to the concentration of the organics.

## *22.3 Phenol from Toluene Oxidation*

### 22.3.1Reactions

Oxidation to Benzoic acid

- Toluene + Oxygen → Benzoic acid + Water
- Catalyst: Cobalt Naphthenate
- Operating conditions: 150 $^{o}$C and 3 atms
- Exothermic reaction

Oxidation of Benzoic acid to phenol

- Benzoic acid + Oxygen → Phenol + $CO_2$
- Catalyst: Cupric Benzoate
- Operating conditions: 220 $^{o}$C and 1.3 – 1.7 atms
- This reaction is also exothermic

### 22.3.2Process technology (Figure 22.2)

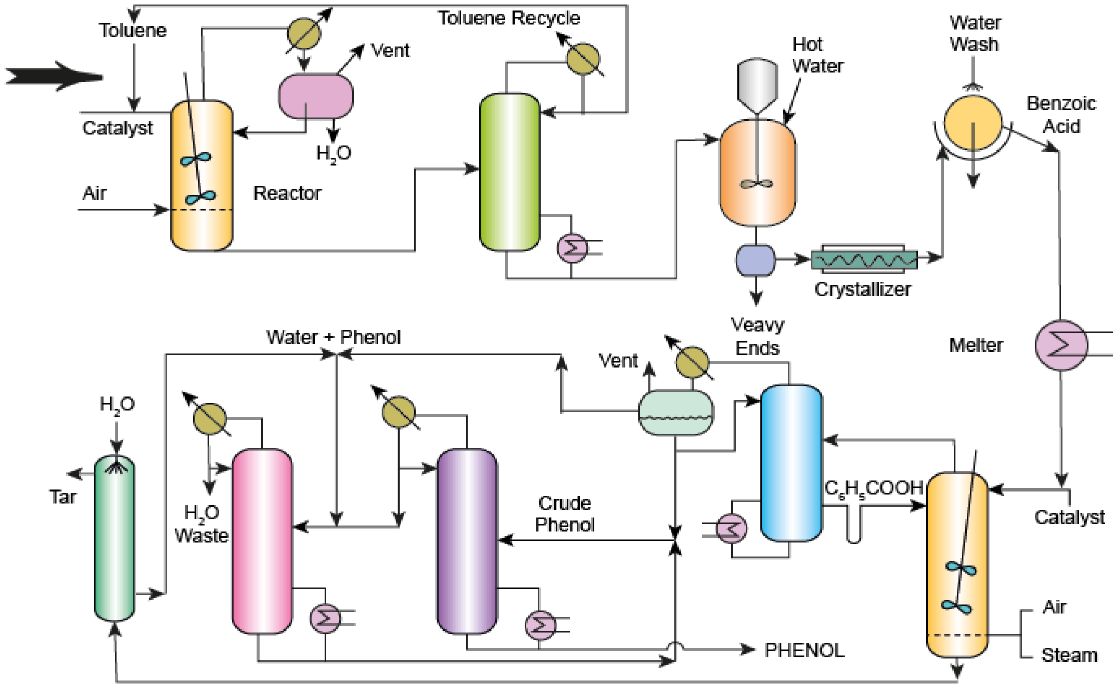


**Figure 22.2 Flow sheet of Phenol manufacture from Toluene Oxidation**

- Fresh and recycled toluene first enter the oxidation reactor
- The oxidation reactor is a gas-liquid reactor in which air is sparged through a column of liquid (toluene)
- To reduce side reactions, toluene is used as a limiting reactant
- The catalyst is fed to the reactor along with the toluene stream
- After reaction, several products are formed including undesired impurities such as benzaldehyde, benzyl alcohol, benzyl benzoate, CO and $CO_2$
- The reactor is facilitated with vent after cooling and partial condensation of the air mixed hydrocarbon vapour stream.

- The liquid product from the reactor then enters a distillation column which separates toluene from the other organics
- The organics then enters a hot water wash unit where hot water extracts benzoic acid. All other impurities don't dissolve in water and leave the wash unit as heavy ends
- The benzoic acid rich hot water stream is sent to a crystallizer where benzoic acid crystals are formed.
- The benzoic acid crystals are once again washed with water to obtain benzoic acid crystals
- The benzoic acid crystals are then melted and fed to the second oxidation reactor
- The second oxidation reactor is fed with air and cupric benzoate catalyst. Steam is also added to the reactor so as to enhance the temperature of the reactants quickly.
- Once again gas liquid reaction is facilitated. Cooling is facilitated by using a jacket or cooling tubes.
- From the reactor two phases are obtained namely vapour and liquid
- The vapour and liquid both consist of phenol and therefore, both are subjected to series of separation steps to extract phenol and enrich the same.
- The vapour enters a fractionating tower which separates the unreacted benzoic acid from other compounds. The top product is obtained after partial condensation followed by phase separation. The phase separator produces three streams namely the vent stream (that consists of $N_2$, CO and $CO_2$), the aqueous water + phenol stream and the organic crude phenol stream. The crude phenol stream is partially sent as a reflux to the fractionators and withdrawn as a product as well.
- The bottom product from the second oxidation reactor consists of organic compounds and is sent to water wash. After water wash, heavy compounds such as tar are removed and phenol is dissolved in water. This water + phenol mixture is mixed with the water + phenol mixture obtained from the fractionators separating benzoic acid.
- The crude phenol is fed to a fractionator to obtain purified phenol as bottom product and phenol + water mixture as a top product. The top product here is an azeotrope.
- The phenol + water coming from three different sources is allowed to enter a distillation column that generates water waste as a top product and a crude phenol stream as a bottom product.

## 22.3.3Technical questions

1. **Why are benzoic acid crystals again subjected to water wash?**

Ans: The benzoic acid crystals could have some water soluble impurities despite having water wash. This is because of the fact that in real life, infinite separation factors don’t exist and components do get distributed in both phases. Therefore, an additional water wash facilitates the removal of these impurities.

2. **Why phenol enters both bottom and top product?**

Ans: The trick in the operation of the second oxidation reactor is to maintain temperature and pressure such that benzoic acid leaves the unit as vapour. This way, benzoic acid can be easily fractionated and sent back to the reactor. However, this has a limit as well i.e., phenol gets evenly distributed between the vapour and liquid phases.

3. **Is there any opportunity for energy integration in the process?**

Ans: Yes, the vapours from the reactor can be heat integrated with the reboilers in the toluene column or any other reboilers in the other two columns.

4. **What exactly happens in the column that is fed with phenol + water mixture, given the fact that phenol forms an azeotrope with water?**

Ans: At atmospheric pressure, phenol forms an azeotrope with water at about 9.4 wt % phenol and 90.6 wt % water. Therefore, crude phenol column shall produce a water rich stream at the top which is the azeotrope and the pure phenol product as the bottom product. From the VLE data (not shown here), it is also apparent that from about 10 wt % phenol to about 90 % phenol, the relative volatility value is pretty low and after 90 % phenol in the feed solution, the relative volatility increases significantly.

Therefore, it makes sense now to understand that crude phenol fed to the first tower splits into azeotrope at the top (with 9.4 wt % phenol) and a purer phenol product at the bottom. Eventually, the phenol + water stream entering the second unit along with the azeotrope composition is improved substantially in its composition to move away from the azeotropic composition (with more phenol in water) and hence, it should again tend to produce a purer phenol product and a waste water product at the top. The waste water product could be again an azeotrope of a different class.

Again, if we alter the pressures of these columns, the VLE data (not shown here) will reduce the phenol composition in the wastewater stream and that’s what would be probably considered to extract maximum phenol using the distillation technology.

Alternatively, extractive distillation process can be used in which toluene can be used as a solvent to alter the relative volatility. Probably, this process is more common presently in the industry than the process outlined in this lecture.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 23: Phenol from Benzene

## *23.1 Introduction*

Phenol can be manufactured from Benzene using several ways

- Benzene hydrochlorination to form Benzyl chloride followed by hydrolysis of benzyl chloride to form phenol.
- Benzene chlorination to form benzyl chloride which is transformed to sodium benzoate and eventually to phenol using NaOH and HCl
- Benzene sulfonate process: In this process, benzene is convered to benzene sulfonate using sulphuric acid and eventually through neutralization, fusion and acidification, the benzene sulfonate is gradually transformed to phenol.
- In this lecture, we restrict our discussion to the manufacture of phenol from
  - Benzene hydrochlorination route
  - Benzene from chlorobenzene route

## *23.2 Phenol using Hydro chlorination route*

### 23.2.1Reactions

First reaction

- Benzene + HCl + Oxygen → Benzyl chloride + Water
- Catalyst: $FeCl_3$ + $CuCl_2$
- Operating conditions: 240$^o$C and atmospheric pressure

Second reaction

- Benzyl chloride + water → Phenol + HCl
- Catalyst: $SiO_2$
- Here, HCl is regenerated and will be recycled.
- Operating conditions: 350$^o$C and atmospheric pressure

## 23.2.2 Process Technology (Figure 23.1)

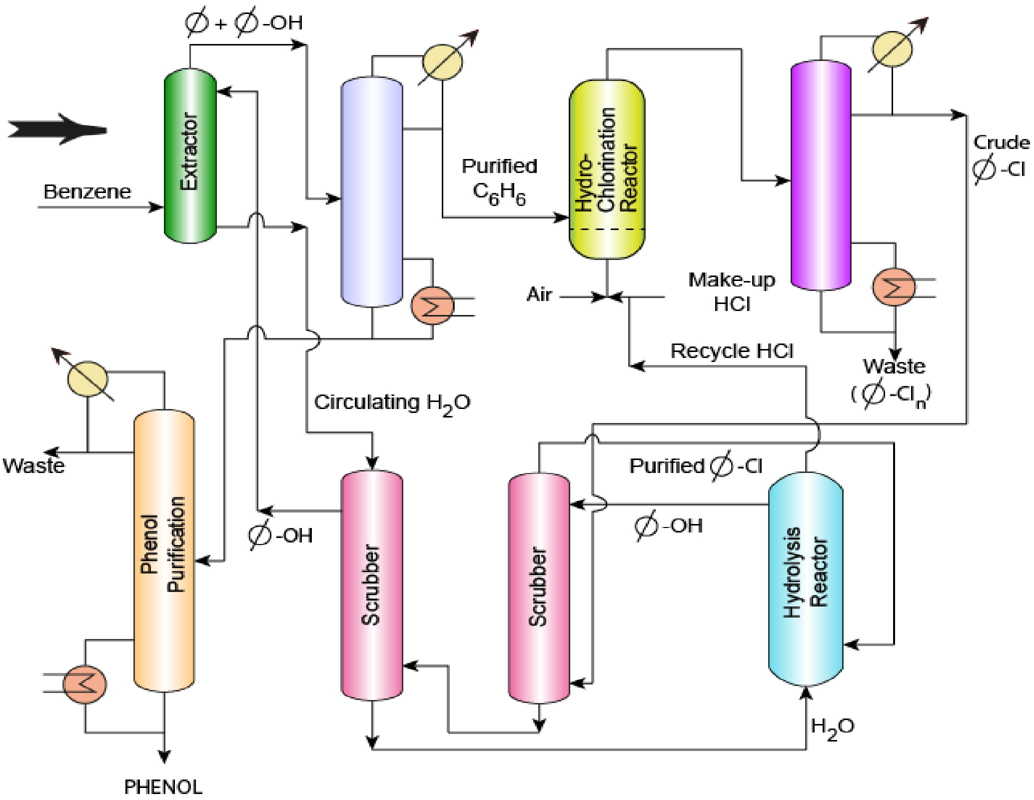


**Figure 23.1 Flow sheet of manufacture of phenol using hydro chlorination route**

- In this process, Benzene is used to extract phenol from phenol +water mixture. This unit is termed as an extraction unit (liquid liquid extraction principle). Therefore, this unit takes up fresh benzene and phenol + water mixture and produces two streams namely water stream (bottom product) and benzene + phenol stream (top product). The water stream is fed to a scrubber unit (i.e., Unit B that will be described later).
- Then onwards, the organic mixture is fed to a distillation column that produces purer benzene as the top product. The bottom product is phenol with other impurities.
- The bottom phenol rich product is sent to the phenol fractionator to obtain waste product as top product and pure phenol as bottom product.
- The purer benzene then enters the hydrochlorination reactor in which a mixture of HCl and $O_2$ is fed at 220 $^{o}$C. Under these conditions, Benzene will be also in vapour state.
- Therefore, the reactor is a gas solid reactor.
- The conversions are pretty low and not more than 20 % of the benzene is converted to benzyl chloride.
- Eventually, the products are sent to two fractionators that separate unreacted benzene, crude benzyl chloride and poly benzyl chlorides as various products. The unreacted benzene is sent back to the hydrochlorination reactor as a recycle stream.

- The crude benzyl chloride then enters an absorber unit A where phenol is used to purify the benzyl chloride from other organic compounds (such as benzene and polybenzyl chlorides).
- The purified benzyl chloride stream then enters the hydrolysis reactor in which water is passed along with benzyl chloride over the silica catalyst. The reactor itself is a furnace with catalyst loaded in the tubes and hot fuel gases are circulated in the shell to obtain the desired higher temperature.
- Under these conditions, both reactants are in vapour state (with the benzyl chloride boiling point of $179^oC$) and therefore, the reaction is also a gas solid reaction.
- After hydrolysis reaction, the product vapors are sent to a partial condenser that separates the HCl from the organic phase.
- The HCl is recycled to the hydrochlorination reactor.
- The phenol rich product stream is sent as a solvent for the scrubber (unit A) that purifies crude benzyl chloride to purer benzyl chloride. The bottom product from the scrubber (i.e., unit A) enters another scrubber (unit B) that receives water from the extractor.
- The unit B enables washing of the phenol to remove any water soluble impurities. The water from the unit B enters the hydrolysis reactor.

## 23.2.3 Technical questions

1. **Discuss the merits of the process from waste minimization perspective?**

In this flow sheet, the raw material itself is used as a solvent to extract the product. Also, one of the reactants (water) is used as another absorbent. The usage of raw materials and intermediates in the process as absorbents itself is very attractive from waste minimization perspective as waste water streams are not produced significantly. Also, the solvent used is benzene itself which reduces the complexity of using another solvent and subsequent safety related issues.

2. **Comment upon the corrosion issues of the processes?**

HCl is very corrosive and therefore, enough precaution shall be taken towards the plant and process design.

3. **What impurities are removed in the unit B scrubber using water?**

Benzyl chloride has limited solubility with water. Therefore, it is expected that benzyl chloride is dissolved to some extent in the unit B scrubber where benzyl chloride as an impurity in minor amounts can be removed from phenol.

4. **Why do you think make up HCl is required?**

Some HCl gets reacted to form poly benzyl chlorides. Some HCl gets lost as a vapour in various operations. Therefore, some make up HCl is definitely required in the process though, HCl is largely regenerated.

5. **Compared to other Benzene based phenol production processes, what advantage this process has towards phenol production?**

In this process, very little quantities of other raw materials are required. These are HCl. Air is inexpensive and is freely available. Therefore, the plant can be build easily as many other auxillary processes are not required provided benzene is available in large quantities in the vicinity. However, one basic drawback is that the fixed costs of units will be high in this case as HCl is involved.

## *23.3Phenol from Chlorobenzene route*

## *23.4Reactions*

- There are three reactions to convert benzene to phenol using chlorination route

### 23.4.1Chlorination

- Benzene + $Cl_2$ → monochloro benzene
- Operating temperature: 85 $^oC$
- Catalyst: Fe or $FeCl_3$ catalyst

### 23.4.2Causticization

- Benzyl chloride + NaOH → sodium benzoate
- NaOH is in aqueous media
- Operating conditions: 425 $^oC$ and 350 atms
- Exothermic reaction

### 23.4.3 Hydrolysis

- Sodium benzoate + HCl (aq) → Phenol + NaCl (aq)
- Operating conditions: Nothing specific

### 23.4.4 Process Technology (Figure 23.2)

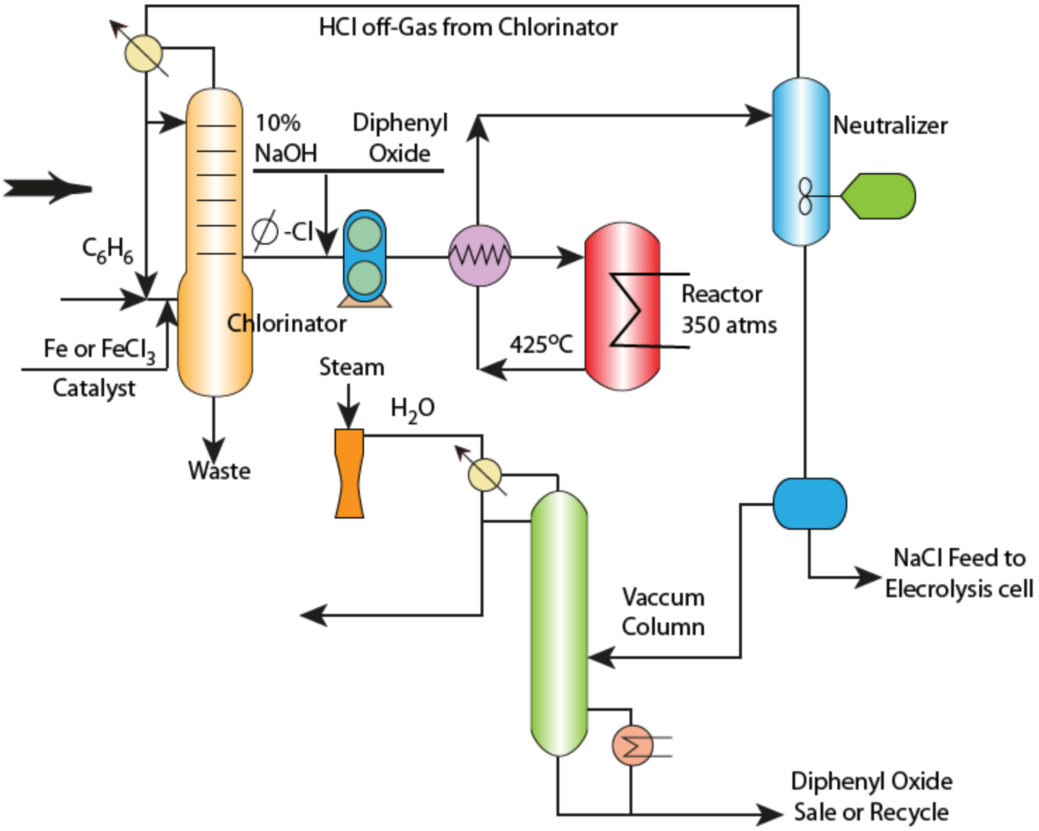


**Figure 23.2 Flow sheet of manufacture of phenol from chlorobenzene route**

- Benzene is first dried. Dry benzene and $FeCl_3$ catalyst enters the chlorination reactor
- After the solid-gas-liquid reaction, the products are further heated up to enter a fractionator
- The fractionator separates benzene as a top product and monochloro benzene as the bottom product. The top product also consists of HCl off gas that is obtained as the vapour stream from the partial condenser.
- The benzene is further cooled and sent back to the reactor and also as a reflux to the fractionator.
- The bottom product monochloro benzene is mixed with 10 % NaOH solution and diphenyl oxide to enter a high pressure pump followed with heat integrated heat exchanger that pre-heats the feed to higher temperature.
- The feed then enters the causticization reactor which has cooling water tubes to control the temperature.
- The product stream is cooled using heat integrated exchanger and then enters a neutralizer that is fed with the HCl obtained from the fractionator partial condenser.
- After neutralization, the product phenol is separated from the aqueous phase using gravity settling principle.

- The organic layer rich in phenol is sent to a vacuum column to separate the phenol from diphenyl oxide (bottom product). The bottom product is partially recycled to enter the cauticization reactor.

### 23.4.5Technical questions

1. **Why is diphenyl oxide added to the causticization reactor?**

Ans: To suppress the formation of more diphenyl oxide at the causticization reactor.

2. **How can you regenerate $Cl_2$ for this process?**

Ans: Brine when subjected to electrolysis will produce $Cl_2$ and NaOH. Therefore, electrolytic process will be beneficial to produce $Cl_2$ and us e it to the requirements as well as produce excess NaOH and sell it too. This way, the process becomes more commercially attractive.

3. **Can the chlorinator and the fractionators be integrated into a single unit where the bottom section is a reactor and the top section is a fractionator?**

Ans: Yes, this is possible, as after chlorination the products are in vapour state and they can enter the trays above the reactor section of a single column. The heavier product in this case is the monochlorobenzene from fractionation perspective and this is the product as well. Therefore, integrating both reactor and separator in a single unit can reduce the costs significantly.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 24: Styrene and Phthalic Anhydride Production

## *24.1 Introduction*

- In this lecture we present the process technology for the production of styrene and pthalic anhydride
- Styrene is produced from benzene via the ethylbenzene route followed by dehydrogenation
- Pthalic anhydride is produced from Napthalene and o-Xylene
- We first present the process technology associated to styrene production

## *24.2 Styrene*

### 24.2.1 Reactions

Alkylation of Benzene

- Benzene + ethylene → Ethyl benzene
- Catalyst: $AlCl_3$ granules
- $C_2H_5Cl$ provides hydrogen and chlorine free radicals
- Operating conditions: $95^oC$ and 1 atm pressure
- Reaction is exothermic

Dehydrogenation of ethylbenzene

- Ethylbenzene → Styrene + Hydrogen
- Reaction is endothermic
- Catalyst: SnO or FeO
- Operating conditions: $800^oC$

### 24.2.2 Process technology (Figure 24.1)

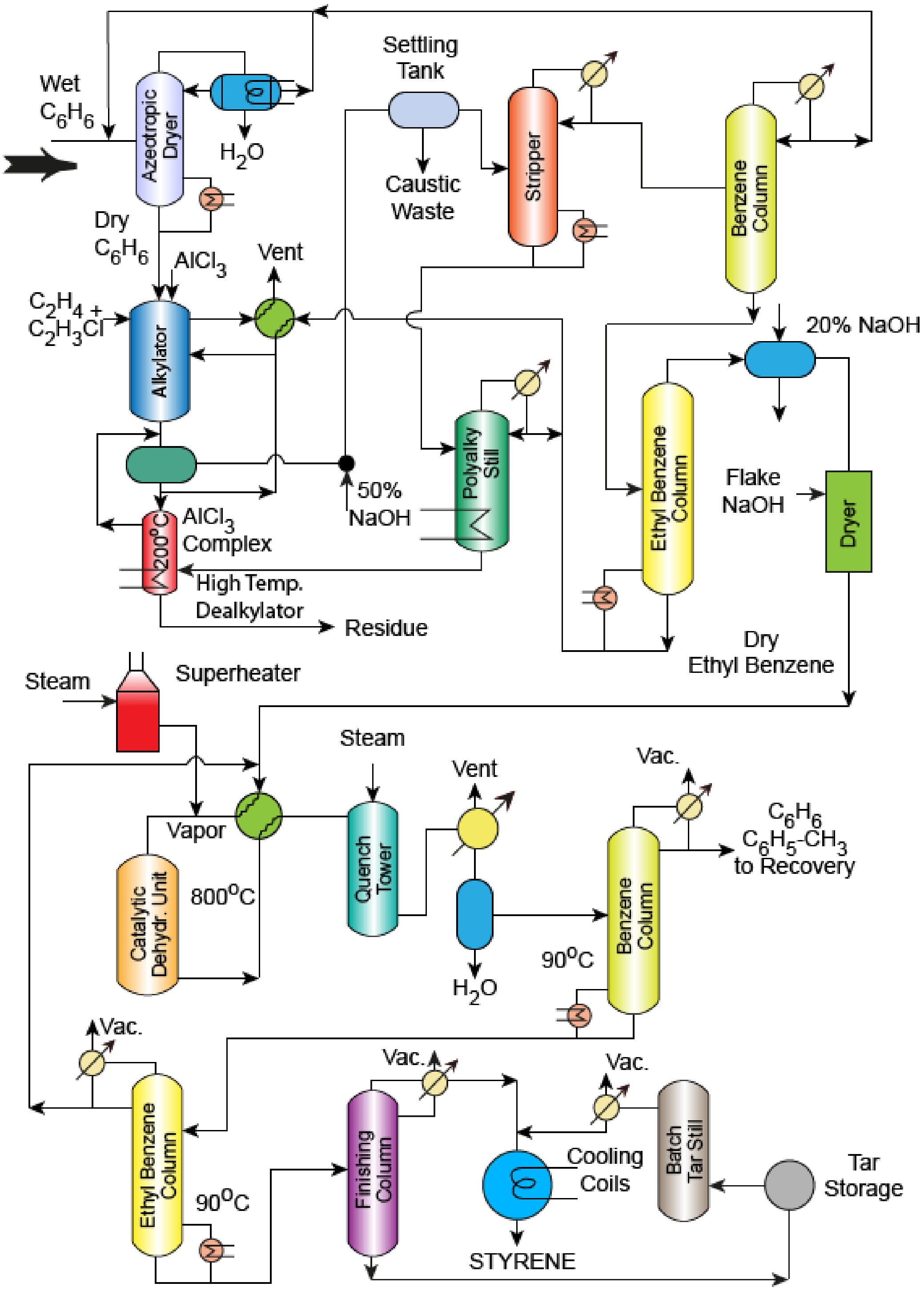


Figure 24.1 Flow sheet of manufacture of styrene

- The process consists of two separate reactor-separator-recycle networks in which one corresponds to the ethylbenzene flow sheet and the other corresponds to styrene flowsheet.
- We first present the flowsheet for ethylbenzene production
- Benzene (wet) is sent first to an azeotropic distillation unit that separates water and produces dry Benzene. Dry Benzene is required so as to avoid

unnecessary reactions in the alkylation reactor as well as damage to the catalyst as alumina can get formed.

- Dry Benzene + Ethylene + Ethyl chloride + $AlCl_3$ enter the alkylator catalyst
- The reactor could be a jacketed tower where water is used as a cooling fluid in the jacket to control the reactor temperature.
- The reactor produces two products namely uncondensible gases and the liquid product in which $AlCl_3$ complex is available. This complex needs to be regenerated and sent back to the alkylator.
- The alkylator product is sent to a cooler which upon cooling to $40^oC$ separates the aluminium chloride complex stream from the product stream. The other stream from the cooler is the ethylbenzene rich product stream.
- The aluminium chloride stream is partially recycled to the alkylator so as to maintain the required catalyst requirements. The other portion of the $AlCl_3$ complex is sent to a dealkylator unit in which the feed is heated to 200 $^oC$. By doing so, the polyethylbenzenes formed in the alkylator are converted to benzene and ethylbenzene (cracking reaction).
- The benzene and ethylbenzene are returned to the cooler.
- The delkylator produces a residue product consisting of tar + $AlCl_3$ mixture.
- From this mixture, $AlCl_3$ is recovered using water extraction as $AlCl_3$ is soluble in water. From there $AlCl_3$ is recovered from the water and returned back to the alkylation reactor.
- The product stream from the cooler consisting of ethylbenzene is mixed with 50 % NaOH to remove acidic impurities. Eventually, after settling waste is eliminated.
- The purified ethylbenzene then enters a stripper that separates ethylbenzene + benzene from the polyalkylbenzenes. The polyalkylbenzenes are sent to a polyalkyl still that separates the benzene + ethylbenzenes from the polyalkylbenzenes (bottom product). The polyalkyl still is operated under vacuum. The polyalkylbenzenes are fed to the dealkylator and the benzene + ethylbenzene rich stream is sent to a heat integrated exchanger that extracts heat from the vent gases and then eventually enters the alkylation reactor.
- The top product from the stripper is ethylbenzene + benzene and it enters a benzene column that separates wet benzene from crude ethylbenzene. The wet benzene is recycled to the azeotropic dryer where it is mixed with fresh wet benzene to enter the azeotropic dryer.
- The crude ethylbenzene is further purified in a fractionator where the bottom product (with benzene) is mixed with the top product of the polyalkyl still. Thereby, the stream enters the heat integrated exchanger.
- The ethylbenzene is further subjected to caustic wash and finally it is sent to a dryer to produce dry ethylbenzene.
- We now move to the dehydrogenation flow sheet.
- The ethylbenzene (dry) is heated with superheated steam to enter the catalytic dehydrogenator. Excess steam is used in this process. The feed pre-heating is

carried out using the product vapour stream. The reaction is gas phase catalytic reaction.

- The vapour stream after cooling with the feed stream in a heat integrated exchanger is fed to a quench tower using steam quenching.
- After quenching, partial condensation of the quenched vapors produces three streams one being the vapour vent, the other being water and the third being the organic phase rich with styrene.
- The styrene rich stream is sent first to a benzene column to recover the benzene + toluene and this is sent to a benzene-toluene distillation column to recover benzene. The benzene is sent to the azeotropic distillation unit as a raw-material.
- The bottom product from the benzene column enters an ethylbenzene column which separates ethylbenzene from the styrene stream. The ethylbenzene stream is mixed with the dry ethylbenzene to enter the catalytic dehydrogenator.
- The bottom product from the ethylbenzene column is the styrene enriched stream and this is sent to the finishing column where styrene is further purified from unwanted impurities such as tar. The tar is further batch distilled to recover styrene from the tar. The styrene finishing column also produces styrene product. Both styrene products from batch still and styrene finishing column are mixed and cooled to store as styrene product.
- All three columns namely benzene, ethylbenzene and finishing columns are operated under vacuum.

## 24.2.3 Uses :

Styrene is mainly used for making plastic toys and model kits. Moreover, housing for machines as well as refrigerator doors and air conditioner cases are made of styrene.

## 24.2.4 Technical questions

1. **Explain how azeotropic distillation unit functions to convert wet benzene to dry benzene?**

Ans: Wet benzene upon heating produces a heterogenous azeotrope at the top and dry benzene at the bottom. Therefore, the unit upon condensation of the top vapors produces two streams namely water and benzene rich wet stream which is recycled back as the reflux stream.

2. **Why is the benzene + ethylbenzene stream returned back to the cooler but not the alkylation reactor?**

Ans: The alkylation reactor should be fed with very important chemicals only. It is possible that the temperatures prevailing in the dealkylator could enable the loss of polyalkylbenzenes to the vapour. Therefore, there is no point in feeding this stream to the alkylator. Instead the stream is sent to the cooler so that any polyalkylbenzenes could be condensed back and sent to the dealkylator again.

3. **Why the $AlCl_3$ complex is partially returned to the reactor?**

Ans: To maintain the required catalyst conditions. If not, then $AlCl_3$ fresh has to be provided to the reactor as $AlCl_3$ forms a complex with the hydrocarbons and would leave the alkylator along with the product streams.

4. **Why do polyalkylbenzenes enter the ethylbenzene rich product?**

Ans: This is the basic problem of the equilibrium separation factors of polyalkylbenzenes between the $AlCl_3$ complex rich product and the ethylbenzene rich product. Since sharp distribution of these compounds is not possible, polyalkylbenzenes get distributed between both these organic phases.

5. **Why there are ethylbenzene + benzenes still available in the bottom product of the stripper?**

Ans: The answer is same as that of question 3 i.e., the phase equilibrium limitations enable the availability of both benzene + ethylbenzene in the polyalkylbenzene stream.

6. **Why the benzene is wet from the benzene column?**

Ans: This is because caustic wash operation enabled the contact with water and some water will enter the organic phase due to phase equilibrium of water with the organic phase. This water therefore enters the benzene stream from the benzene column.

7. **Why caustic wash followed by drying is carried out is carried out for the ethylbenzene stream?**

Ans: Caustic wash removes any undesired impurities where as dryer removes the water. Both water and acid are important compouds which if not eliminated contribute significantly to side reactions during the heating process with superheated steam. Therefore, totally dry and acid free conditions are targeted for ethylbenzene.

8. **Why vacuum is used in the polyalkyl still unit?**

a) To enhance relative volatility of components that can be easily removed
b) To reduce dissociation of polyalkyl components in the column

9. **Why steam quenching but not water quenching is adopted?**

Ans: Water quenching can give rise to additional reactions. Steam quenching does not allow condensation and hence is safe in that sense not to trigger any unwanted reactions of the styrene and ethylbenzene.

**10. What gases are removed in the vent following quenching tower?**

Ans: Gases such as hydrocarbons that are resultant of undesired cracking are removed as non-condensibles in the partial condenser. These are vented out.

**11. Why tar consist of styrene?**

Ans: Styrene being organic compound has affinity to get dissolved in the tar. Therefore, the batch still is used to extract styrene from the tar.

**12. Why vacuum is used for the separation of benzene, toluene, ethylbenzene and styrene?**

Ans: All these compounds are closely boiling systems. By going for vacuum distillation, we are able to enhance the relative volatility of the components and hence better separation. The increasing order of higher vacuum levels is applied for these three columns in series i.e., benzene column, ethylbenzene column and finishing column.

## *24.3 Pthalic Anhydride*

### 24.3.1Reactions

- Basic raw material is Naphthalene or o-xylene
- Naphthalene + $O_2 \rightarrow$ Pthalic anhydride + $H_2O$ + $CO_2$
- O-Xylene + $O_2 \rightarrow$ Pthalic anhydride + Water
- Side reaction products: Maliec anhydride, Complete combustion products: $CO_2$ and water
- Catalyst: Vanadium pentoxide
- Operating conditions: 340 - 385 $^{o}$C
- Reaction is highly exothermic

## 24.3.2Process technology (Figure 24.2)

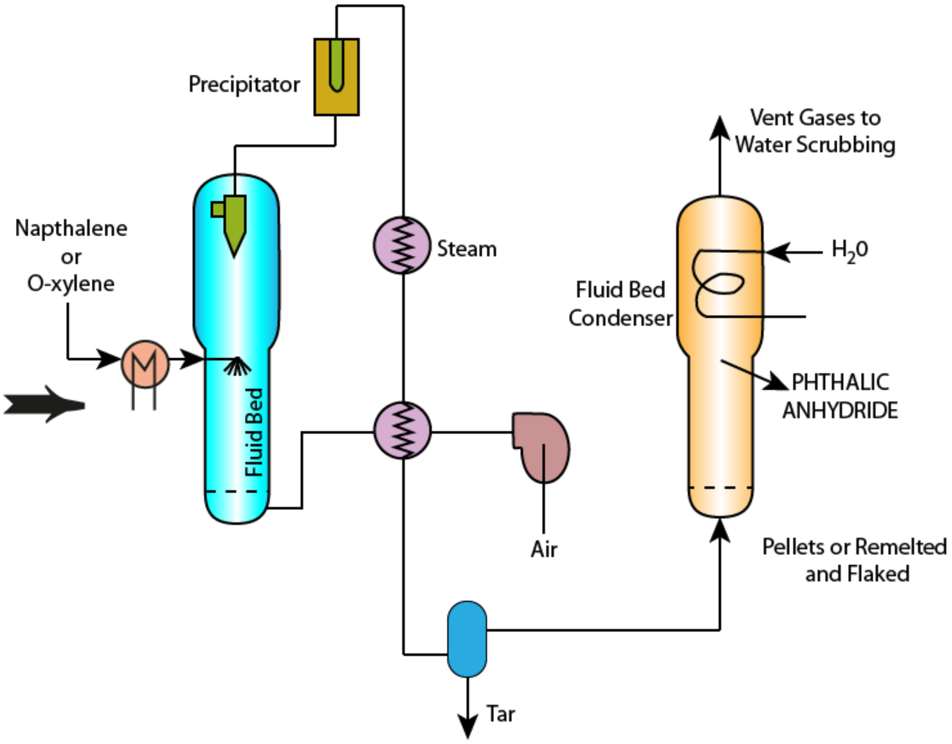


**Figure 24.2 Flow sheet of manufacture of phthalic anhydride**

- In this lecture, we present the usage of both multitubular reactor or fluidized bed reactor for the production of pthalic anhydride.
- While multitubular reactor is demonstrated for o-xylene, the fluidized bed reactor is demonstrated for naphthalene
- Ortho xylene to Pthalic anhydride (Fixed bed reactor)
    - Air is filtered and compressed to enter a air pre-heater
    - O-xylene is also separately vaporized to generate the o-xylene vapour
    - The o-xylene and compressed air enter a multitubular reactor. The reactor design is essentially a shell and tube set up where the catalyst is held in the tubes.
    - Salt solution is circulated to cool the reactor in the shell side. The salt solution that gets heated up is sent to a waste heat recovery boiler to generate process steam.
- Napthalene to Pthalic anhydride (Fludized bed reactor)
    - Napthalene and air are allowed to enter the fluidized bed. Napthalene in molten form is sprayed on to the fluidized bed of catalyst in air.
    - The operating temperature is about 600 $^{o}$C in this case.
    - Eventually, the vapors (+ catalyst dust) enter a cyclone unit to separate the catalyst particles and the vapors from the cyclone separator.
    - The fluidized bed is supplemented with cooling tubes in which salt solution is circulated to eventually obtain steam from the waste heat recovery boiler.

    - The fluidiized bed reactor does not provide higher yields of maleic acid
- Separation network (common for both fluidized bed reactor and packed bed reactor technologies)
    - The reactor effluent (vapour) is sent to a steam generator where the vapors are cooled to condense the pthalic anhydride and the boiler feed water is converted to steam. Here, pthalic anhydride is just cooled to a temperature slightly above its dew point.
    - After cooling the pthalic anhydride, the condensed pthalic anhydride is sent to switch condensers that enable the generation of crude product. The switch condensers enable the generation of pthalic anhydride solid product.
    - The condensers generate maleic anhydride and fumaric acid as the non-condensibles from the switch condensers.
    - The crude product is subsequently melted, distilled and sent to a crystallization process or pellization process to obtain high purity product.

## 24.3.3 Uses :

Phthalic anhydride is used as a versatile intermediate in organic chemical reactions, mainly because it is bifunctional and is cheaply available. It may also be used in the manufacture of phathalate plasticizers like DOP, DEP etc.

## 24.3.4Technical questions

1. **Why is the fluidized bed operated at a higher temperature?**

Ans: The advantage of fluidized bed reactor is to achieve maximum mass transfer and if this principle is better exploited then it is also possible to alter the selectivity of the process. Therefore, fluidization bed is operated at $600^oC$ so that no maleic anhydride is produced and a higher yield of pthalic anhydride is obtained.

2. **Is it justified to use spray of the feed in the case of fluidized bed reactor where as packed bed reactor received the vaporized feed stream?**

Ans: Well, since fludization involves better mass and heat transfer effects when compared to packed bed reactor and since fludized bed reactor is operating at a far higher temperature than the packed bed reactor, it is easy for us to understand that the sprayed feed (i.e., naphthalene) will vaporize instantaneously and will undergo the desired reaction. Also, it is worthy to note that for better facilitating these variations, the gas hour space velocity and air to feed ratio of the fluidized reactor is chosen totally different from those existing in the packed bed reactor.

3. **How do switch condensers assist in generating the crude pthalic anhydride solid product?**

Ans: The switch condensers operate like an on and off switch involving the crystallization of pthalic anhydride and once these crystals are formed they are allowed for partially melting the same (by offing the condensation process) and this way, the flakes melt from the condenser tubes to obtain as a crude pthalic anhydride.

When the crystallization is on, it implies that cooling fluid is circulated and when crystallization is off, then hot fluid is circulated. These are circulated in an on and off mode and hence we got the name as switch condensers.

4. **Why are the switch condensers not called as switch crystallizers but switch condensers?**

Ans: Here, the vapors are received above the dew point of the pthalic anhydride and they are subjected to cooling. Since phthalic anhydride is sublime (solid generating vapour), the crystallization process is called as switch condensation.

5. **In the flowsheet shown, the non-condensible gases such as $CO_2$ are not shown to be vented out. Where do you think they will be vented out and why?**

Ans: $CO_2$ is vented out along with non-condensible gases from the switch condensers. Other than this, there is no other place to remove the same as the product gases are sent to these units only. In case of packed bed reactor technology, the vent also consists of maleic anhydride and fumaric acid which are absorbed in a scrubber using water as a solvent.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012

# Lecture 25: Manufacture of Maleic Anhydride and DDT

## *25.1 Introduction*

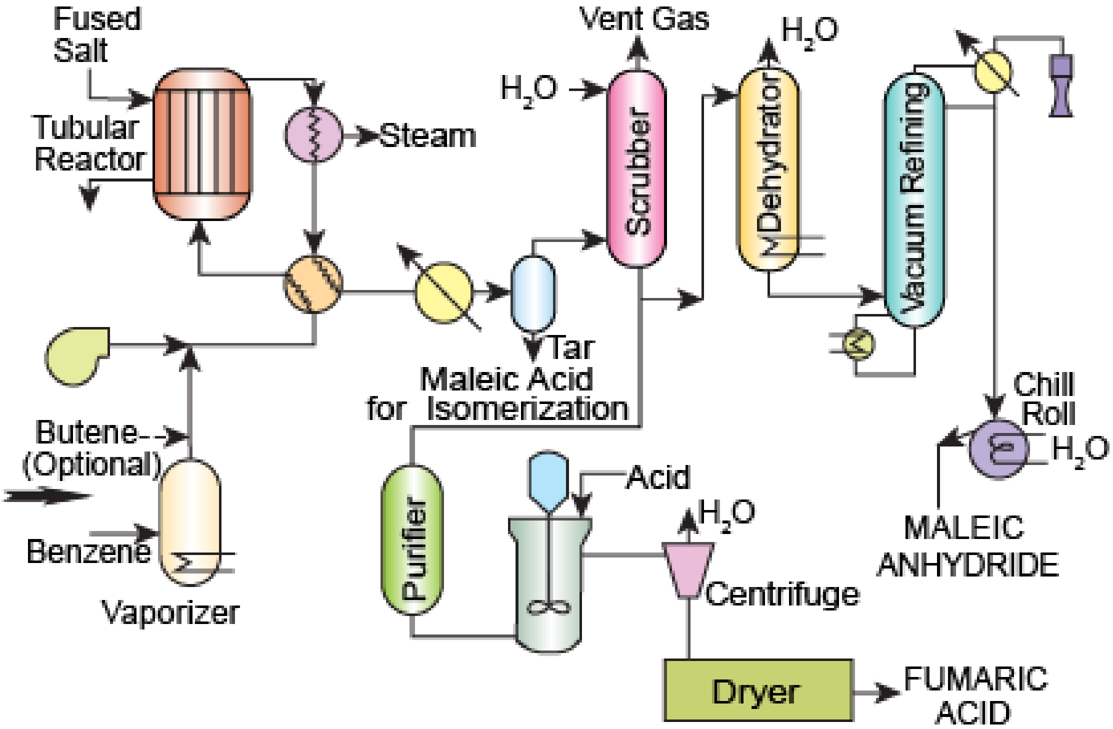
- In this last lecture for the petrochemicals module, we demonstrate the process technology for Maleic anhydride and DDT.
- Maleic anhydride is manufacture from benzene by butane oxidation
- DDT is a pesticide and is manufactured from benzene, chlorine and ethanol using sulphuric acid as a catalyst.
- We next present the process technology for maleic anhydride. Along with this compound, fumaric acid is also produced as another product.

## *25.2 Maleic anhydride &Fumaric acid*

### 25.2.1 Reactions

- Benzene + $O_2$ (Air) → Maleic anhydride + $H_2O$ + $CO_2$
- Reaction is exothermic
- Operating temperature is 400 – 500 $^{o}$C
- Catalyst is $V_2O_5$
- For fumaric acid, the reaction is Maleic acid →Fumaric acid.
- Fumaric acid is an isomer of Maleic acid.
- HCl is used as a catalyst for the isomerisation reactor at normal pressure and temperature.

### 25.2.2 Process technology(Figure 25.1)



- The process technology is similar to phthalic anhydride production.
- Benzene or butane is first vaporized in excess air.
- Then the mixture enters the catalytic tubular reactor (with shell arrangement). The catalytic reactor is circulated with salt solution so as to absorb the heat generated using the reaction.
- The reactor products enter a waste steam recovery boiler where the boiler water is converted to steam.
- The product vapors eventually enter an integrated heat exchanger to exchange heat with the pre-heated feed stream.
- Eventually, the vapors are condensed followed with gravity settling to remove tar as a product in the gravity settling. The vapors then enter a water scrubber to obtain 40 % maleic acid solution. The leaving gases consist mainly of $CO_{2.}$
- The maleic acid from the absorber is partially sent to a dehydrator that removes water using azeotropic distillation principle. The purified maleic anhydride product is further sent to vacuum distillation to obtain the maleic anhydride product.
- The dilute maleic acid solution is partially sent to an isomerisation unit where HCl is used as the isomerisation catalyst.
- After reaction, the product is sent to a centrifuge that separates water from the fumaric acid.
- Eventually, fumaric acid is sent to a drier to obtain dry fumaric acid.

## 25.2.3 Uses :

Maleic anhydride can be used as a highly reactive and versatile raw material. It can be used in the manufacture of alkyd resins, which in turn are used for making paints and coatings. It can also be used in making agricultural chemicals like herbicides, pesticides and plant growth regulators.

## 25.2.4 Technical questions

1. **Whyisbenzene separately vaporized in excess air ?**

Ans. To avoid the formation of explosive compositions, benzene is separately vaporized and then mixed with air. The lower flammability limit of benzene-air mixture is 1.35 % and the upper flammability limit of benzene is 6.35 %. Therefore, with such low levels of flammability limits, heating the benzene in hot process air can keep the process safe. Directly generating benzene vapors and mixing it with air is more dangerous.

2. **Explain in brief how azeotropic distillation of maleic acid is carried out to generate maleic anhydride.**

Ans. The aqueous maleic acid is fed to the azeotropic distillation column which is fed with an azeotropic agent such as xylene. The water is removed along with xylene as overhead vapors as a minimum boiling heterogenousazeotrope as the top product and the bottom product is the maleic anhydride. The heterogeneous azeotrope can be easily separated from the xylene with gravity settling principle and the recovered xylene is fed back to the distillation column as the reflux stream.

3. **Explain why waste steam recovery boiler is kept before heat integrated exchanger from the vapour products perspective**

Ans. The reaction is highly exothermic and heating the feed to a high temperature is not desired. Had it been so, the waste steam recovery boiler would be kept after the heat integrated exchanger. This way, we generate good quality process steam from waste heat recovery boiler.

4. **Explain how the usage of centrifuge is justified from process technology perspective**

Ans. From physical property data, the solubility of maleic acid and fumaric acids are 68 g/100 ml water and 0.63 g/100 ml water respectively. This indicates that while maleic acid is soluble in water, fumaric acid is not. Therefore, after isomerisation reaction, the fumaric acid solids rich solution is sent to a centrifuge so as to separate the solids from the water. This clearly indicates how physical properties play an important role in choosing the separation process.

5. **Can the process steam generated from the waste heat recovery boiler be also used for reboiler requirements in the azeotropic distillation unit, benzene vaporizer, vacuum distillation unit etc**. ?

Ans. Yes, this way we reduce the total utility requirements in the process. In fact the exact steam requirements (fresh) cannot be estimated unless we have a good idea of the total energy balances for the system.

6. **Why is vacuum distillation required for maleic anhydride refining ?**

Ans. Maleic anhydride tends to polymerize upon aging and heating. Therefore, heating the maleic anhydride in vacuum conditions reduces the boiling point. Also, maleic anhydride is very corrosive and corrosiveness of any compound enhances with temperature. With all these limitations, vacuum distillation would suite the requirement.

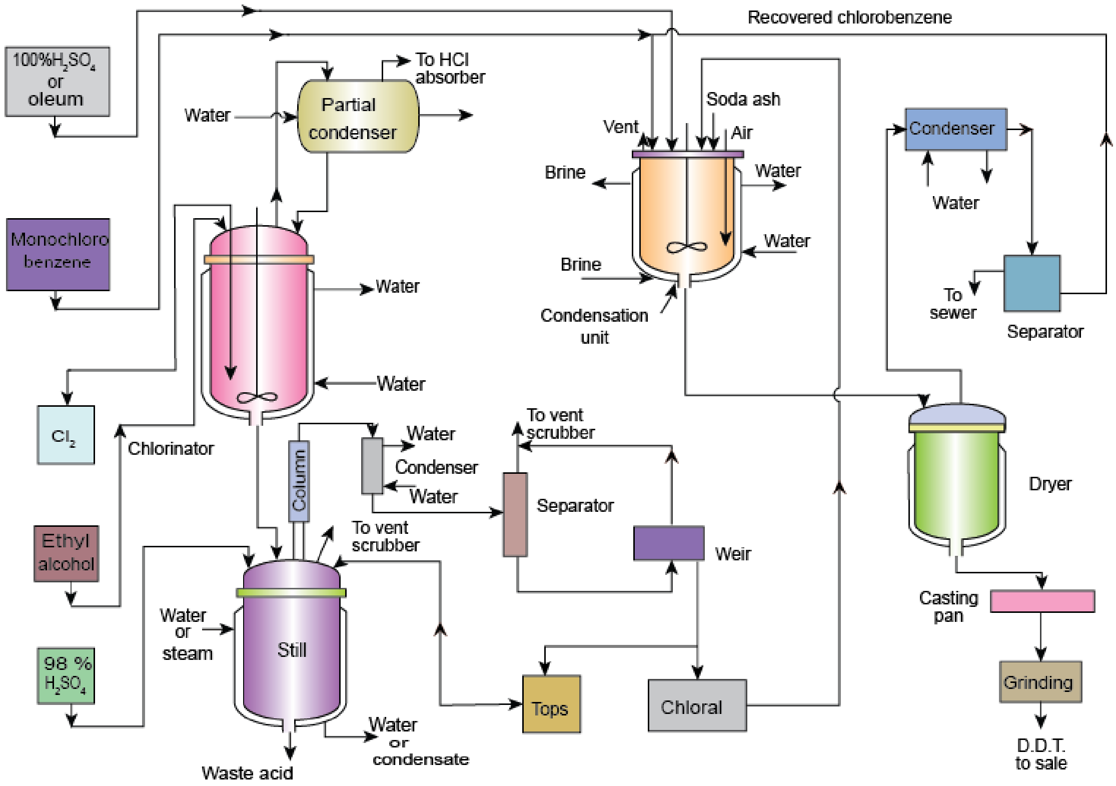
## *25.3 DDT*

### 25.3.1 Reactions

- DDT refers to Dichlorodiphenyltrichloroethane.
- DDT is produced by a reaction between monochlorobenzene and chloral in the presence of Oleum as catalyst.
    - Monochlorobenzene + Chloral → DDT + $H_2O$
- Therefore, to prepare DDT, first we need to prepare Chloral and purify it to the highest standard.

- Chloral is prepared by first forming chloral hydrate using chlorination of benzene route.
- The reaction for chloral is presented as
  - $4\ Cl_2 + C_2H_5OH + H_2O \rightarrow Cl_3CCH(OH)_2 + 5\ HCl$
- Then chloral hydrate is allowed to distill in the presence of sulphuric acid which dessicatesthe chloral hydrate to chloral.

## 25.3.2 Process Technology



- In the process technology, we first discuss the process technology of chloral which is an important ingredient.
- Dry chlorine is first absorbed into ethanol at room temperature conditions. In this process, the alcohol turns to a syrupy fluid. The operation occurs in a chlorination tank which produces chloral hydrate and HCl.
- From the chlorination tank, HCl is separated by using partial condenser. The uncondensibleHCl is sent for gas recovery using scrubbing. The liquid stream from the partial condenser is sent back to the chlorinator.
- The condensate from the chlorination tank is sent to a still, where distillation is facilitated in the presence of sulphuric acid which acts as a dessicant. Eventually, the still is operated at high temperature and for this purpose, steam is used for heating purposes. To control the operation, cooling water is also circulated in the jacket, as chloral hydrate conversion to chloral is a sensitive reaction.
- After the reaction, the batch still produces the waste acid as a product at the bottom and the clear chloral liquid at the top along with the vent gases.

- Eventually chloral is treated with lime to remove dissolved acidic impurities.
- The purified crude chloral is further sent to distillation in another still to remove chloral hydrates present in the stream. Therefore the second distillation unit is also operated in the presence of $H_2SO_4$.Vapors released during this step (from the partial condenser) are sent to the vent scrubber.
- Eventually, chloral is produced from the distillation unit and chloral hydrate is recycled back to the chloral hydrate converter to chloral.
- To manufacture DDT, purified chloral, monochlorobenzene, oleum are allowed to enter the DDT condensation unit.
- After condensation, the organic layer and spent acid are withdrawn. The organic layer consists of DDT and monochlorobenzene. This is first neutralized with soda ash.
- After reaction, the organic layer is sent to a dryer where the vapors generated from dryer enter a total condenser followed with gravity settling separator. The gravity settling unit separates monochlorobenzene from other organic impurities. The monochlorobenzene is recycled back to the condensation unit that is meant for preparing the DDT.
- The Dryer produces DDT powder which is sent for casting/pelletization process to obtain the DDT in either flakes or in pellets for sale.

With this flowsheet, we finish Module 2 in which process technology for good number of petrochemicals has been elaborated. We next move to the third module namely polymer technology.

## 25.3.3. Uses :

DDT is mainly used as a pesticide. DDT was the first of the modern insecticides. However, the use of this chemical has been restricted to some degree due to its harmful ill effects.

## 25.3.4Technical questions

1. **Whyis the chloral hydrate converter fed with steam and water alternatively?**

Ans. The chloral hydrate conversion to chloral takes good amount of time and switch type heating and cooling is required. Heating only with steam will enable faster decomposition of chloral which is very reactive and unstable. Therefore, the switch type heating is enabled in this case.

2. **Why is air circulated in the DDT condensation unit?**

Ans. In the DDT condensation unit, two liquids need to be thoroughly mixed. For this purpose, air is sparged so that interfacial area of the reactants enhances drastically due to the sparging effect.

3. **DDT is a solid but the organic layer from the DDT condensation unit does not have any solid. Why?**

Ans. DDT is soluble in most organic solvents but not in water. Therefore, upon drying, the liquid mass consisting of dissolved DDT in monochlorobenzene gets generated as a solid product.

4. **Whyarevapors released from the still despite knowing the fact that no HCl is produced from the still?**

Ans. Due to the high temperature of the still, it is possible that some chloral hydrate decomposes to unwanted compounds such as HCl, chloroform and ethanol. These compounds will be non-condensible at the condenser operating temperatures and therefore, these are vented out.

5. **Discuss what technology you would adopt to recover the $H_2SO_4$ from the spent solutions.**

Ans. The sulphuric acid stream from the units will have higher concentrations of organics. Therefore, technology should be targeted that enables the recovery of these organics. Multiple effect evaporator appears to be suitable in this regard to concentrate the sulphuric acid as well as eliminate the organic impurities. The regenerated sulphuric acid with its regained original strength can be reused for the DDT condensation and chloral hydrate conversion operations.

**References:**

Dryden C. E., Outlines of Chemical Technology, East-West Press, 2008

Kirk R. E., Othmer D. F., Encyclopedia of Chemical Technology, John Wiley and Sons, 1999-2012