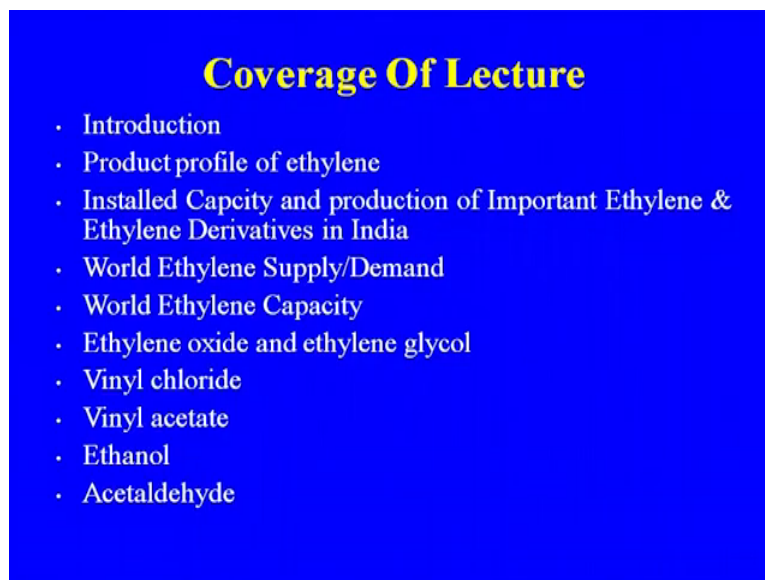


Chemical Technology
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Module - 7
Petrochemical
Lecture - 5
Ethylene Derivatives: Ethylene Oxide, Ethylene Glycol, Ethylene Dichloride, Vinyl Chloride

We are discussing the module 7 of the organic Chemical Technology course, and the lecture 5 will be discussing about the Ethylene Derivatives, Ethylene Oxide, Ethylene Glycol, Ethylene Dichloride, which is major outlet for Vinyl Chloride. And some of the other actually, the ethylene derivative, which will be discussing, one is the ethanol because the importance of ethanol is always there, because one of the source of the ethylene is still ethanol in India. So, an another important chemical, which will be discussing about acetaldehyde, already we have this discuss about the vinyl acetate in detail. So, acetaldehyde that is one of the another very important derivative of ethylene.

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Coverage Of Lecture

- Introduction
- Product profile of ethylene
- Installed Capacity and production of Important Ethylene & Ethylene Derivatives in India
- World Ethylene Supply/Demand
- World Ethylene Capacity
- Ethylene oxide and ethylene glycol
- Vinyl chloride
- Vinyl acetate
- Ethanol
- Acetaldehyde

This will be the coverage of the lecture, introduction, product profile of ethylene, installed capacity and the production of the important ethylene and ethylene derivatives in India, world ethylene supply demand, world ethylene capacity. And what are the products, the feed stock for the ethylene, ethylene oxide and ethylene glycol, because this is the ethylene oxide and MEG plant, that is the integral part of the large.

All the petrochemical complexes, whether it is the reliance or the Panipat refinery, where they are making having the cracker IPCL in or even in case of the Gandhar unit of the reliance industry. In all the cases, we are making the ethylene oxide from the ethylene and then the ethylene glycol. Another major outlet for the ethylene, that has been the vinyl chloride through the ethylene dichloride, cracking of the ethylene dichloride. Then vinyl chloride if use the monomer for the poly vinyl chloride, one of the largest consume polymer that we are using in the different application.

Another product vinyl acetate, already we discussed about the vinyl acetate while discussing the synthesis gas, because vinyl acetate both the routes are available. And some of the units, which are making the ethanol from the molasses route, they are also making the vinyl acetate. Ethanol, ethanol - why ethanol here, I am discussing the ethanol that has been the one of the major route for ethylene, even before coming of the petrochemical then this acetaldehyde.

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Introduction

Ethylene is one of the most versatile petrochemicals and its production has steadily increased over the years.

Ethylene is called as king of chemicals and surpasses all organic chemicals in production and in amount sold. Ethylene is the basic building block for petrochemicals.

Ethylene, ethylene is one of the most versatile chemical and it is production has steadily increase over the years. And ethylene is called as a king of chemicals and surpass all organic chemicals in production and in amount sold. Ethylene is the basic building for a large number of the petrochemicals.

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Introduction

Because of its ready availability at low cost and high purity & reactivity, ethylene has become one of the important raw materials for large number of petrochemicals and products

Because of its ready availability at low cost and high purity and reactivity, ethylene has become one of the important raw material for large number of the petrochemicals and the products. Ethylene has replaced the earliest route of the production of vinyl chloride, acetaldehyde, vinyl acetate and other chemicals through the acetyl route. As I told you earlier also, the birth of the chemical was actually through the calcium carbide route, acetylene route.

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Introduction

Ethylene has replaced the earliest route of production of vinyl chloride, acetaldehyde, vinyl acetate and other chemicals through acetylene route. Large tonnage of ethylene is being used for the manufacture of polyethylene, ethylene oxide, ethylene glycol and styrene.

But now, because of the coming of the large number of the complexes and at the same time, the availability of the ethanol, now the ethylene that has being manufacture either through the, from the cracker plant or from the molasses route. Because again molasses route, the cost of production is higher in comparison to the petrochemical route. But with the rising cost of the chloride and the at the same time, raw basic raw material for the petrochemical complexes, the molasses route of the ethanol and from ethanol to ethylene, that can play a very important role.

Last time, the ethylene is being used for the manufacture of the polyethylene, polyethylene is the another one of the major product, apart from the poly vinyl chloride because the poly vinyl, poly ethylene that has revolutionized the packaging industry. Ethylene oxide, ethylene glycol and also the styrene ethyl benzene, we are making where, we need the ethylene.

So, that is also one of the major outlet for the ethylene and this the reason why, the some of the petrochemical, there are also just like (()) Panipat they are going for the manufacture of the SVR. But earlier route of the styrene, that was the again through the your ethanol route. These are the some of the major outlet for the ethylene, apart from the as I told you the earlier that the polyethylene, that is one of the major product of any petrochemical complex LDD and the various grade of the polyethylene that is available again.

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Product Profile of Ethylene	
Product	Uses
Polyethylene LDPE, LLDPE, HDPE	Films, moldings, pipes, cable covering, netting
Ethylene oxide & Ethylene glycol	Antifreeze, polyester, solvents, detergent ,textile, ethanol amine
Styrene	Synthetic rubber and polystyrene
Ethyl alcohol	Industrial solvent and Chemical intermediates

Detail of the polythene, polyethylene that will be discuss while discussing the polymer so these are the some of the grades of the LDPE polyethylene LDPE, LLDPE or the HDPE. Another major outlet, which is finding major application in the chemical industry that is, ethylene oxide and ethylene glycol. You see, the ethylene glycol, that is one of the major chemical that we are using in the manufacture of the polyester and so the this the importance in case of the... Another important outlet that has been the (()) that you are making which is going to the surfactant industry.

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Product Profile of Ethylene	
Product	Uses
Acetaldehyde (from ethyl alcohol)	Acetic acid (Peracetic acid), Acetic anhydride, Cellulose acetate, Vinyl acetate, Pyridine, Butyraldehyde (ethyl hexanol)
Olefin	n-Butenes, Synthetic detergent, Oxo alcohols, Synthetic lubricants

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Product Profile of Ethylene	
Product	Uses
Chlorinated Solvents	Trichloroethylene, Perchloroethylene
Ethyl Chloride	Tetraethyl lead, Chemical intermediates
Vinyl Acetate	Polyvinyl acetate, Polyvinyl alcohol
Vinyl Chloride	Polyvinyl chloride(PVC)

Acetaldehyde as I told you, the acetaldehyde that is one of the important, you are organic chemical that you are making from the ethylene. And so the usage of the acetic acid, peracetic acid, acetic anhydride which is again we are getting use in case of the cellulose. From the ethyl alcohol, cellulose state vinyl, it may be acetaldehyde from the ethyl alcohol route also you can make because both the routes are available olefin, n butanes, synthetic detergent, oxo alcohols, etcetera.

Chlorinated solvent, ethyl chloride, vinyl acetate and vinyl chloride, these are the major actually outlet for the... This is the install capacity while discussing the your petrochemical, the overall view of the petrochemical and then the starting the raw material and the various product that you are gave me. These are the some of the major outlet for the from the ethylene derivatives which are making ethylene, ethylene oxide.

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Installed Capacity and Production of Important Ethylene & Ethylene Derivatives in India		
Product	Installed capacity 2008-09 000MT	Production 2009-10, 000MT
Ethylene	2841	2515
Ethylene oxide	120	117
Monoethylene glycol	820	738
Acetaldehyde	238	59.2
Acetic anhydride	59	43.42
Ethanol amine	10	7.0
Ethyl acetate	132.0	103.96

This is the install capacity, this is the production, ethylene oxide, mono ethylene glycol, during the MEG manufacture, we are getting both the MEG, DEG and TEG.. Then the acetaldehyde, acetic anhydride, ethanol amine, as I told you the ethanol amine is finding wide application for the more of the sole gases and then the ethyl acetate.

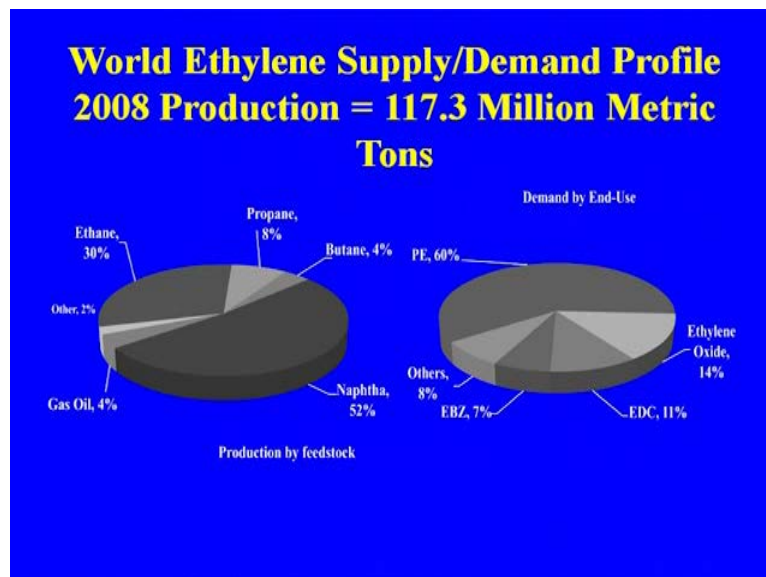
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Ethylene Complexes

	Company	Location	Capacity, tpy
1	Formosa Petrochemical Corp.	Mailiao, Taiwan, China	2935000
2	Nova Chemicals Corp.	Joffre, Alta	2811792
3	Arabian Petrochemical Co.	Jubai, Saudi Arabia	2250000
4	ExxonMobi Chemical Co.	Baytown, Tex.	2197000
5	Chevron Philips Chemical Co.	Sweeny, Tex.	1865000
6	Dow Chemical Co.	Terneuzen, Netherlands	1800000
7	Ineos Olifins & Polymers	Chocolate Bayou, Tex.	1752000
8	Equistar Chemicals LP	Channelview, Tex.	1750000
9	Yanbu Petrochemical Co.	Yanbu, Saudi Arabia	1705000
10	Equate Petrochemical Co.	Shuaiba, Kuwait	1650000

These are the some of the major ethylene complexes in the world, already I discussed while discussing the cracker plant. This is the install capacity of the ethylene, this is the how the raw material again some of the things we discussed about the, while discussing the cracker plant. Because the basic source is the, mother plant is the naphtha cracker or the gas cracker, from where we are getting ethylene.

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So, again the major product is the 52 percent is from the naphtha, rest of the other natural gas, ethane, propane, butane or it may be the gas oil and this is the demand of the end

use, that you are having. So, one of the major use of the, this is the about the polyethylene, you see the major portion that is going to the polyethylene then the ethylene dichloride for making of the PVC. So, these are the some of the major outlet for the ethylene and this is the reason, why the importance of the ethylene is there.

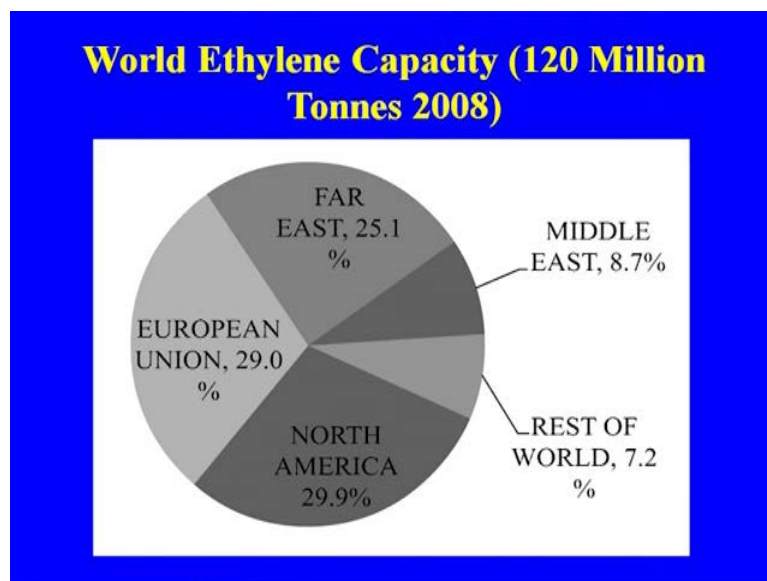
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**Global Ethylene Capacity Growth
(-000'Tons)**

Major Region	2008 Capacity	2013 Capacity	08 to '13 Delta
Middle East / Africa	19,711	34,461	14,751
Asia Pacific	39,617	56,349	16,732
America's	40,421	40,434	12
Europe	30,953	31,293	340
World Total	130,702	162,537	31,836

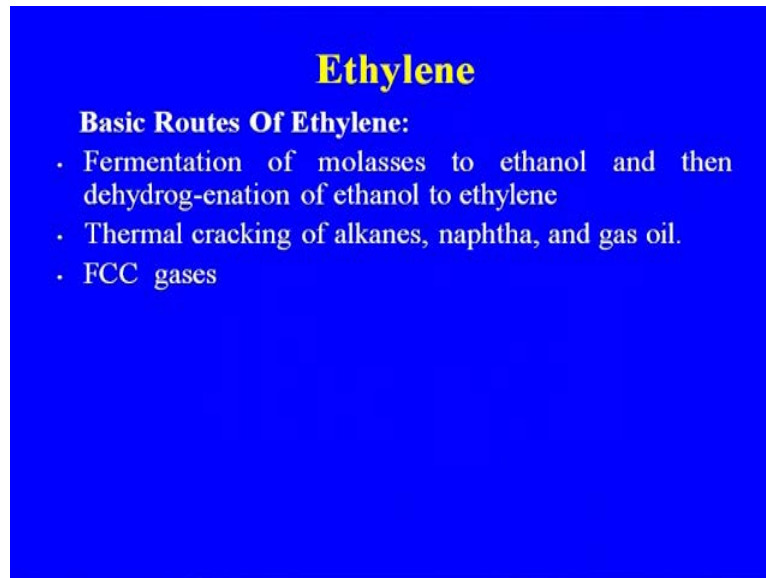
Again the global ethylene capacity that is the, how the capacity change that is there, addition of the capacity is there.

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World ethylene capacity middle East, this is the European union, North America and the rest of the world. So, the major North America is still, it is the major part, the ethylene basic route of ethylene.

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Ethylene

Basic Routes Of Ethylene:

- Fermentation of molasses to ethanol and then dehydrogenation of ethanol to ethylene
- Thermal cracking of alkanes, naphtha, and gas oil.
- FCC gases

As I told you, the earlier method of getting the ethylene, that was the fermentation of molasses to ethanol. And then dehydrogenation of the ethanol to ethylene and the another route that is, there is the thermal cracking of the alkanes, naphtha and gas oil. The FCC gases because as I while discussing the C 4, C 5 gases I discussed that the FCC gases, they contains dilute steam of the ethylene also. Although it is not being recovered but in the future definitely that may play important role, the recovery of the ethylene from the FCC gases.

Another route for the getting of the, that was the apart from these three process the dehydrogenation process of the paraffin, which you are using for the propylene also. So, dehydrogenation of the ethane that can be a that is the, on purpose means, the the plant itself a ethylene is there, you can produce the without going for the cracking dehydrogenation.

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Ethylene

Major portion of the ethylene is still met through cracking of naphtha and natural gas - ethane and propane. In India, naphtha and natural gas are the two major sources of ethylene.

Ethanol from molasees is also used as feed stock from some of the plant in India

So, as I told you, major portion of the ethylene is still met through the cracking of the naphtha and natural gas, ethane and propane. In India, naphtha and natural are the two major source of the ethylene, apart from the some of the units, which are still making the ethylene from the molasses route from the ethanol. And two major plants, which are there and which played very important role in the development of the chemical industry in India.

That is, the Indian glycol and the vam organic, now jubilant organize, which are still operating and that is a vam or jubilant organizer, that is large integrated plant we are having. And so I will discuss while discussing the ethanol, what are the product profile of the alcohol to ethylene route. Let us discuss about the ethylene oxide because most of the cases where, we are having the one major plant is polyethylene plant. Another is the ethylene oxide, PVC, ethylene dichloride, (()) because the they need their distilled one, huge amount of the chlorine also. But, the you see the PVC, that is one of the very important actually outlet for the ethylene also so let us discuss now the ethylene oxide.

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Ethylene Oxide(EO)

Ethylene oxide is one of the important petrochemical intermediate.

Some of the major EO derivatives are in the manufacture of ethylene glycols, glycol ethers which is made by reaction of ethylene oxide and alcohols, ethanol amines. Surfactant industry is one of largest user of EO

Ethylene oxide is one of the important petrochemical intermediate, some of the major ethylene oxide derivatives in the manufacture of the ethylene glycols. As I told you, the MEG, DEG, TEG, glycol ethers, which is made by reaction of the ethylene oxide and alcohol. Ethanol amines, surfactant industry one of the largest user of the ethylene oxide where, the ethylene oxide that is where, we are making the ethoxalate, that is more valued product and this is the Indian glycol, they are making the ethoxalate.

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Major Producer of Ethylene Oxide

Naphtha , Natural gas:

- Reliance Industries, Vadodara, Hazira, Nagothne, Gandhar
- IOC Panipat Refinery

Molasses Based:

- Indian Glycol
- SM Dychem

New plant: ONGC, Brahmaputra cracker

These are the major actually units, which are based on the naphtha and the natural gas, which are having the ethylene oxide plant at the Reliance industry, Vadodara, Hazira plant, Nagothne plant, Gandhar plant. These are all units are making ethylene oxide IOC panipat refinery, molasses based plants are the Indian glycol and SM dychem. New plant ONGC and Brahmaputra cracker, ONGC also going to have one petrochemical complex near Gandhar where, the Reliance industry, they have already having a big naphtha gas cracker plant. And then the large number of products, they are petrochemical and the finished product they are manufacturing.

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Product Profile of Ethylene Oxide	
Product	Uses
Ethanol Amines	Detergent, Soap solvent, Cosmetics, Morpholine
Mono Ethylene Glycol	Polyester, Staple fiber yam, PET Bottles, Film
Diethylene Glycol	Coolants, Pesticides, Rubber Compounding, Plasticizer, Polyurethane, Alkyl Resin
Tri ethylene Glycol	Natural gas conditioning agents plasticizer

These are the major outlet of the products, which you are getting from the ethylene oxide, ethanol amines, mono ethylene glycol, diethylene glycol, triethylene glycol that is, detergent, soap solvent, cosmetics, morpholine, polyester, staple fiber, PET bottles where, we are using the MEG for making the PET. PET ranging because we are having the polyester that is going to be your synthetic fiber. And PET resin that is using for the packaging means, bottles and other containers we are making from the PET. A film are the PET films, coolants, pesticides, rubber compounding, plasticizer, polyurethane, alkyl resin and the natural gas conditioning agents.

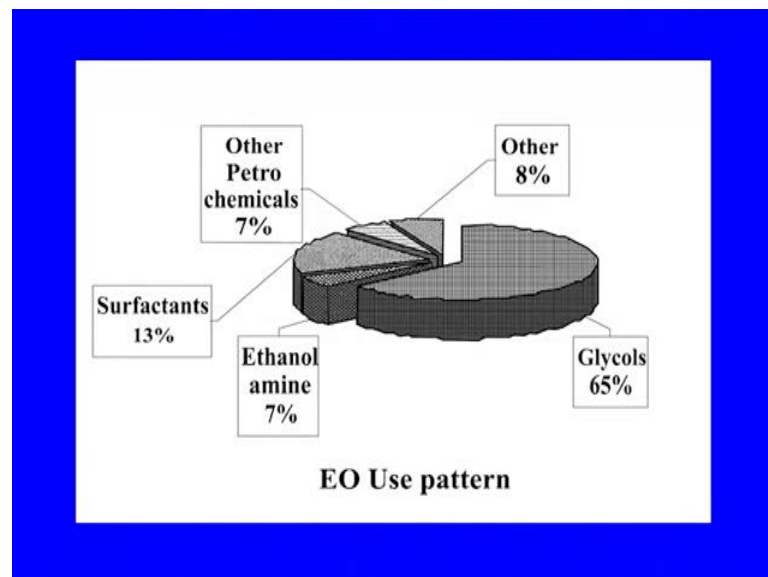
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Product Profile of Ethylene Oxide

Product	Uses
Polyethylene Glycol	Pharmaceuticals, Brake Fluid, cosmetics
Non-ionic surfactants, Ethoxylates	Textile auxiliaries, Binders, Dyes, Pesticides, Pharmaceuticals, Cosmetics
Glycol Ethers	Brake Fluid and Protective Coating

Poly ethylene glycol, non ionic surfactants, ethoxylates and glycol ethers, these are the others some of the outlet for the more valuated product of the ethylene where, they are finding an application. And the pharmaceuticals industry, fluid textile, dyes then the brake fluid that is, glycol ether that we are using.

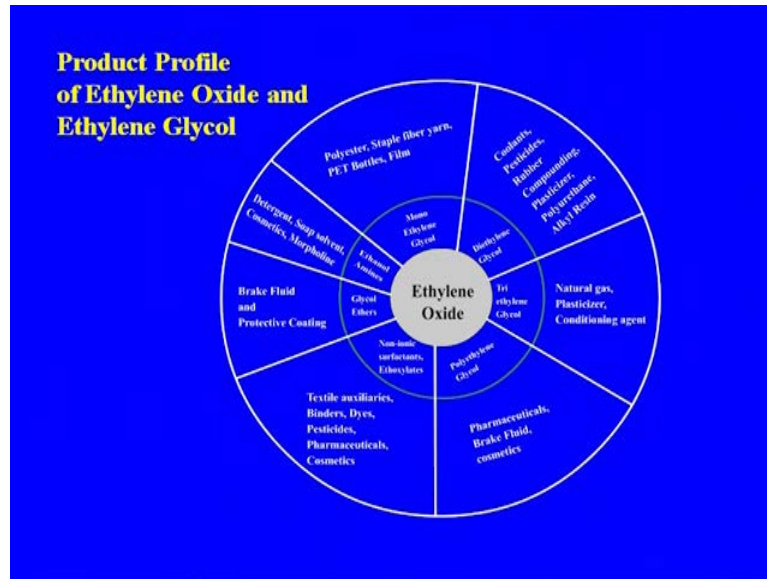
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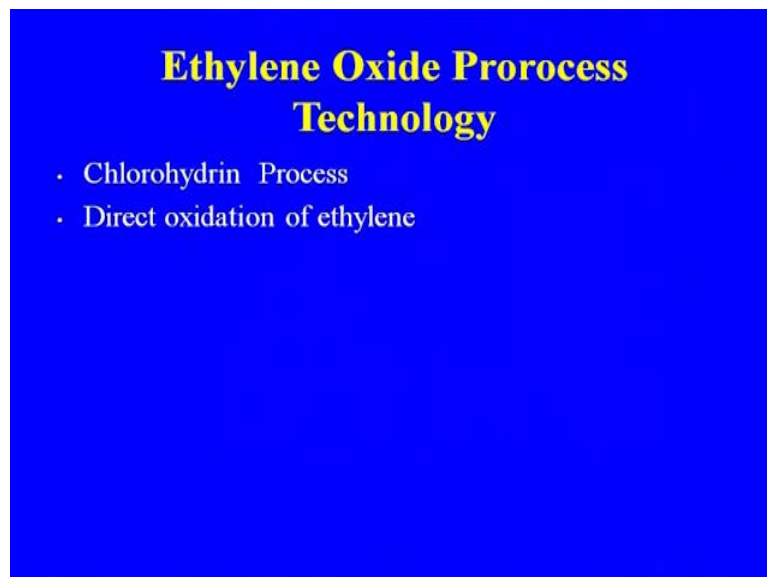
These are how the ethylene oxide used pattern, that the major portion you see the ethylene glycol ethylene glycol. Because during the process as I told you the, all the three are formed but you can optimize the condition of the from... So, that the higher

portion of the, major portion is the MEG by adjusting the water to your ratio. So, this is the how the and the one of the another major outlet trajectory in the surfactant industry and ethanol amine is 7 percent. So, these are the some of the major outlet for ethylene oxide and you can realize the importance of the ethylene oxide in the petrochemical industry.

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Ah these are the product profile of the ethylene oxide from the ethylene, these are the major products derived from the and they are finding the application in the various area.

Monoethylene glycol, diethylene glycol, triethylene glycol, poly polyethylene glycol and the non ionic surfactants, ethoxylate and the (()). These are the major outlet for ethylene oxide and from where, you can see the large amount of the petrochemical intermediate, that you are making. Now, let us discuss the process of ethylene oxide, there are two processes as chlorohydrin process and direct oxidation of the ethylene.

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Chlorohydrin Process

- **Chlorohydrin Process** : In the chlorohydrin process, ethylene is reacted with chlorine and water to give an aqueous solution of ethylene chlorohydrin and hydrogen chloride, which after reacting with calcium hydroxide produces ethylene oxide.

Chlorohydrin process, in chlorohydrin process, ethylene is reacted with chlorine and water to give an aqueous solution of ethylene chlorohydrin and hydrogen chloride, which after reacting with calcium hydroxide produces ethylene oxide. This was the earlier process, that was being used for the manufacture of the chlorohydrin route for the ethylene oxide. But you see there, here it is the involvement of the chlorine is there, production of hydrogen chloride there. So, highly chlorosive nature is there, that has to be avoided and so you because of that reason, now we are having the ethylene, direct oxidation of the ethylene.

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Chlorohydrin Process

- $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{HOCl} + \text{HCl}$
- $\text{C}_2\text{H}_4 + \text{HOCl} \longrightarrow \text{CH}_2\text{OH-CH}_2\text{Cl}$
- $\text{CH}_2\text{OH-CH}_2\text{Cl} + \text{Ca}(\text{OH})_2 \longrightarrow$
 $\text{CH}_2\text{CH}_2\text{O} + \text{CaCl}_2 + \text{H}_2\text{O}$

Corrosion problem
Disposal of Calcium chloride

This is the reaction that is taking place in case of the chlorohydrin process and the chlorohydrin that is going for the manufacture of ethylene dioxide. So, corrosion problem, one another byproduct you can say, the waste you are generating that the calcium chloride. So, these are the two major problems, which relate to the use of the oxidation process of the chlorine ethylene sorry not chlorine, ethylene.

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Ethylene Oxide By Direct Oxidation Process

Various steps

- Ethylene oxide synthesis,
- Ethylene oxide scrubbing,
- Ethylene oxide purification, and CO_2 recovery.

Ethylene oxide by direct oxidation process, various steps involve in case of the ethylene oxide ethylene by oxidation process, ethylene oxide synthesis, ethylene oxide scrubbing.

Because during the process, lot of this CO₂ is also evolve, so CO₂ that has to be separated by scrubbing, ethylene oxide purification and CO₂ recovery section. So, these are the three major section in case of the, your ethylene oxide by the oxidation process.

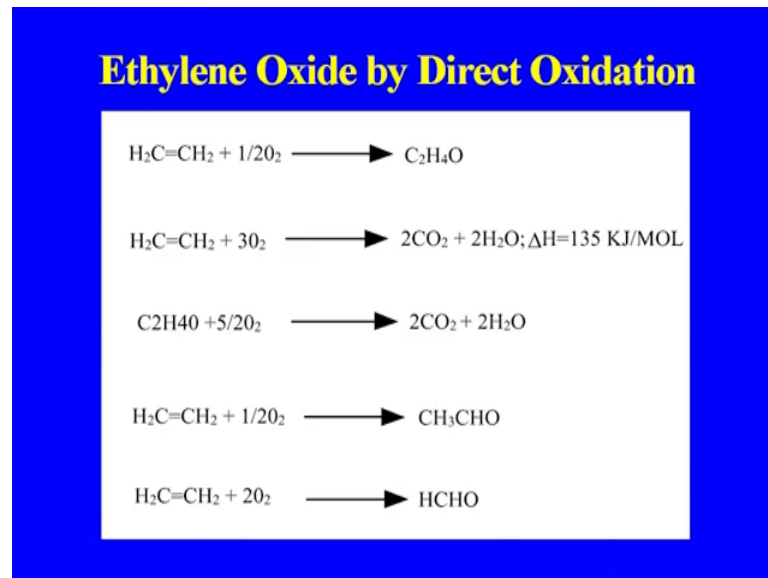
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Ethylene Oxide by Direct Oxidation Process

In the direct oxidation process, ethylene (after removal of sulphur) and oxygen produced by air separation are reacted safely under optimum conditions for making ethylene oxide in presence of silver catalyst containing an initiator, which is usually alkaline earth or alkaline metal deposited on solid support.

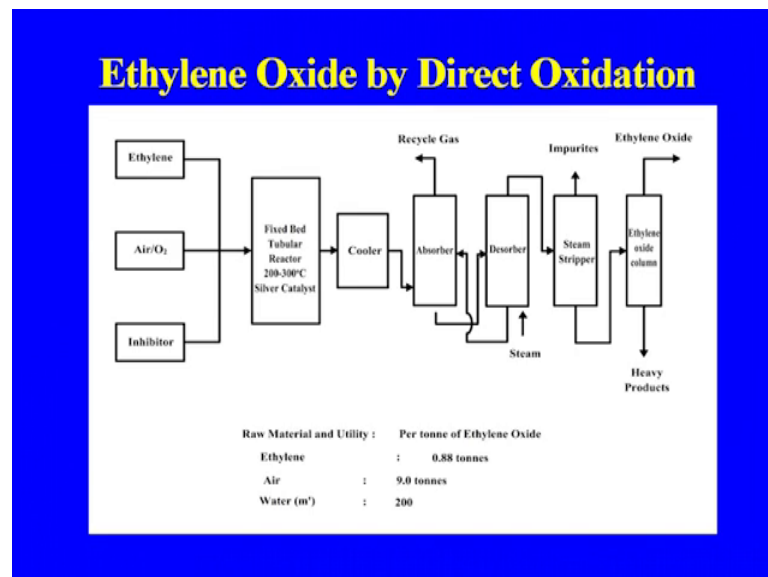
In the direct oxidation process, ethylene after the removal of the sulphur here also and the oxygen produces by air separation because the oxygen definitely that has to be from the air. And so there are it reacted safely under optimum condition because lot of the safety involve. Here, in case of the ethylene oxide process, because because of the (()) of the ethylene and the oxygen mixer. So, the separation are reactor safely under optimum condition for making ethylene oxide in presence of the silver catalyst, that we are using here containing an initiator, which is usually alkaline earth or alkaline metal deposited on solid support.

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This is the reaction that is taking place and in the reaction, if you see that we are also getting some of the side reaction also there. Undesirable side reaction, which are not unavoidable, this the CO₂ formation, huge amount of the CO₂ that is formed there in the process and so that has to be removed continuously.

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So, this is the process, we are having the flow diagram for making of the ethylene oxide, ethylene air inhibitor, that is going to the fix bed. Tubular reactor where, the temperature you know around 200 to 300 degree centigrade cooler than absorber, as I told you the CO

2 that has to be removed. So, the finally, it is going to the steam stripper and ethylene oxide heavy hence, you are removing and then the ethylene oxide you are getting as a top chloroform here.

So, this is the actually the process flow diagram, this is the requirement of the raw material per ton of the ethylene oxide, ethylene air and the water. So here, one of the process major problem that is the side reaction, which are there where, this CO₂ is formed or the formaldehyde is formed so that has to be minimized. But CO₂ formation always be there as per the reaction and so that has to be removed and that can be stored, that can be utilize for some of the value added product.

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Ethylene Oxide By Direct Oxidation Process

The reactor temperature is one of the most critical parameter in ethylene oxide synthesis and is measured at large number of locations in the catalyst bed.

An efficient and reliable heat transfer system is also very important.

So, the reactor temperature is one of the most critical parameter in ethylene oxide synthesis and is measured at large number of locations in the catalyst bed. Because temperature that is playing a very important role here. Because you will have to suppress the side reaction, which is taking place and efficient and reliable heat transfer system is also very important.

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Ethylene Oxide

The flammability of ethylene oxide poses a serious problem in the operation of ethylene oxide plant.

The main hazards in ethylene oxide process are the potential formation of flammable oxygen/hydrocarbon mixtures and auto-ignition of these oxygen/hydrocarbon mixtures.

The flammability of ethylene oxide, as I told you discuss by the safer condition, that has to provided because the flammability of ethylene oxide poses a serious problem in the operation of ethylene oxide. The main hazards in the ethylene oxide process are the potential formation of the flammable oxygen and hydrocarbon mixtures and auto ignition of these oxygen hydrocarbon mixtures. So, here proper precaution has to be taken so that, the and as you know, the oxidation reaction, this is the oxidation reaction.

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Characteristics of Ethylene Oxide

Characteristics	Values
Purity, percent	99.9
Appearance	Clear colorless liquid
Water, ppm (max.)	100
Aldehyde as CH ₃ CHO, mg/kg	20
Carbon dioxide, mg/kg	10
Nonvolatile residue, mg/kg	10
Color (Pt-CO), (max.)	10

So, always it will be exothermic and exothermic control of the temperature, that is very important and that is why, the monitoring of the temperature at the various section of the reactor, that is very important.

This is the requirement of the ethylene oxide, the property of ethylene oxide that is required. So, the various appearance, water contain aldehyde, carbon dioxide, nonvolatile residue, color, this is the ethylene glycol formed of Reliance industry, courtesy Reliance industry. And I will be discussing now, about the ethylene glycol form because that is one of the again, as I told you, the one of the major unit in case of the cracker plant or the petrochemical complexes.

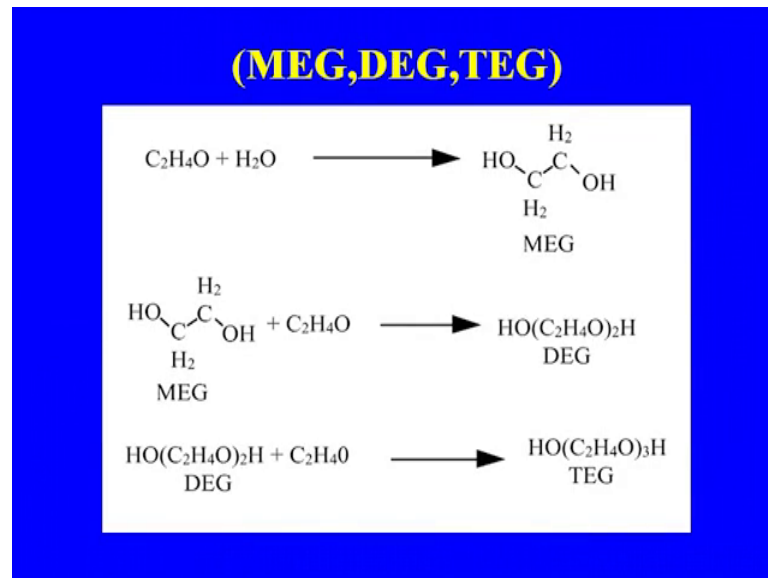
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Mono-, Di-, Tri- Ethylene Glycols (MEG,DEG,TEG)

- 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: H₂O ratio 10:1 to maximise MEG production.
- By Products DEG,TEG

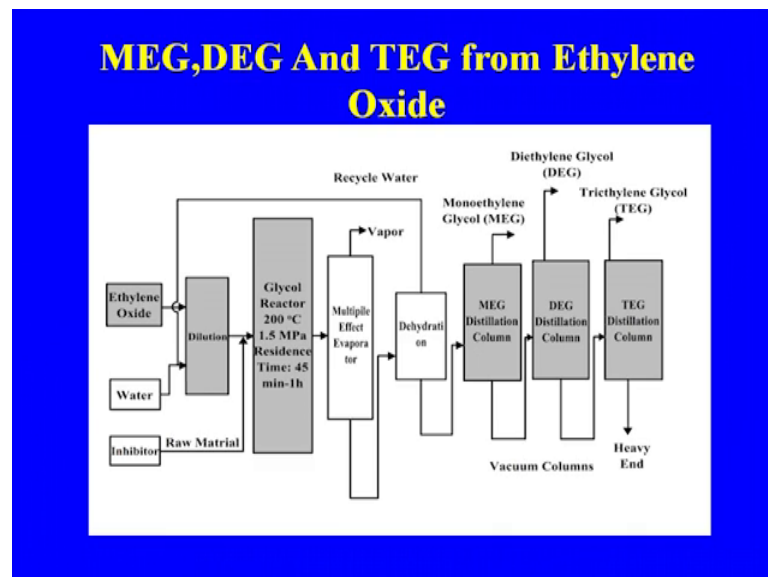
Mono MEG, DEG, TEG, mono di tri ethylene glycol, the major petrochemical and find application in manufacture of polyester. And as the antifreeze accounts for 70 percent of the ethylene oxide production, ethylene oxide preheated to 195 degree centigrade then the EO H₂O ratio because here that is very important. The ratio of the ethylene oxide and water to maximize because here our interest is to have more and more MEG and less DEG and TEG but always that will be there and so there will be as a byproduct soap.

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This is the reaction that is taking place during the manufacture of the ethylene glycol from the ethylene oxide and the here, you see the various reaction that is taking place MEG, DEG, TEG. So, this is the how the, why the we are controlling the ratio of the ethylene oxide to water, to have the maximum MEG.

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This is the process flow diagram for MEG and here, if you see the ethylene oxide then the water, inhibitor, that is going to the dilution. After dilution, it is going to the glycol reactor, this is the temperature, (()) your pressure condition residence time is about, this is

the residence time. And then this is the actually the multiple effective operator and during the process because here, you will have to control the ethylene oxide to water ratio to maximize the yield of the MEG.

So, this will go to multiple effect evaporator, dehydration and then you will be getting the MEG recycle water, that will go to the system. MEG that will go to the MEG column, DEG column, TEG column, they are three fractionating column where, we are separating depending upon the boiling point. So, mono ethanol ethylene glycol, ethylene diethylene glycol and the triethylene glycol, heavy end so this is the process for the manufacture of the MEG. Here, one of the very important parameter, which you have to control for the maximize reproduction of the MEG that is, the ethylene to water ratio. Now, let us discuss another important petrochemical, which is derived from methylene, that is the phenyl chloride, which is being used for the manufacture of the poly vinyl chloride.

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Vinyl Chloride

Vinyl chloride is one of the major ethylene derivatives and has gained worldwide importance because of its industrial use as raw material for Polyvinyl Chloride (PVC) polymer, the second largest tonnage commercial polymer after polyethylene.

So, vinyl chloride is one of the major ethylene derivatives and has gained worldwide importance, because of its industrial use as raw material for poly vinyl chloride. Polymer, the second largest tonnage commercial polymer polymer after poly ethylene.

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Vinyl Chloride

About 95% of the present vinyl chloride production worldwide is used in polymer production or copolymer application. Another important use of vinyl chloride is in the production of vinylidene chloride.

About 95 percent of the present vinyl chloride production, worldwide is used in polymer production or the copolymer application. Another important use of the vinyl chloride is in the production of vinylidene chloride, which is being used as the comonomer in some of the synthetic fiber industry. These are the three technology available earlier route, I discussed at the acetylene route and still one of the unit in India. They are making vinyl chloride and the poly vinyl and the PVC from the acetylene route, that the serum chemical and fertilizer and Kota unit.

They are still making the PVC through this route so that was the older unit and the second process, that was development direct chlorination method or the direct chlorination of the... But here, again the HCL was form and so in order to avoid it because they highly corrosive nature was there and the handling of the HCL. So, direct chlorination that has been placed with the oxy chlorination process, which is now being use in most of the petrochemical complexes. Vinyl chloride as I told you the, let us discuss about the historical background of the production of the vinyl chloride.

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Vinyl Chloride From Acetylene Route

- Vinyl chloride has been made since 1930s from calcium carbide route. The process involve reaction of acetylene with hydrochloric acid in vapour phase over a catalyst mercuric chloride supported on active carbon at a temperature between 370 and 450k depending on the age of the catalyst

Vinyl chloride has been made since 1930's from the calcium carbide route, that was the earlier route which was available. Because if you talking about the 1930's, no petrochemical complex, the petroleum refinery that was the at the developing stage. The process involve the reaction of the acetylene with the hydrochloric acid in vapor phase over a catalyst mercuric chloride, supported on active carbon at a temperature of 370 degree centigrade and depending on the age of the catalyst.

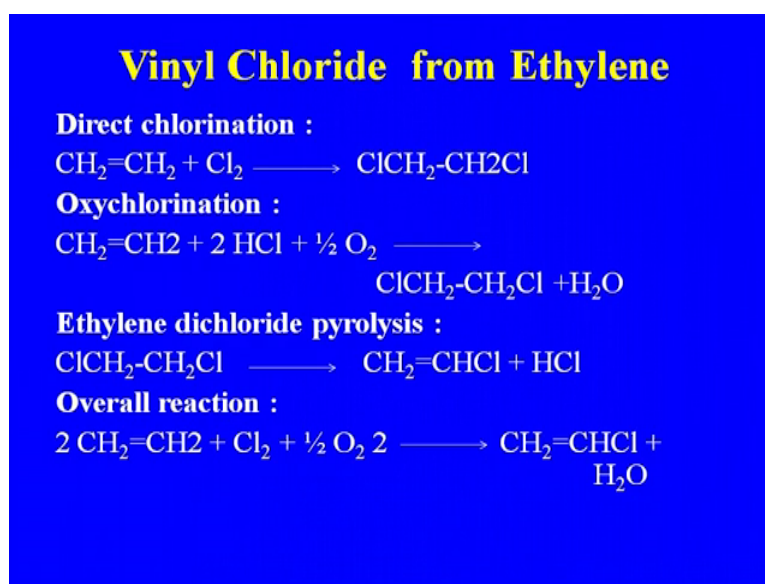
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Vinyl Chloride From Acetylene Route

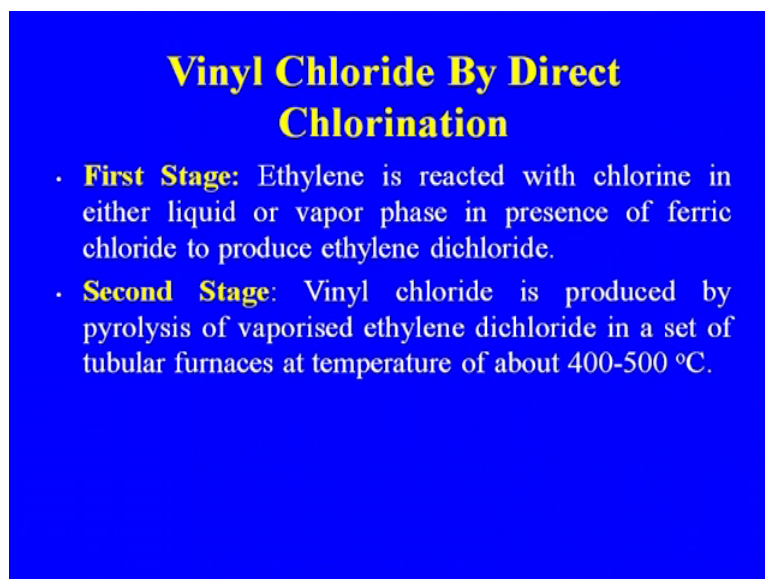


So, this was the actually, they are real route for making and this is the reaction we are getting the acetylene and acetylene after the chlorination, that the that is here then then it will go to for the formation of the vinyl chloride. So, direct chlorination process where, we are using, no this is not the, we are not using the oxygen.

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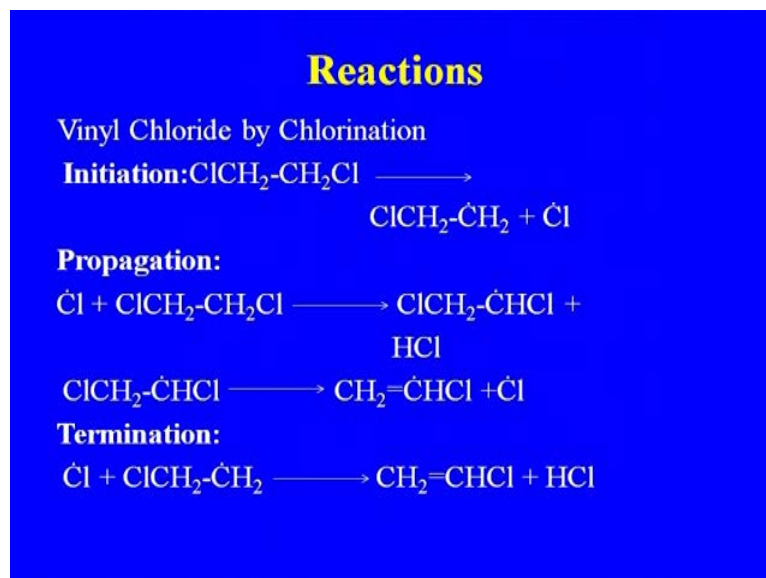


So, if you see the reaction in case of the these two reaction, di direct chlorination and oxychlorination. Here again, in case of the oxic here, HCL is also formed but here, in case of the oxychlorination, this HCL, whatever the HCL, that is consume in the

processes. So final stage in case of the vinyl chloride is, from whichever route you are getting the vinyl ethylene dichloride then the cracking of the ethylene dichloride to your this vinyl chloride.

The in case of the vinyl chloride, direct chlorination method, the first stage is the ethylene is reacted with chlorine in either liquid or vapor phase in presence of the ferric chloride to produce ethylene dichloride. Second stage, that the cracking of the ethylene dichloride so the vinyl chloride is produced by pyrolysis of vapor vaporized ethylene dichloride in a set of tubular furnaces at a temperature of about 400 to 500 degree centigrade. So, this is the process that was being used in case of the direct chlorination of the ethylene for making the vinyl chloride.

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This is the series because the reactions that will change that is, the initiation, propagation and termination stage are there and so these are the various reactions that are taking place. Here, you see the one of the major constant, that was the production of the HCL but in the other process, the HCL that is being used in the process itself. Now, let us discuss about the oxychlorination process, because now all the vinyl chloride manufacturing, they are based on the oxy chlorination process.

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Oxychlorination Process

The original process of manufacture of vinyl chloride by ethylene chlorination and cracking of ethylene dichloride has been replaced by oxychlorination process in which no hydrochloric acid is formed as byproduct.

The original process of manufacture of vinyl chloride by ethylene chlorination and cracking of ethylene dichloride has been replaced by oxy chlorination process. In which, no hydrochloric acid form as a byproduct, which was a problem in case of the direct chlorination process already we have, I discussed that point.

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Oxychlorination Process

The process involves production of ethylene dichloride by exothermic reaction of ethylene, hydrochloric acid and oxygen

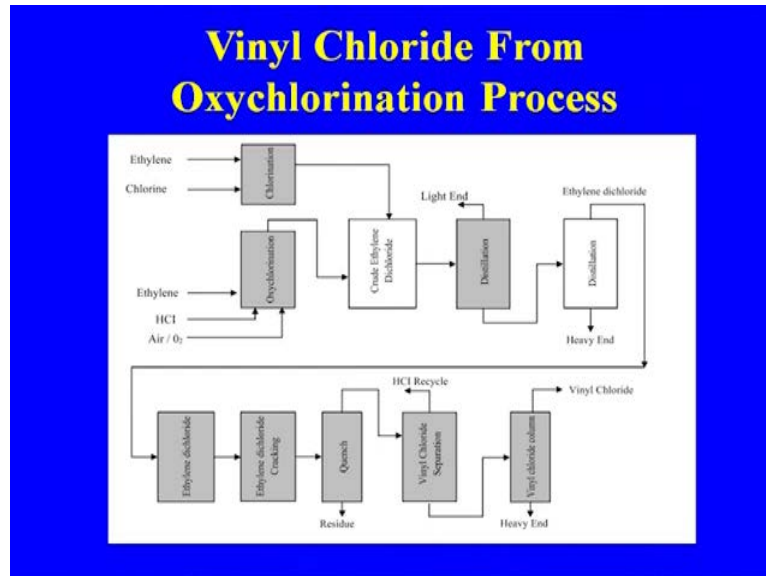
Liquid phase: at about 170-180 °C in at 15-20 atm pressure in presence of copper chloride in either fixed or fluidised bed reactor.

Vapor phase reaction: the temperature and pressure are 200-220 °C and 20-50 atm pressure.

In case of the oxy chlorination process, the process involves production of ethylene dichloride by exothermic reaction of ethylene, hydrochloric acid and oxygen. Because here the what about the hydrochloric acid is produce in the process that is being utilize.

So, liquid phase or the vapor phase reaction, that may be there so this is the, how the reaction that is, the various condition that involves.

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This is the reactor typical reactor, which you are getting ethylene and chlorine and then it is going to the various stages of the... Then the ethylene dichloride, ethylene dichloride then the cracking, you are getting the vinyl chloride. Then the HCL, which you are getting after the cracking of EDC, that will go to the that will be recycle that will be used in the system. So, this is the oxy chlorination that is taking place and the ethylene, HCL, HCL this HCL that will be recycling the system.

And so the ethylene dichloride finally, it will go for the cracking processes already, I have discussed about the vinyl acetate. But only I am mentioning here because one of the route is the ethylene route, is also for making out the vinyl acetate, which they in case of the vam organic or jubilant organization, they are making the vinyl vinyl acetate that route.

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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.

So, it is one of the very important derivatives of ethylene, which is used as intermediate for manufacture of the poly vinyl chloride, poly vinyl acetate, poly vinyl butyral.

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Vinyl Acetate

Global use pattern

Adhesives (23%), paints and coating (29%), textiles (21%), plastics (17%), paper and board (10%). Consumption pattern of vinyl acetate in India is polyvinyl acetate emulsions & resins (50%), polyvinyl alcohol (25%), ethylene vinyl acetate (10%), others (15%).

Global use for pattern, this is the adhesives, paints, textile, plastic paper and board, consumption pattern of the vinyl acetate in India is, this is the poly vinyl acetate emulsion and resins that is, 50 percent. That is major outlet, poly vinyl alcohol 25 percent, ethylene vinyl acetate 10 percent, others 15 percent, this is the used pattern of the... So, these are the two routes, again the same ethylene route, which I told you that

the acetylene, that was the earlier route and the many of the petrochemical, which are now we are making.

Because now, the 90 percent of the chemicals we are organic chemicals we are manufacturing from the petrochemical. But earlier, it was the acetylene route, which was available for making a large number of the chemical. So, ethylene route that is now what we are using and the acetylene route, ethylene route may is the why, the ethylene route I am telling here. Because ethylene for getting ethylene to vinyl acetate, ethanol route that is also available, this is the about the process technology.

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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.

Ethylene route has replaced the traditional process of manufacture of vinyl acetate from the acetylene route. The production of vinyl acetate through acetylene route, which was developed by Wacker 1930, involves reaction of the acetylene and acetic acid in liquid phase. So, that process that has been take place with the use of the ethylene in the major raw material.

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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 in presence of palladium and cupric chloride catalyst.

So, vinyl acetate is made by reaction of ethylene with acetic acid by liquid phase process or by vapor phase process in presence of the palladium and cupric chloride catalyst. This is the process, which now being used for the, even the the units which are making the vinyl acetate from the ethylene, from molasses route alcohol to ethylene so they are using this process.

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Vinyl Acetate From Ethylene Route



These are the reaction series of reaction that is taking place and the catalyst, which are using palladium catalyst.

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Use Of Vinyl Acetate

Polyvinyl Alcohol; Surface coating adhesives, Textile resins, Textile size, Grease proofing paper, Vinyl emulsifier, Thickener, Viscosity regulators, Adhesives,

Use of vinyl acetate, already I have discussed about the, what are the various issues of the vinyl acetate.

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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

The whose outlet is there for the vinyl acetate and the importance of the, already I discuss in the previous lecture also. Now, let us discuss ethanol because here, I am discussing ethanol separately again because the we discussed about the ethanol while discussing the sugar and the fermentation industry. But here, I am discussing the ethanol because there is alternative route for making of the ethanol through the ethylene route,

which is not being practised in India. But but at the same time, ethanol is not important from the (()) point of view, it is also one of the very important feed stock.

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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 produced 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.

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

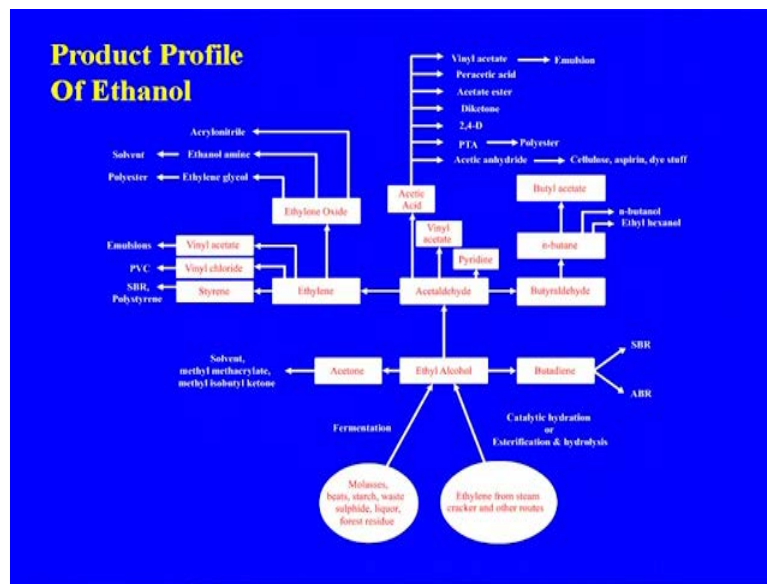
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Ethanol

However, ethanol in India is still manufactured through molasses route. Some of the important chemicals which are made through petrochemical route are still made through ethanol route at some places in India.

Ethanol in India is still manufactured through the molasses route so some of the important chemicals, which are made through the petrochemical route are still made through the ethanol route, as I discussed while discussing the petrochemical the raw material for the organic chemical industry. Ethylene from ethanol, that is providing a basic raw material from many of the intermediates, which are we are making from the ethylene, from the your cracker plant which you are getting.

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This is the actually the process various large number of the product, which you are saying from here that is, from... But only difference here, this is the from the ethanol route, ethanol tree you can say, only difference from a petrochemical and this route is only that from ethanol to ethylene. In case of the petrochemical, directly it reform ethylene to ethanol.

So, in case of the alcohol based chemical industry, what you are doing, we are doing the going for the from the ethanol we are going for the ethylene and from ethylene, in large amount of product, that we are making. Two important complexes, which I told you, I have been discussing time to time because the nature as provided alternative raw material. Only thing, how to explode these raw material, how to explode the possibilities of this these raw material that is important.

This was the reason, why the, even during the initial stages number of the plants because the alcohol is available from the molasses route, they started manufacturing some of the

very important PET chemical organic chemical. And in this jubilant organization and in the Indian glycol (()), these are the two other units in Somaiya organic in Barabanki. Now, it is closed because of this some reason (()), another major unit was there, which is started making with all our this four units were in you UP. Because, the UP that has been all of their sugar producing state, another is the king that was in Maharashtra. Maharastra also the ethanol because the sugar producing state is there and so the they are making from the ethanol to some of the chemical.

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Ethanol

Various routes for manufacture of ethanol

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

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Ethanol by Vapor Phase Hydration of Ethylene

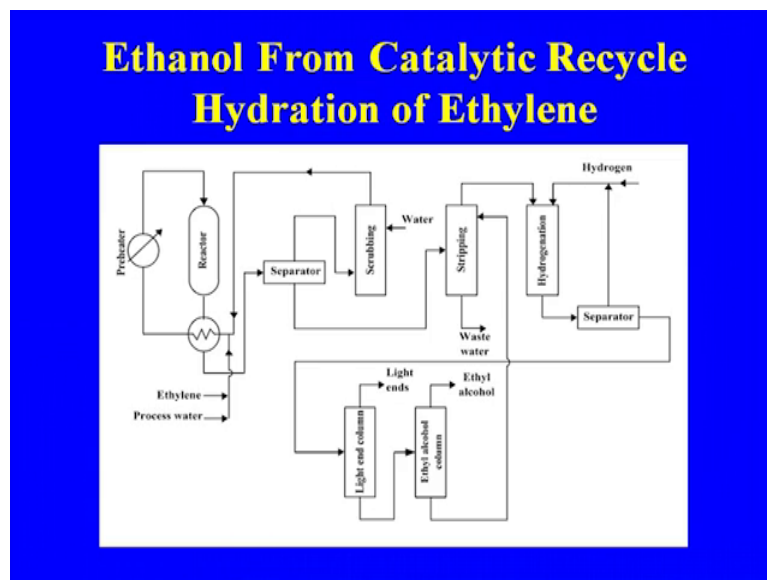
An ethylene rich gas is mixed with water and heated to about 300 °C and passed on to fixed bed catalytic reactor where catalytic hydration of ethylene takes place



So, for the ethanol as I told you, the fermentation route, catalytic hydration of the ethylene or ethylene esterification and the hydrolysis, these are the three routes available. And so the first route is from the molasses route and the second, this second route that may be used for the making of the ethanol from the ethylene.

So, this is the reaction that is taking place, the vapor phase hydration of the ethylene, I am not going in detail about the alcohol part because the again what we are interested from the petrochemical or organic chemical feed stock, that is the ethylene. So, ethylene why to convert ethylene to ethanol again, only I am saying that the, from the ethanol you can get back the ethylene. And so the how to get the ethylene from the ethanol, where you are having the molasses as raw material for ethylene.

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So, this is the process we are using in case of the ethanol by hydration by vapor phase hydration of the ethylene that you are getting the ethanol. This is the process, that we are using for from the using the ethylene for making of the ethanol. Now, let us discuss one of the very important product of the ethylene that is, the acetaldehyde.

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Acetaldehyde

Acetaldehyde is one of the most important intermediates for the manufacture of a large number of organic chemicals like acetic acid; acetic anhydride; pentaerythritol; butanol; peracetic acid; chloral, 2-ethyl hexanol, pyridine, picolines, vinyl acetate, 1,3-butylene alcohol, etc.

Acetaldehyde is the one of the most important intermediate for the manufacture of a large of the organic chemicals like acetic acid, acetic anhydride, pentaerythritol, butanol, peracetic acid, chloral, 2 ethyl hexanol, pyridine, vinyl acetate, 1 3 butylene alcohol. You see the, some of the product where you are seeing, these are all major products, which manufactured by Jubilant organization through the ethanol route, ethanol to... So the because the they are the alternative route for making of the steroid, one is from the ethylene route another is from the ethanol route.

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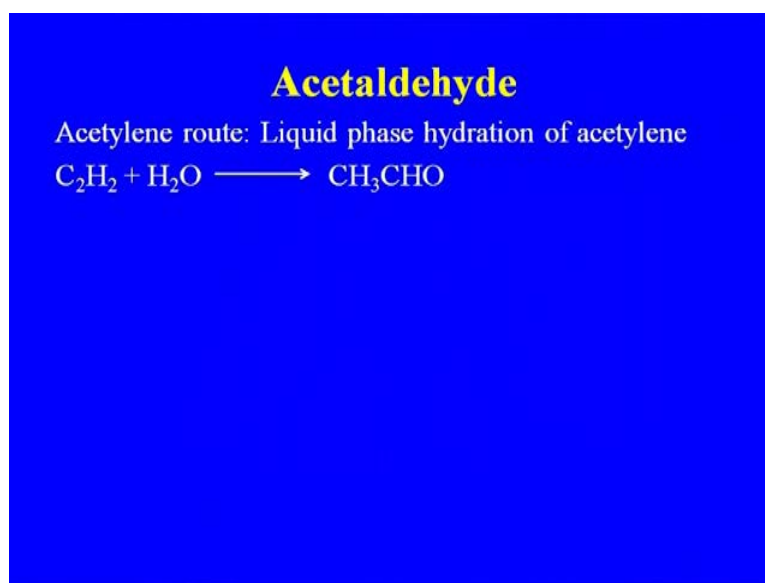
Acetaldehyde

- Process Technology
- Some of the commercial processes for the manufacture of acetaldehyde are:
- Liquid phase hydration of acetylene.
- Dehydrogenation or partial oxidation of ethanol.
- Oxidation of butane, propane/butane mixture.
- Liquid phase oxidation of ethylene.

The process technology the again here the same acetylene, which I was telling, that the acetylene in the earlier process was the liquid phase, hydration of the acetylene, dehydrogenation or the partial oxidation of the ethanol. That is the process where, the ethanol is available on the molasses route, they are using oxidation of the butane, propane, mixture, liquid phase oxidation of ethylene.

The last classes that is from the petrochemical point of view, that is very important and this is because we are getting from the from the your C 4 gases, you can get or from the natural gas you can separate and this can be used for the production of acetaldehyde. Because in during this process of making from butane, propane is, number of the other chemicals are also formed. So, this is the various technology, that is available for the manufacture of acetaldehyde.

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This is the acetylene route liquid phase hydration of the acetylene where, you are getting the acetaldehyde, this process is no more it has been used.

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Acetaldehyde

Oxidation and Dehydrogenation of Ethanol: Ethanol route for the manufacture of acetaldehyde is being used by those industries where ethanol is produced through fermentation of molasses.

There are two routes for manufacture of acetaldehyde from ethanol – vapor phase oxidation of ethanol and dehydrogenation of ethanol.

Oxidation and dehydration of ethanol, ethanol route for the manufacture of acetaldehyde is being used by those industries where, ethanol is produced through the fermentation of the molasses. They are two routes for manufacture of acetaldehyde from ethanol that is, the vapor phase oxidation of the ethanol and dehydrogenation of the ethanol.

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Acetaldehyde

- **Oxidation of Ethanol:**



- **Dehydrogenation of Ethanol:**



This is the process that is taking place, while the reaction that the oxidation of ethanol or the dehydrogenation of the ethanol.

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Acetaldehyde

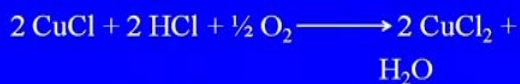
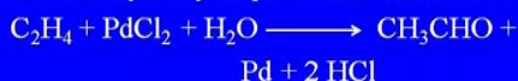
Acetaldehyde by Liquid Phase Oxidation of Ethylene: Commercialisation of ethylene route for manufacture of acetaldehyde began in 1960 and remains the widely accepted route because of availability of cheap ethylene from petrochemical complexes

Acetaldehyde by liquid phase oxidation of the ethylene, commercialization of the ethylene route for manufacture of the acetaldehyde began in 1960 and remains the widely accepted route, because of the availability of the cheap ethylene from the petrochemical complexes means, the cracker plants.

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Acetaldehyde

Acetaldehyde by Liquid Phase Oxidation of Ethylene



This is the reaction that is taking place in case of the liquid phase, again the palladium catalyst that we are using.

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Acetaldehyde

Oxidation of Hydrocarbons: Vapor phase oxidation of hydrocarbons, butane or propane/butane mixture at 370 °C yields acetaldehyde along with a wide range of chemicals including formaldehyde, methanol, acetone, glycols, etc. Because of formation of a wide range of byproducts, the purification section is complex and highly specialised.

Oxidation of the hydrocarbon, which I told you the vapor phase oxidation of the hydrocarbon, butane, propane, butane mixture yields acetaldehyde along with a wide range of the chemicals including the formaldehyde, methanol, acetone, glycol. So, these are all the mixture of the large number that has to separated and that was the actually the because here, we need the purification. The whole process complex and highly specialize in because of that reason, that direct from the ethylene route that is, more preferred in case of the manufacture of the acetaldehyde.

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Product Profile Of Acetaldehyde

Product	Uses
Pyridine, Picoline	Solvent, Drugs, Dyes, Agricultural chemicals
Chlor-aldehydes	Insecticides, Fungicides, Disinfectants
Acetaldol	1,3-Butylene Glycol (Polyesters), Urethane coating, Humectant, Printing ink, Crotonaldehyde, n-butyl alcohol, n-butyric acid anhydride, 2-ethyl hexanol, Rubber accelerator, Sorbic acid
Paraldehyde	Rubber accelerator, Antioxidant dye, stuff

These are the some of the product profile of the acetaldehyde and this is the pyridine and picoline, these are the two very important product. Even in case of Jubilant organization, they are making and which are finding use in the drugs, dyes, agriculture chemicals and this is the again, you see the while discussing the coal chemicals I told you, the route of the pyridine and picoline, even they through the coke oven plant also that was available. But with the coming of the development of this technology, now we are able to make from the ethylene route, from the acetaldehyde. So, pyridine and picoline, these are two very important valuable product of the Jubilant organization, which is being used for making of the agro chemicals.

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Product Profile Of Acetaldehyde	
Product	Uses
Per-acetic acid	Epoxidation reaction, Reagent in caprolactam, Synthetic glycerols
Penta-erythritol	Alkyl resin, Stabilizer, Plasticizers, Chlorinated polyether resin, Intumescent
Acetic, anhydride	Acetyl salicylic acid, Cellulose acetate, Esters
Acetic acid	Cellulose acetate, Vinyl acetate Chloro-acetic acid Ammonium acetate
Lactic acid	Food and, beverages, lactates, adhesives, Leather processing

Then, the chloral aldehydes, that is being used insecticide, fungicide, recent times acetyl parahaldehyde, rubber accelerator, anti oxidant of the and the in the dyes stuff industry. Peracetic acid, epoxi epoxidation reaction, reagent in the caprolactam then the synthetic glycerols, penta erythritol, acetic anhydride, the acetyl salicylic acid, cellulose acetate, esters, acetic acid, lactic acid, which are different use of these products are there. But starting material, that may be the from that is from the acetaldehyde, these are manufacture I am not going on detail on these.

Every product, which you are getting, how we are getting from acetaldehyde but these are the various products, which are available and they are finding wide application. This is the importance, why we are making the acetaldehyde, the acetaldehyde is considered

one of the very important derivative of the ethylene so far, the chemical industry is concerned, Because in so far, the PVC or the poly ethylene is concerned, that is going to the polymer industry but as a chemical feed stock, this is the importance, why the we are interested in the acetaldehyde.

So, we discuss about the ethylene, ethylene derivatives here, I did not discuss the cracker, already we have discussed how we are getting the ethylene from the cracker plant. The next lecture will be the another important petrochemical, that we are getting through the, from the cracker plant at the propylene. Propylene, that is one of the very important, where the same, the various product which you are getting the same propylene oxide as ethylene oxide or propylene glycol.

But, some of the other important products are also there, propylene because that is been used for the acrylonitrile, manufacture of the acrylonitrile and so the what are the various routes for getting the, apart from the your this cracker route, the the dehydrogenation of the paraffin, that is another important. What are the various technology because one of the technology which is coming, which I did not discuss there in case of the synthesis gas that is, the methanol to propylene, methanol to olefin technology.

So, all these things about the propylene on purpose means, the propylene from dehydrogenation, propylene from the cracker. From already we have discussed, we will be discussing in that the, how the propylene, what are the various technology available for the conversion of the paraffin's to the propylene and the methanol to propylene technology. Because that is going to the future source, the important source because that will go along with the cracker plant that is, the methanol to olefin, because the natural gas, where that will be used for the making of the methanol and methanol to olefin.

And that technology also coming from the coal gasification route, coal to polymer, coal to plastic, that is the same route coal to methanol and methanol to, again we are going for the propylene. So, that is the technology available and that is, we are going to at the China, they are going to have the coal chemical where, they are going to implement this technology. And in the future also, you may say, may see some of the plants, which are based on the methanol to olefin technology. So, these are the things that will be discussing in the next lecture that is, the about the propylene and their derivatives.