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COURSE MATERIAL

PETROLEUM AND PETRO CHEMICAL TECHNOLOGY UNIT IV SCH1308

UNIT IV CHEMICALS FROM METHANE AND ETHANE

1.0 Petrochemicals: Overview

1.1Introduction

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.

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.

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."

1.2 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.

1.3 Manufacture of Methanol from Synthesis Gas

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

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.

Process Technology

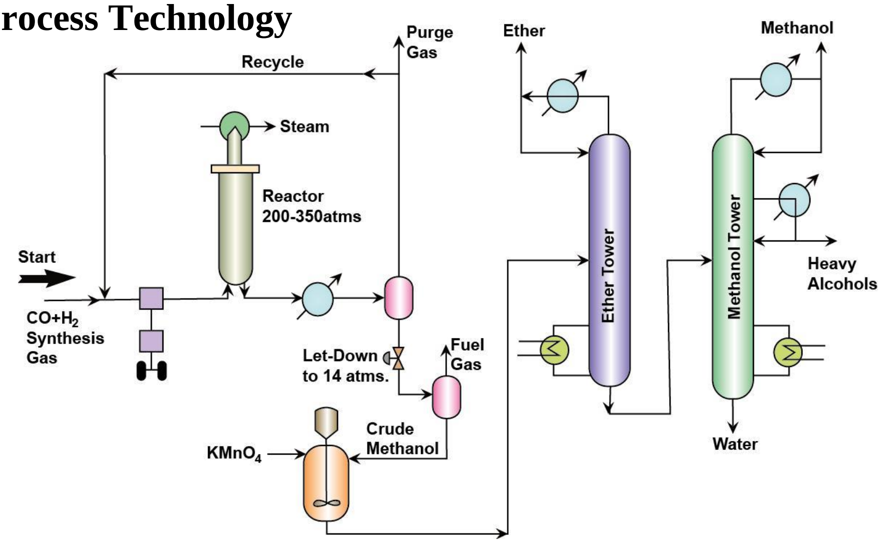


Figure: Flow sheet of manufacture of Methanol from Synthesis Gas

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.

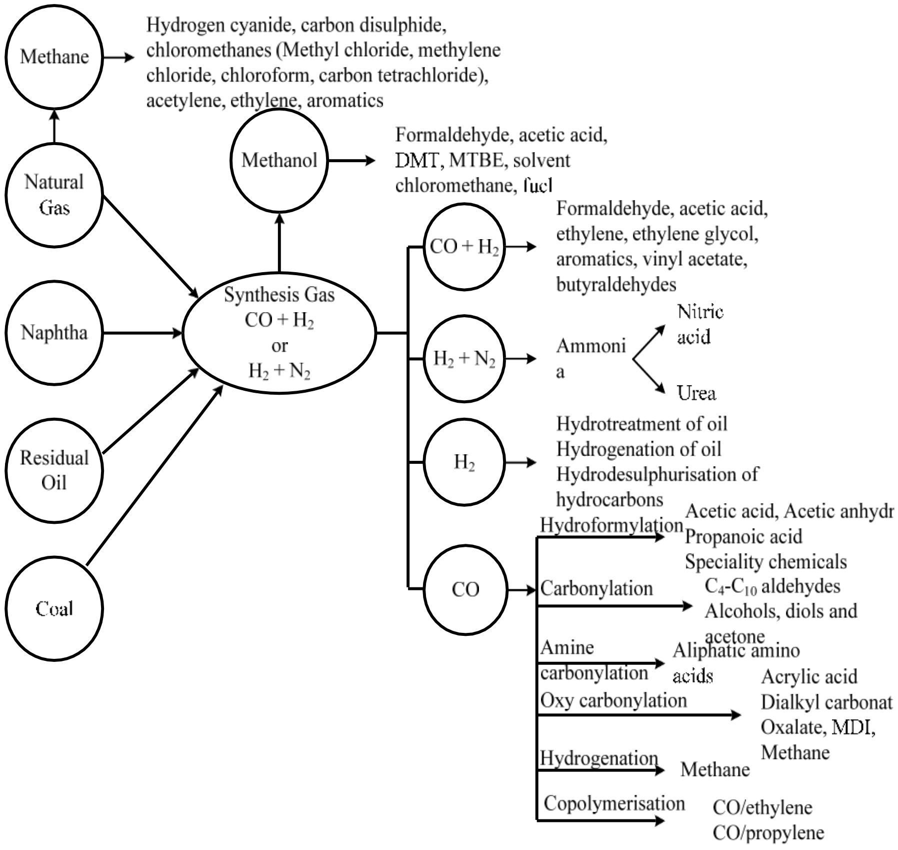
The liquid stream then enters a mixer fed with $KMNO_4$ so as to remove traces of impurities such as ketones, aldehydes etc.

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.

Methane and synthesis gas are important petrochemical feedstock for manufacture of a large number of chemicals, which are used directly or as intermediates, many of these products are number of which are finding use in plastic, synthetic fiber, rubber, pharmaceutical and other industries. ‘Synthesis gas’ is commonly used to describe two basic gas mixtures - synthesis gas containing CO, hydrogen and synthesis gas containing hydrogen and nitrogen for the production of ammonia. Major requirements of synthesis gas in world scale petrochemical are given.

Some of the emerging technologies in utilization of synthesis gas and methane for the production of petrochemicals, are Fischer-Tropsch synthesis, oxidative coupling of methane with chlorine to yield ethane and ethylene, methanol to olefin technology (MTO). Fischer-Tropsch synthesis is being studied in great detail world over and it is promising to be a future technology for manufacture of olefins from synthesis gas. CO that can be separated from synthesis gas either by cryogenic or by pressure swing adsorption is a promising feedstock for production of a variety of products. Product profile of methane, synthesis gas and CO based building blocks are given in Figure BELOW



1.4 SYNTHESIS GAS

Methane and synthesis gas are important petrochemical feedstock for the manufacture of a large number of chemicals, which are used directly or as intermediates, a number of which are finding use in plastic, synthetic fiber, rubber, pharmaceutical and other industries. 'Synthesis gas' is commonly used to describe two basic gas mixtures - synthesis gas containing CO, hydrogen and synthesis gas containing hydrogen and nitrogen for the production of ammonia.

Petrochemical derivatives based on synthesis gas and carbon monoxide have experienced steady growth due to large scale utilization of methanol and development of a carbonylation process for acetic acid and Oxo synthesis process for detergents, plasticizers, and alcohols. Recent market studies show that there will be a dramatic increase in demand of CO and syngas derivatives .

Methanol is the largest consumer of synthesis gas. The reformed gas is to meet certain requirements with regard to its composition. It is characterized by the stoichiometric conversion factor, which differs from case to case

1.5 RAW MATERIALS FOR SYNTHESIS GAS

Various raw materials for synthesis gas production are natural gas, refinery gases, naphtha, fuel oil/residual heavy hydrocarbons and coal. Although coal was earlier used for production of synthesis gas, it has now been replaced by petroleum fractions and natural gas. Petrocoke is the emerging source for Synthesis gas. Coal is again getting importance alone are with combination of petroleum coke. Various Routes for Synthesis gas and Ammonia and Methanol manufacture is shown in Figure. Reactions in the manufacture of synthesis gas by Steam reforming and Partial oxidation in Table

Process Technology

Various synthesis gas production technologies are steam methane reforming, naphtha reforming, auto-thermal reforming, oxygen secondary reforming, and partial oxidation of heavy hydrocarbons, petroleum coke and coal.

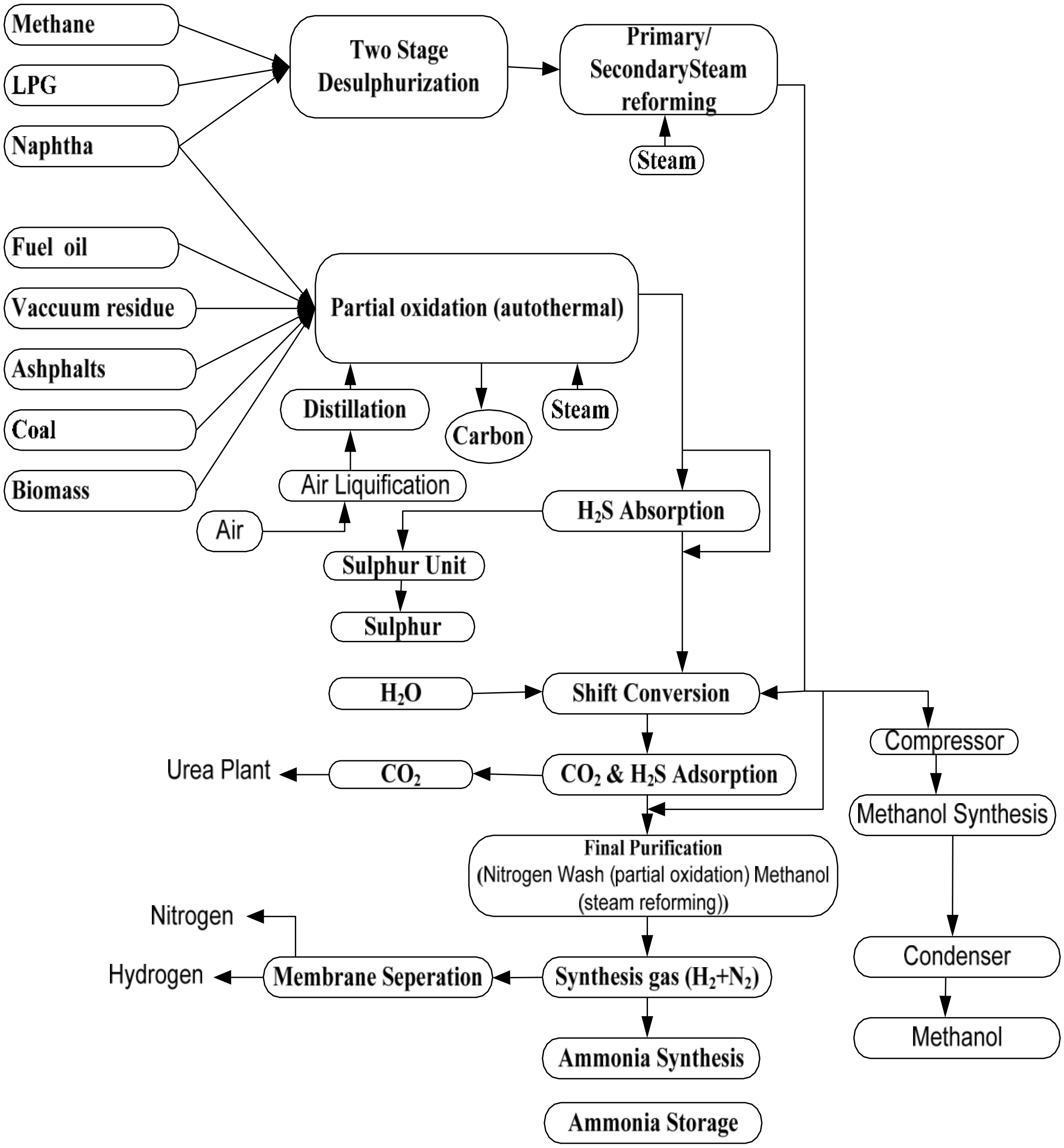
Various steps involved in synthesis gas production through steam reforming are:

- Desulphurization of gas
- Steam reforming and compression

- Separation of CO_2

Various available synthesis gas generation schemes are:

- Conventional steam reforming
- Partial oxidation
- Combined reforming
- Parallel reforming
- Gas heated reforming



Various Routes for Synthesis gas and Ammonia and Methanol manufacture

Reactions in the manufacture of synthesis gas by Steam reforming and Partial oxidation

Process steps	Reaction	Process Condition
Desulphurisation: 1st Stage First Stage 2nd Stage Second Stage	$C_2H_5SH + H_2 \rightarrow H_2S + C_2H_6$ $C_6H_5SH + H_2 \rightarrow H_2S + C_6H_6$ $C_4H_4SH + 3H_2 \rightarrow H_2S + C_4H_9$ $CS_2 + 4H_2 \rightarrow 2H_2S + CH_4$ $COS + H_2 \rightarrow H_2S + CO$ $CH_3SC_2H_5 + H_2 \rightarrow H_2S + CH_4 + C_2H_4$ $H_2S + ZnO \rightarrow ZnS + H_2O$	Al-Co-Mo Al-Ni-Mo Catalyst 350-400 ^{o}C Zinc oxide absorbent 200-500 ^{0}C
Steam reforming two stages	$C_nH_m + 1/4(4n-m)H_2O \rightarrow 1/8(4n+m)CH_4 + 1/8(4n-m)CO_2$ $CH_4 + H_2O \rightarrow CO + 3H_2$ $CO + H_2O \rightarrow CO_2 + H_2 \rightleftharpoons$	Nickel catalyst 800 ^{o}C Endothermic reaction
Partial Oxidation	$C_nH_m + [(2n+m)/4 \rightleftharpoons]O_2 \quad nCO + m/2\ H_2O$ $C_nH_m + \rightleftharpoons nH_2O \quad nCO + (n+m/2)\ H_2$ $2CO \quad \rightleftharpoons C + CO_2$ $CO + H_2 \quad C + H_2O$	Exothermic reaction

1.6 METHANOL

Methanol was first obtained by Robert Boylein in the year 1661 through rectification of crude wood vinegar over milk of lime and was named adiaphorous spiritusliglorum. The term methyl was introduced in chemistry in 1835. Methanol is one of the largest volume chemicals produced in the world. Methanol consumption can be separated into three end use categories – chemical feedstock, methyl fuels, and miscellaneous uses. About 71% of the current global consumption of methanol is in the production of formaldehyde, acetic acid, methyl methacrylate, and dimethyl terephthalate. The global methanol industry has experienced very fundamental and structural changes and has settled down considerably.

1.7 METHANOL PROCESS TECHNOLOGY

From the early 1800s until 1920s, the distillation of wood to make wood alcohol was the source of Methanol. The most common industrially favored method for the production of methanol was first developed by BASF in 1923 in Germany from synthesis gas utilising high pressure process using zinc-chromic oxide catalyst. However, due to high capital and compression energy costs compounded by poor catalyst activity, high-pressure process was rendered obsolete when ICI in the year 1966 introduced a low-pressure version of the process at 5-10 MPa and 210-270 ^{o}C, with a new copper-zinc oxide based catalyst of high selectivity and stability.

Process steps involved in the production of methanol are:

- Production of synthesis gas using steam reforming or partial oxidation
- Synthesis of methanol
- High-pressure process (25 – 30 MPa)
- Medium pressure (10-25 MPa) process
- Low-pressure process (5-10 MPa)

Figure BELOW illustrate the production of methanol from steam reforming of natural gas and naphtha.

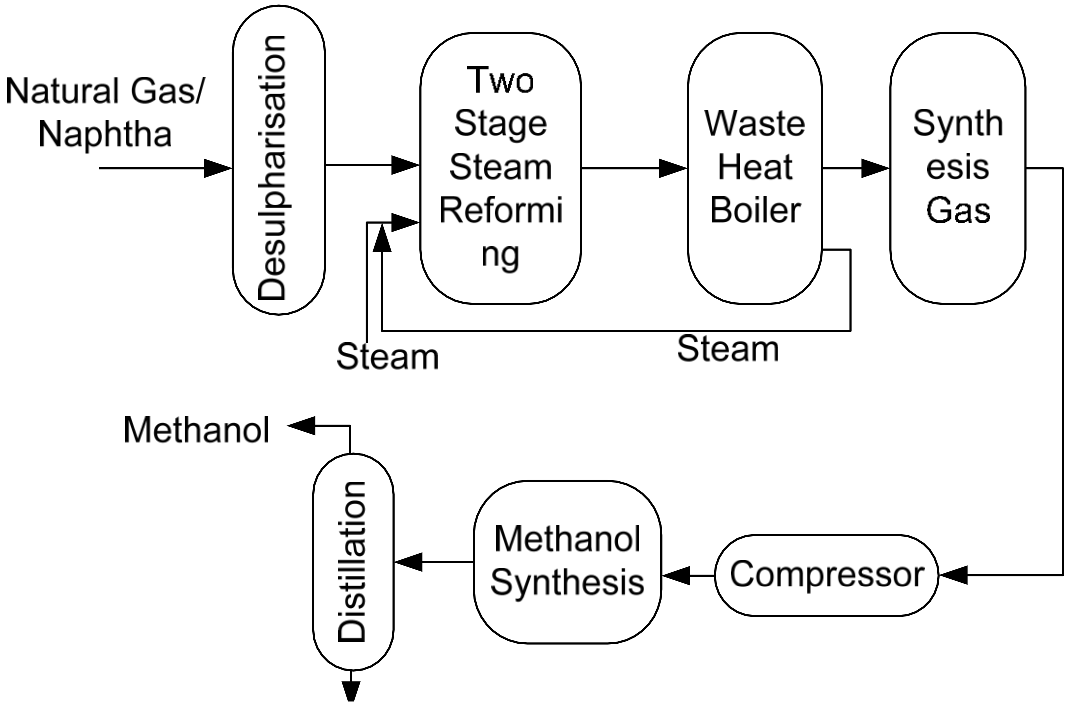


Figure : Methanol from steam reforming of Natural gas and Naphtha

The major reactions take place during methanol synthesis converter can be described by following equilibrium reactions:

$CO + 2\ H_2 \rightarrow CH_3OH$ $\Delta H298\ ^0K = -90.8$ kJ/mol

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ $\Delta H298\ ^0K = -49.5$ kJ/mol

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H300\ ^0K = 41.3$ kJ/mol

The first two reactions are exothermic and proceed with reduction in volume. In order to achieve a maximum yield of methanol and a maximum conversion of synthesis gas, the process must be effected at low temperature and high pressure.

After cooling to ambient temperature, the synthesis gas is compressed to 5.0-10.0 MPa and is added to the synthesis loop which comprises of following items – circulator, converters, heat exchanger, heat recovery exchanger, cooler, and separator. The catalyst used in methanol synthesis must be very selective towards the methanol reaction, i.e. give a reaction rate for methanol production which is faster than that of competing

2.0 Formaldehyde

Introduction

In this lecture, we present the production technology for formaldehyde .
Formaldehyde is produced from methanol

Formaldehyde production

Reactions

Oxidation: $CH_3OH + 0.5\ O_2 \rightarrow HCHO + H_2O$

Pyrolysis: $CH_3OH \rightarrow HCHO + H_2$

Undesired reaction: $CH_3OH + 1.5\ O_2 \rightarrow 2H_2O + CO_2$

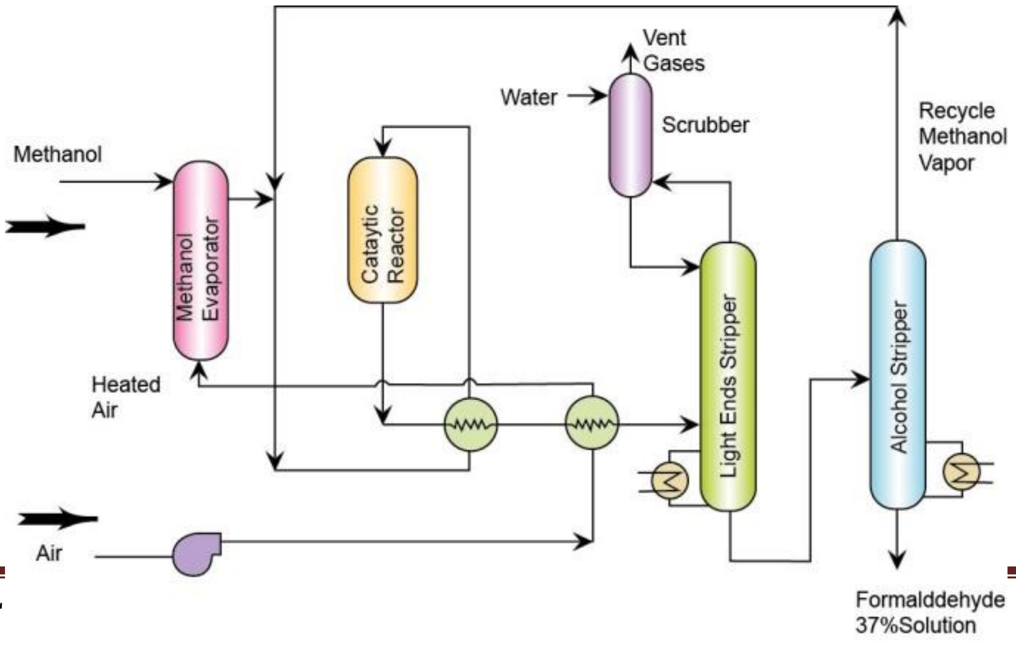
In the above reactions, the first and third are exothermic reactions but the second reaction is endothermic. The reactions are carried out in vapour phase.

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

Operating temperature and pressure: Near about atmospheric pressure and 500 – 600 ^{o}C

Process Technology :

Air is sent for pre-heating using reactor outlet product and heat integration concept.



Flow sheet of Formaldehyde production

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 ^{O}C.

The feed ratio is about 30 – 50 % for $CH_3OH: O_2$

After reaction, the product is a vapour mixture with temperature 450 – 900 ^{O}C

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).

3.0 Hydrocarbon Steam Cracking for Petrochemicals

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.

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.

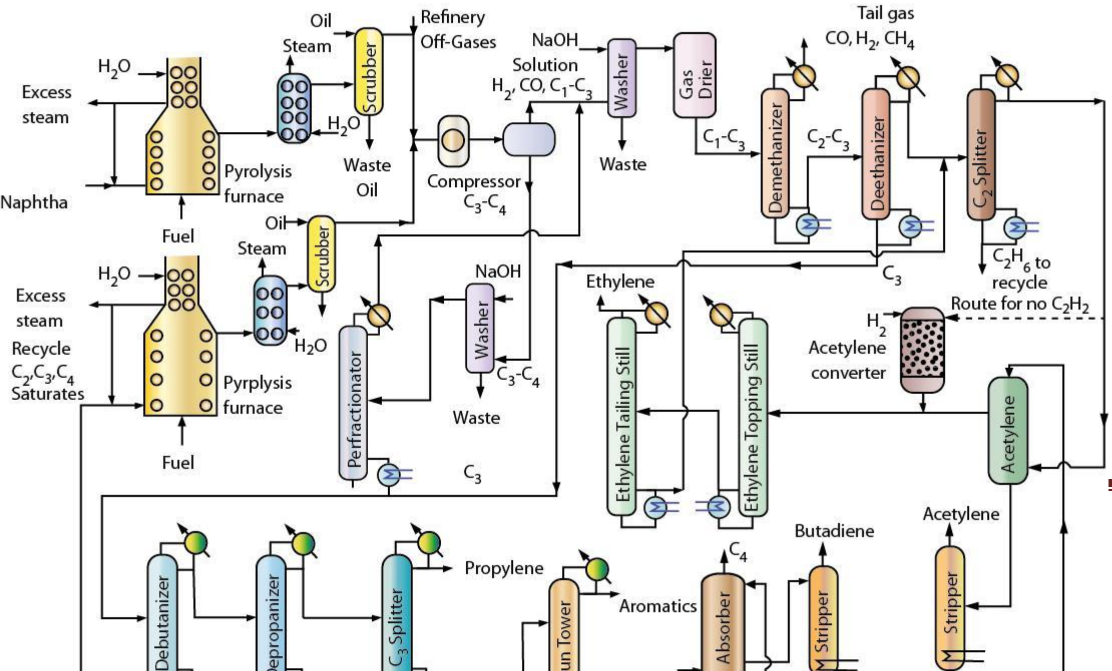
Important separation tasks: Elimination of CO and CO_2, Purification of all products such as ethylene, acetylene etc.

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 ^{o}C (Vapor phase reaction).

Process technology



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 ^{O}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_2s 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. The saturates mixture is recycled to the saturates cracking furnace as a feed stream.

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.

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.

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).

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.

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.

4.0 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

Ethylene dichloride

Reactions

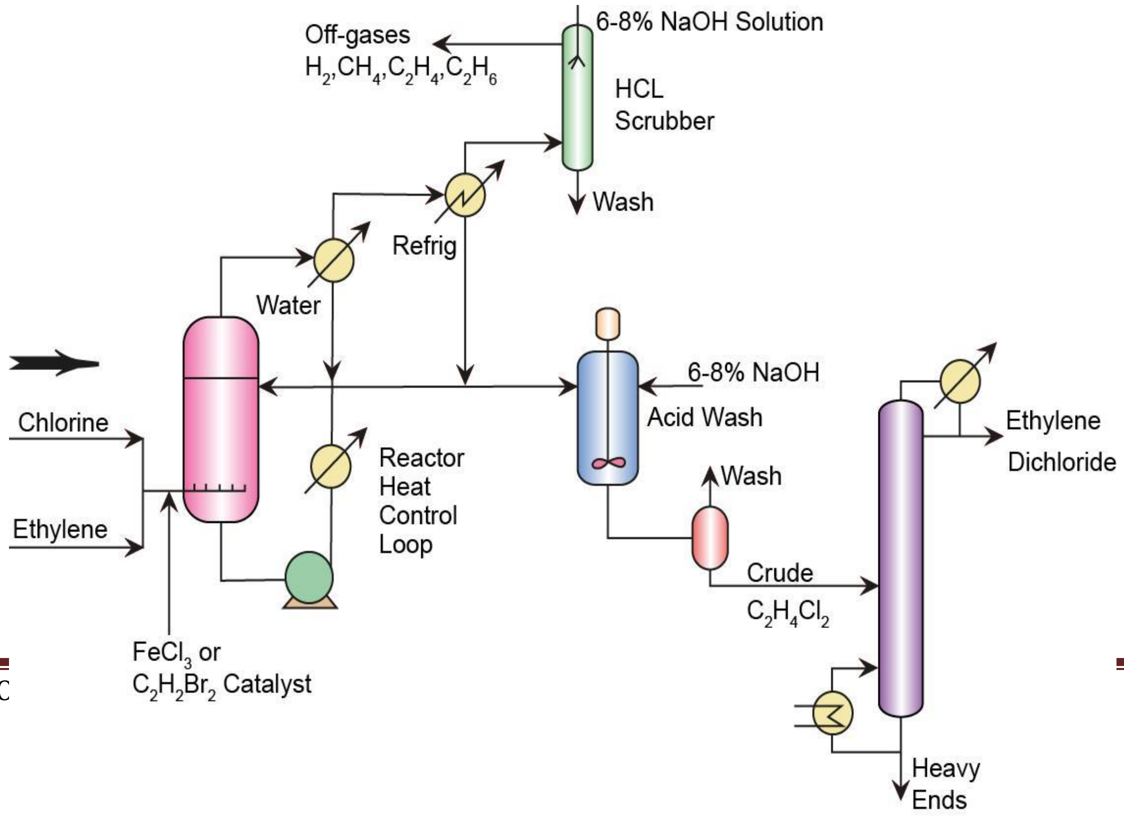
$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

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

Process Technology



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 ^{O}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.

4.1 Vinyl chloride production

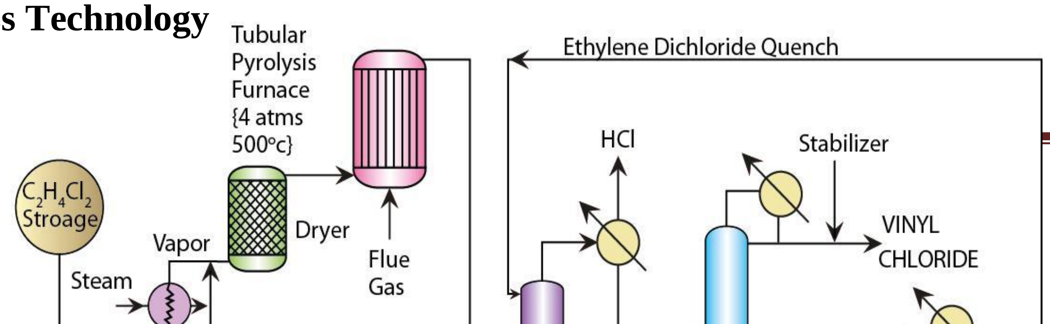
Reaction

$C_2H_4Cl_2 \rightarrow CH_2CHCl + HCl$

Charcoal is used as the catalyst

The reaction is a reversible gas phase reaction

Process Technology



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 ^{O}C. 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.

5.0 FORMALDEHYDE

Some major intermediates derived from formaldehyde are chelating agents, acetal resins, 1,4-

butanediol, polyols, methylene diisocynate. It is also used for the manufacture of wide variety of chemicals, including sealant, herbicides, fertilisers, coating, and pharmaceutical.

Formaldehyde is commercially available as aqueous solution with concentration ranging from 30-56 wt.% HCHO. It is also sold in solid form as paraformaldehyde or trioxane. The production of formaldehyde in India has been growing at a fairly constant rate during last ten years. There are presently about 17 units in India. Installed capacity and production of formaldehyde during 2003-04 was 2.72 lakh tonnes and 1.89 lakh tonnes respectively.

Various industrial processes for manufacture of formaldehyde using silver and iron- molybdenum catalyst are given below:

Catalyst	Process licensor
Silver catalyst processes	Bayer, Chemical construction, Ciba, DuPont, IG Farben, CdF Chemie process, BASF process, ICI process,
Iron-molybdenum catalyst processes	Degussa process, Formox process, Fischer-Adler, Hiag-Lurgi, IFP-CdF Chimle Lumus, Motedisous, Nikka Topsoe, Prolex

Product Profile of Formaldehyde

Product	Uses

Formaldehyde	Thermosetting resin: Phenol, Urea Melamine, Formaldehyde resins Hexamethylenetetramine, Plastic & pharmaceuticals 1,4-Butadiol Methylene diisocyanate Fertiliser, Disinfectant, Biocide Preservative, Reducing agent, Corrosion inhibitor Polyaceta resin p-formaldehyde Pentaerythritol (Explosive-PETN),Alkyl resins

Process diagram for manufacture of formaldehyde using silver and iron-molybdenum catalyst is shown in Figure

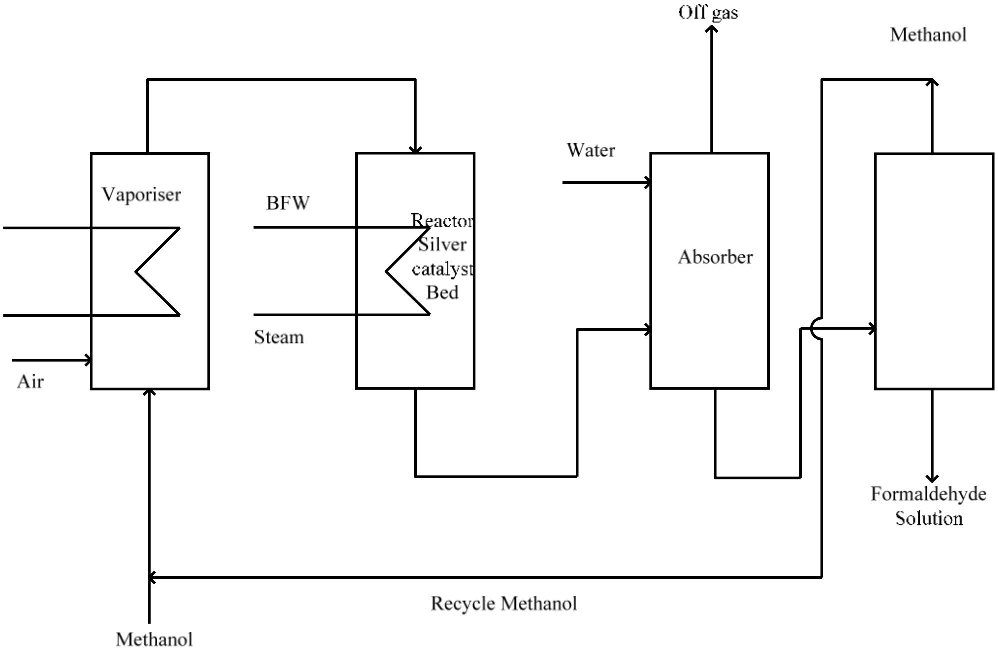


Figure : Formaldehyde Using Silver Catalyst

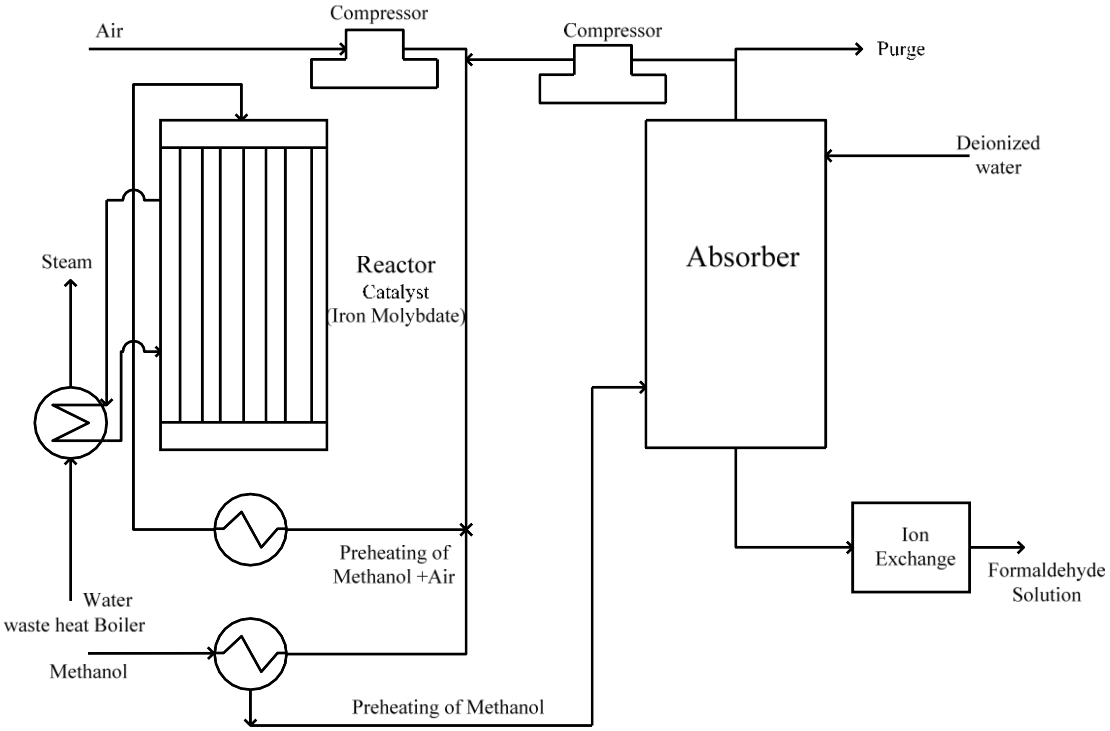


Figure : Formaldehyde from Iron Molybdenum Catalyst

6.0 ACETYLENE

Various Routes for Acetylene:

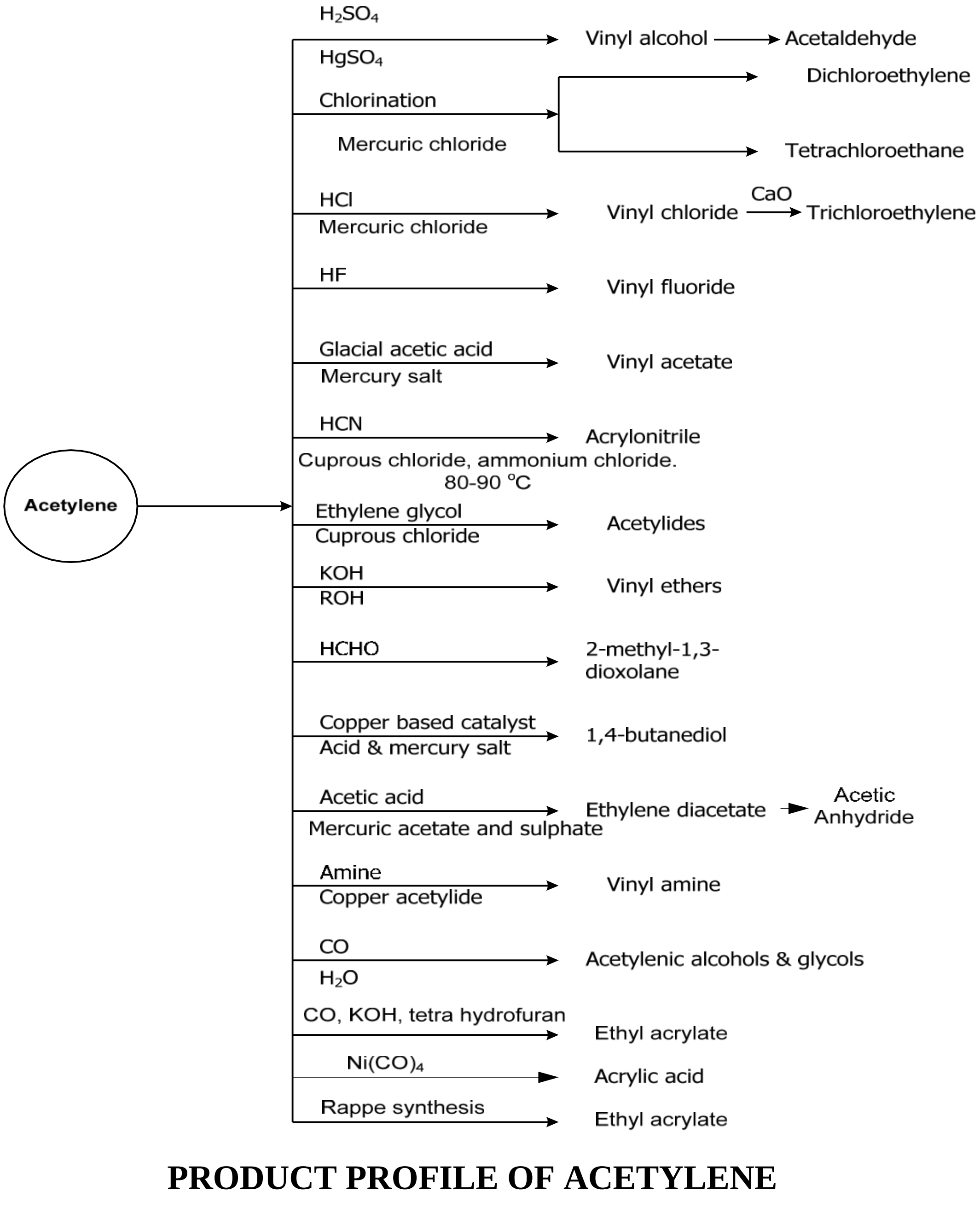
Calcium Carbide Route: This is the oldest method for production of acetylene and still acetylene is produced by this process in small scale as well large scale. Calcium carbide is produced by reacting lime with coke at temperature 2,000-2,100 ^{o}Cin an electric furnace**.** Two processes produce acetylene from calcium carbide process: Wet process and Dry process. Dry process is preferred as in case of calcium hydroxide, which is produced during the process (is produced in the form of dry calcium hydrate).

$CaC_2 + 2\ H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

Acetylene from Cracking of Hydrocarbons: Cracking of hydrocarbons such as methane, ethane, propane, butane, ethylene, and natural gas can make acetylene.

- $2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2$
- $C_2H_4 \longrightarrow C_2H_2 + H_2$
- $C_4H_{10} \longrightarrow C_2H_2 + C_2H_4 + 2\ H_2$

Product Derived from Acetylene: Acetylene is extremely reactive hydrocarbon and was initially was used for the manufacture of large number of chemicals which are now being derived from acetylene route.



PRODUCT PROFILE OF ACETYLENE

Acetaldehyde:

$HC{\equiv}CH + H_2O \longrightarrow CH_3CHO$

rAc ylorit ile: $HC{\equiv}CH+HCN \longrightarrow HC{=}CH{=} CH2{=}CHCN$

Chlorinated solvents:

$HC{\equiv}CH+2Cl_2 \longrightarrow CH_2Cl_2CHCl_2 \longrightarrow CHCl = CCl_2+HCl$

$CHCl = CCl_2+ Cl_2 \longrightarrow CH_2Cl_2CCl_3 \longrightarrow CCl_2 = CCl_2+HCl$

Vinyl acetate:

$HC{\equiv}CH+CH_3COOH \longrightarrow CH_2 = CHOOCCH_3$

Chloreprene

$HC{\equiv}CH+CH_3COOH \longrightarrow CH_2 = CHOOCCH_3$

$CH_2 = CHOOCCH_3+Cl_2 \longrightarrow CH_2{=}CClCH{=}CH_2$

Vinyl Chloride and Vinylidene Chloride

$HC{\equiv}CH+HCl \longrightarrow CH_2 = CHCl$

$CH_2 = CHCl+Cl_2 \longrightarrow CH_2 ClCHCl_2$

$CH_2 ClCHCl_2 \longrightarrow CH_2 = CCl_2+HCl$

Vinyl fluoride:

$HC{\equiv}CH+ HF \longrightarrow CH2{=}CHF$

Reactions in Acetylene derived Chemicals

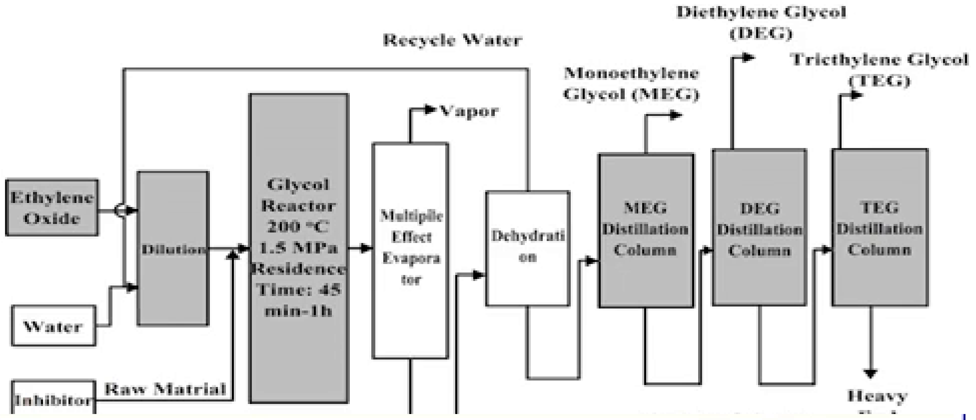
7.0 ETHYLENE GLYCOLS

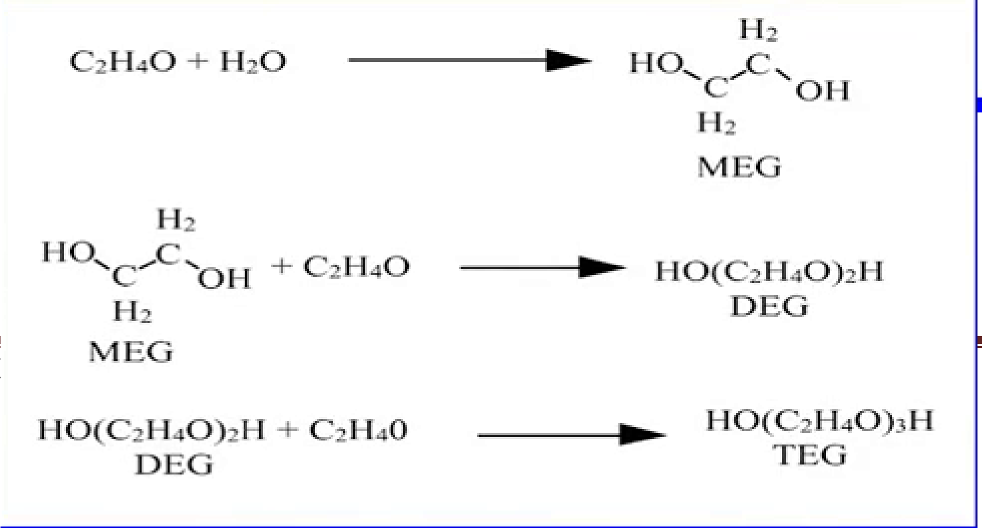
Mono-, Di-, Tri- Ethylene Glycols (MEG,DEG,TEG)

A major petrochemicals and find application in manufacture of polyester and as antifreeze accounts for 70% of Ethylene oxide production. Ethylene oxide preheated to 195°C

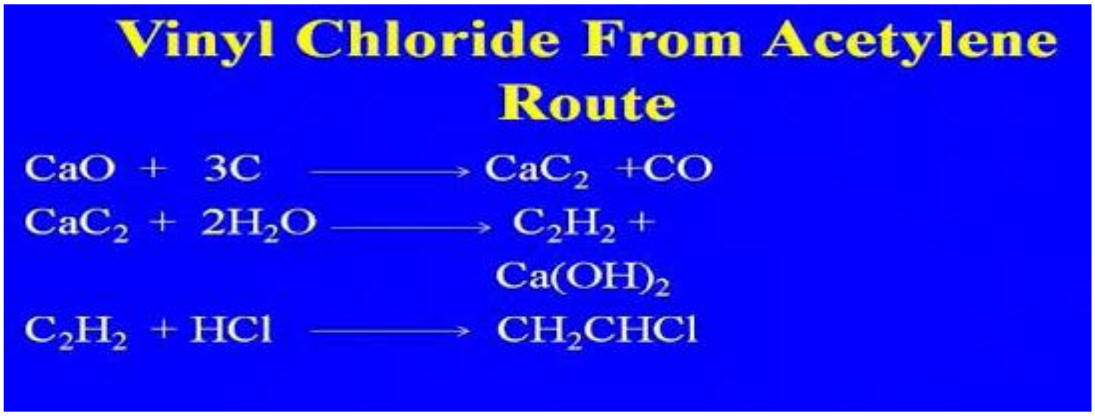
EO: H_20 ratio 10:1 to maximise MEG production.

By Products DEG,TEG





8.0 VINYL CHLORIDE

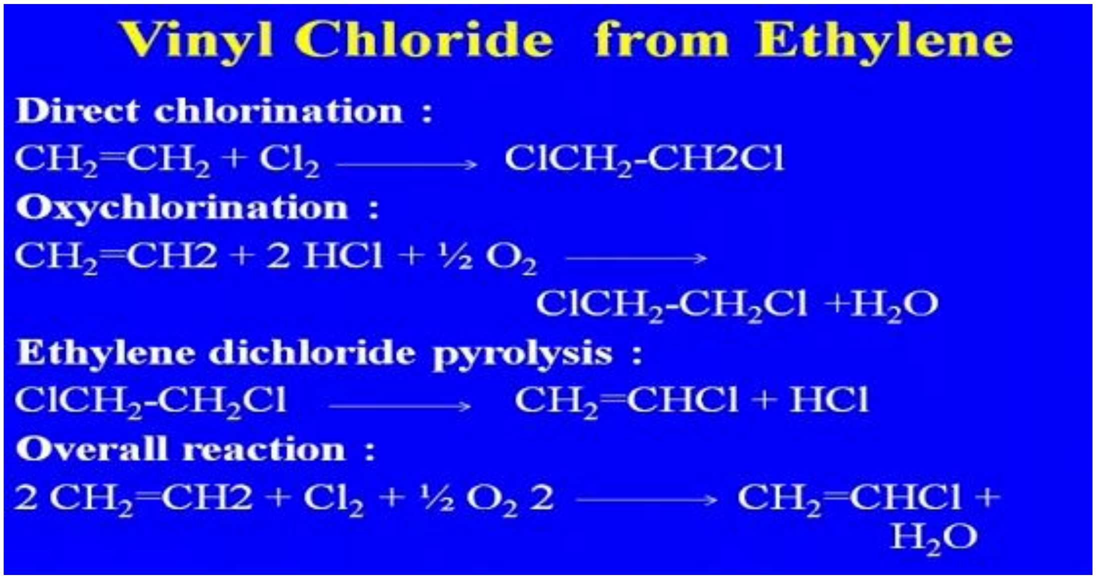


Vinyl Chloride From Acetylene Route

$CaO + 3C \longrightarrow CaC_2 + CO$

$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

$C_2H_2 + HCl \longrightarrow CH_2CHCl$



Vinyl Chloride from Ethylene

Direct chlorination :

$CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2\text{-}CH2Cl$

Oxychlorination :

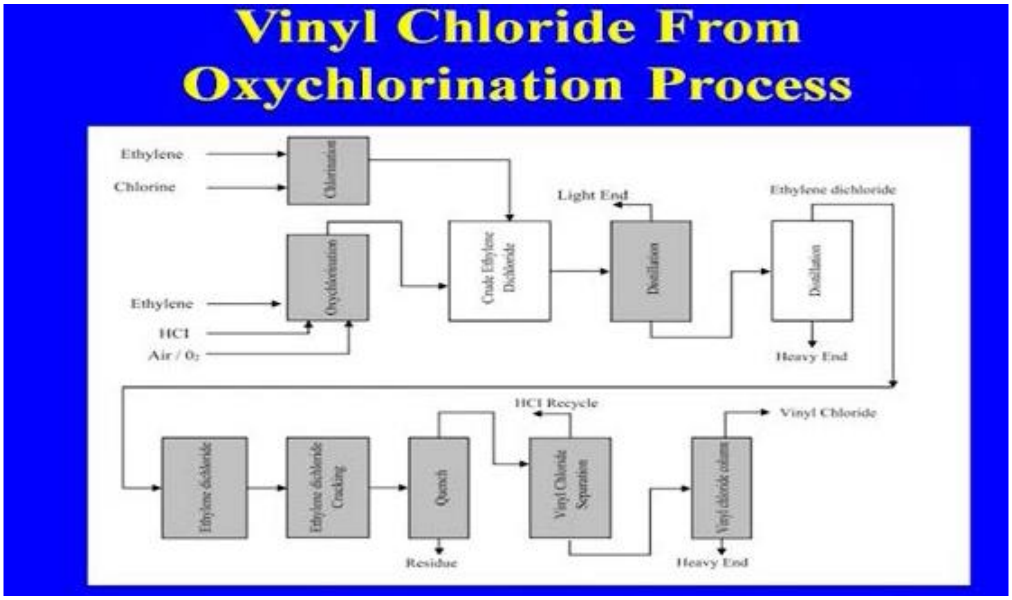
$CH_2{=}CH2 + 2\,HCl + \frac{1}{2}\,O_2 \longrightarrow ClCH_2\text{-}CH_2Cl + H_2O$

Ethylene dichloride pyrolysis :

$ClCH_2\text{-}CH_2Cl \longrightarrow CH_2{=}CHCl + HCl$

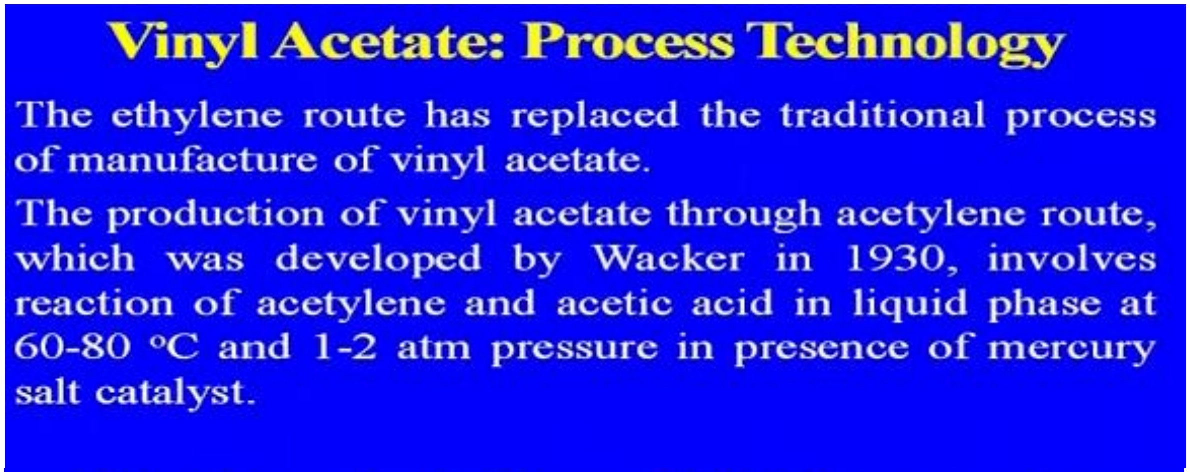
Overall reaction :

$2\,CH_2{=}CH2 + Cl_2 + \frac{1}{2}\,O_2\;2 \longrightarrow CH_2{=}CHCl + H_2O$



Vinyl Chloride From Oxychlorination Process

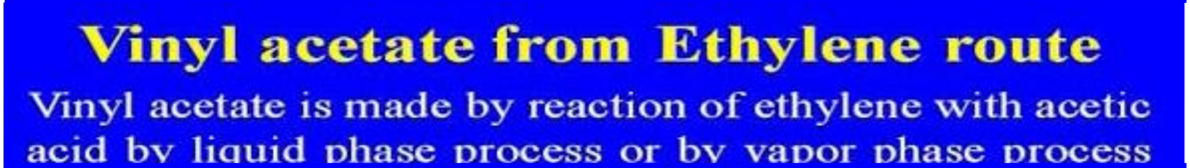
9.0 VINYL ACETATE



Vinyl Acetate: Process Technology

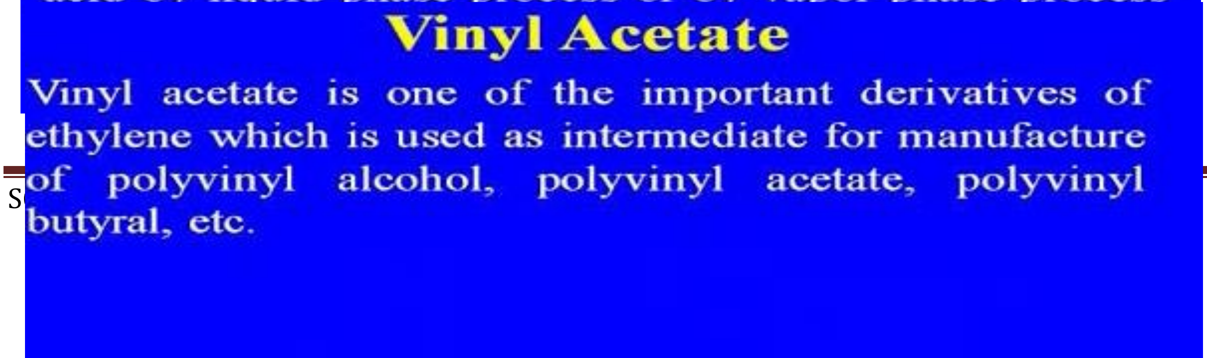
The ethylene route has replaced the traditional process of manufacture of vinyl acetate.

The production of vinyl acetate through acetylene route, which was developed by Wacker in 1930, involves reaction of acetylene and acetic acid in liquid phase at 60-80 °C and 1-2 atm pressure in presence of mercury salt catalyst.



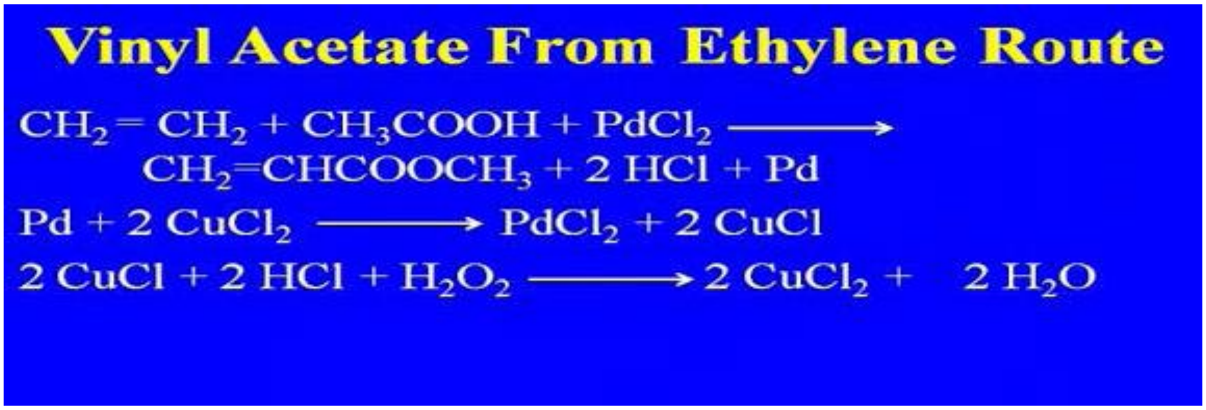
Vinyl acetate from Ethylene route

Vinyl acetate is made by reaction of ethylene with acetic acid by liquid phase process or by vapor phase process



Vinyl Acetate

Vinyl acetate is one of the important derivatives of ethylene which is used as intermediate for manufacture of polyvinyl alcohol, polyvinyl acetate, polyvinyl butyral, etc.



Vinyl Acetate From Ethylene Route

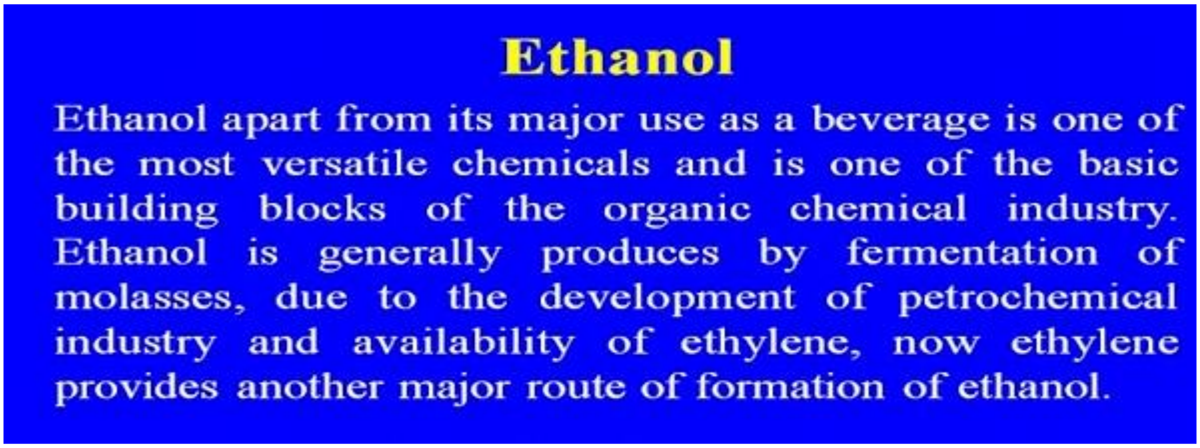
$$CH_2=CH_2 + CH_3COOH + PdCl_2 \longrightarrow CH_2=CHCOOCH_3 + 2\,HCl + Pd$$

$$Pd + 2\,CuCl_2 \longrightarrow PdCl_2 + 2\,CuCl$$

$$2\,CuCl + 2\,HCl + H_2O_2 \longrightarrow 2\,CuCl_2 + 2\,H_2O$$

Use of Vinyl Acetate

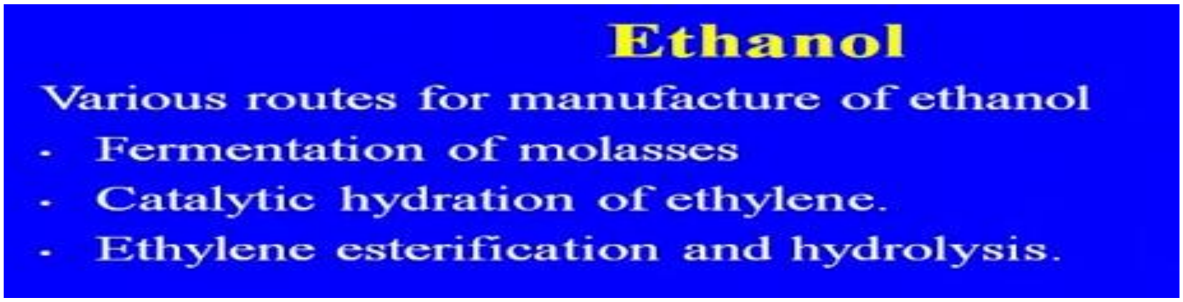
Vinyl Acetate	Ethylene Vinyl Acetate Copolymers	Textile and Paper Coating
	Vinyl chloride comonomers	VC-VAC, LP Records, VC-VAC Coating
	Polyvinyl Butryaldehyde	Safety Glass



Ethanol

Ethanol apart from its major use as a beverage is one of the most versatile chemicals and is one of the basic building blocks of the organic chemical industry. Ethanol is generally produces by fermentation of molasses, due to the development of petrochemical industry and availability of ethylene, now ethylene provides another major route of formation of ethanol.

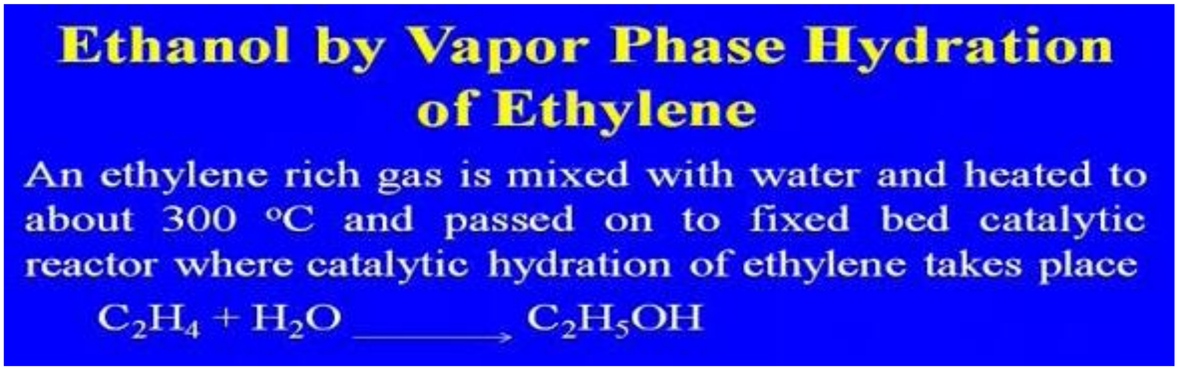
10.0 MANUFACTURE OF ETHANOL



Ethanol

Various routes for manufacture of ethanol

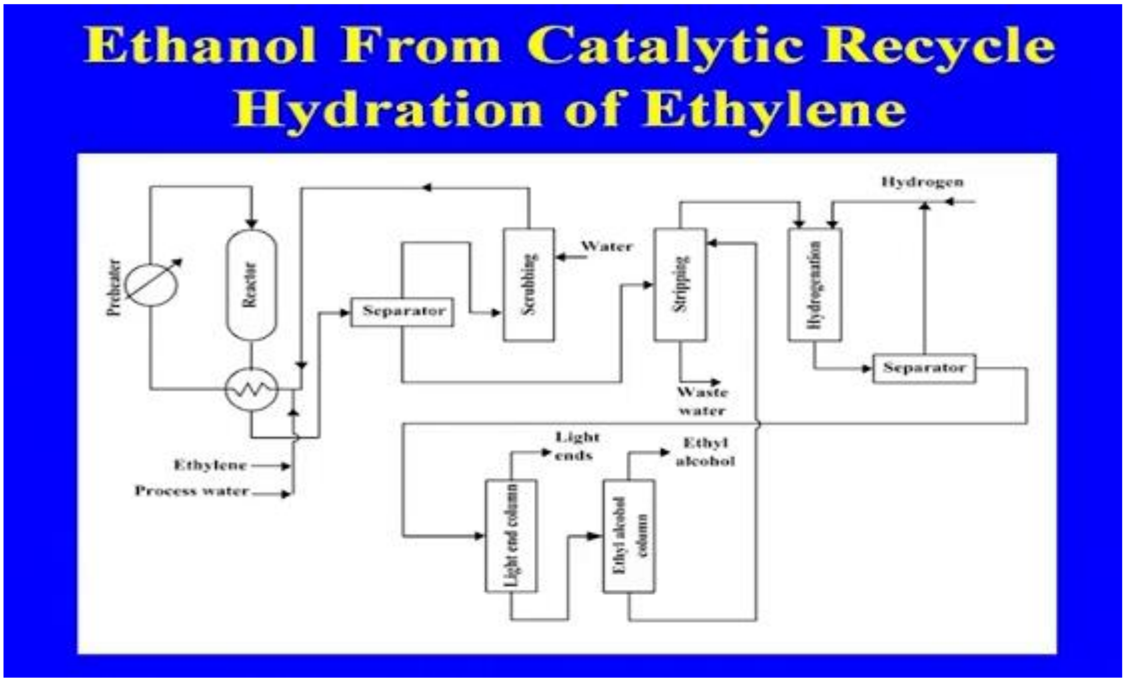
- Fermentation of molasses
- Catalytic hydration of ethylene.
- Ethylene esterification and hydrolysis.



Ethanol by Vapor Phase Hydration of Ethylene

An ethylene rich gas is mixed with water and heated to about 300 °C and passed on to fixed bed catalytic reactor where catalytic hydration of ethylene takes place

$$C_2H_4 + H_2O \longrightarrow C_2H_5OH$$



Ethanol From Catalytic Recycle Hydration of Ethylene

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