

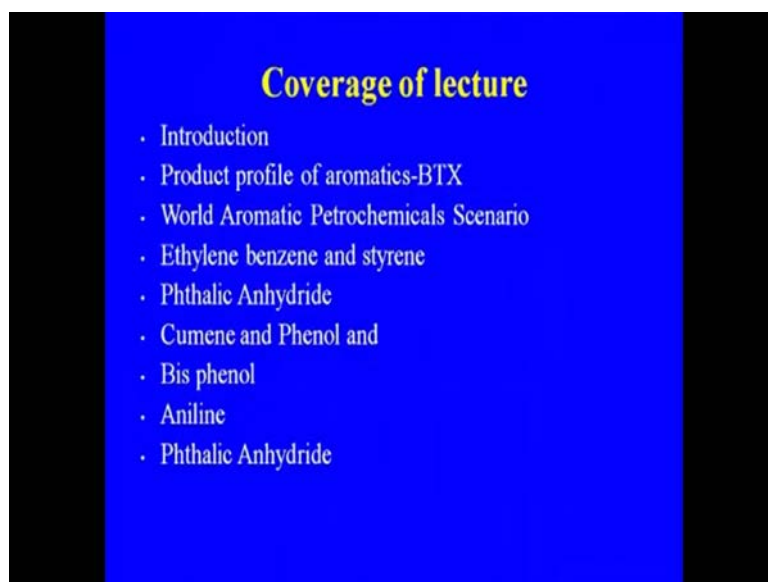
Chemical Technology
Prof. Indra D. Mall
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Module - 7
Petrochemical
Lecture - 8
Aromatic Product Profile, Ethyl Benzene and
Styrene, Cumene and Phenol, Bisphenol, Aniline

We are discussing module 7 of the organic chemical technology course and in the module 7 we are discussing about various petrochemicals which being manufacture. Already we have taken 7 lectures on the petrochemical and that was the introduction to the petrochemical then, it was the naphtha cracking, recovery of the FCC gases.

Then, we discuss about the synthesis gas ethylene and the propylene derivatives. Now, today will be discussing about a very important topic, already we discussed in the last lecture about the aromatic production. So, will be discussing aromatics product profile, ethyl benzene, styrene, cumene, phenol, bisphenol, aniline and ethylic anhydride also.

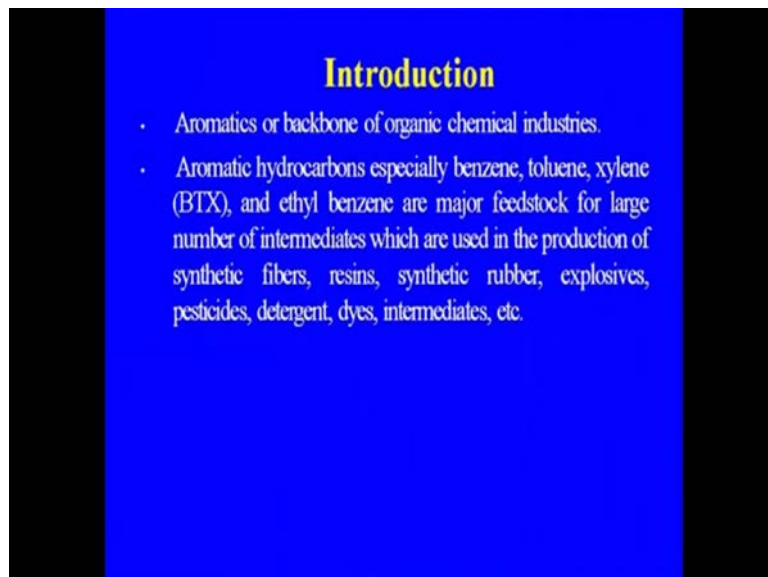
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The coverage of the lecture will be introduction, product profile of aromatics- benzene, toluene, xylene, world aromatic petrochemicals scenario, ethyl benzene and styrene manufacture. Because for the manufacture of styrene we need the ethyl benzene and for the ethyl benzene ethylene and the benzene and so that is the styrene that is the major outlet is for

the manufacture of the resins and synthetic rubber. Another important product of BTX is the phthalic anhydride, cumene and the phenol, bisphenol, aniline.

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So, aromatics as we discussed in case of this, is the ethylene is the king of the chemicals where, aromatic is the backbone of organic chemical industries. And before coming of the cracker there was the aromatics in some other format and one of the route was your coal, open gas, coke open gas and already we discussed about the coal chemical and the aromatics, different type of the aromatics which we are getting and even you see them.

Now, we are talking about the ortho xylene, perthalic anhydride, earlier it was the naphthalene route, which was produced from the coke oven plant. So, this is how the importance of the aromatics happens. But actually the availability of the aromatics that was more, only after the coming of the catalytic reforming because you see the requirement of the aromatics are huge.

And if you see the product profile of aromatic, the aromatic hydrocarbon especially the benzene, toluene, xylene BTX and ethyl benzene are major feedstock for the large number of the intermediates which are used in the production of the synthetic fiber. You take the case of the benzene we are producing the cyclohexane, cyclohexane to caprolactam. Similarly, other xylene to your para-xylene to TPA purified terephthalic acid or the DMT.

Similarly, resins: Various resins we are making poly styrene resin one of the important resin synthetic rubber, synthetic rubber SPR and another rubbers are there where you are using the huge amount of the aromatics explosive, TNT that was the one of the a very important explosive during the world war 1, world war 2. And so, TNT that played important role.

So, pesticide and benzene hexa chloride, which are called the gammexane. That was the first pesticide which was made from this benzene. That was the benzene hexa chloride after the DDT that was ban on the DDT. Detergent linear alkyl benzene: I already discussed about the linear alkyl benzene and the importance of the linear alkyl benzene where we are using the benzene for the alkalization process, dyes and intermediates where the huge amount of the aniline that will bring used for the production of the dyes intermediate.

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Derivatives of Benzene		
Cumene	Phenol	Adipic acid, Aniline, Bisphenol-A, Caprolactam, Phenolic resin, Pesticides, Dyes, Rubber chemicals
	Acetone	Methyl Isobutyl Ketone, Methyl Methacrylate, Solvent, Methyl Isobutyl Carbinol

These are the some of the derivatives of the benzene: So, from the benzene to cumene, cumene to phenol and acetone because during the manufacture of phenol from the cumene we are also getting acetone as bi product. So, the phenol outlet is for adipic acid aniline, bisphenol that is one of the very important product of the phenol which is going for the manufacture of the poly carbon. Then, the caprolactam, phenolic, resin, pesticide, dyes, rubber chemicals. Acetone- methyl isobutyl ketone, methyl methacrylate, solvent, methyl isobutyl carbinol.

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Cyclo-hexane	Caprolactam Nylon 6, Nylon 66, Adipic acid
Linear Alkyl Benzene	Detergent

Cyclo hexane that is another derivative of the benzene that we are making and that is going for the manufacture of the caprolactam nylon 6, nylon 66, adipic acid. Linear alkyl benzene that is going for the manufacture of the detergent, the biodegradable detergent. And with the coming of the linear alkyl benzene there has been lot of change in your detergent industry because of the availability of the raw material from the petrochemical route.

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Maleic Anhydride	Acids (fumaric, malic); lubricating oil additives; copolymers; agricultural chemicals, unsaturated polyester resin, 1,4-butanediol (Resins, polyurethane solvent,
Chloro Benzene	Aniline, phenol, DDT, chloro-nitrobenzene, biphenyl

Another derivative of the benzene that is the maleic anhydride which is finding the wide application as lubricating oil additives, copolymers, agriculture chemicals, unsaturated

polyester resin; 1, 4 butanediol. These are the some of the product outlet of the maleic acid. Chloro benzene: Chloro benzene was the route for the aniline all the nitro benzene that we are using. So, for making that, the chloro benzene chlorination of the benzene that was the routes; so aniline, phenol, DDT, chloro-nitrobenzene, biphenyl.

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Derivatives of Benzene		
Nitro Benzene	Aniline	Dyes and intermediates, rubber chemicals, drugs and pharmaceuticals, photographic chemicals, iso-cyanate.
BHC	Pesticides	
Ethyl Benzene	Styrene	Polystyrene, SBR, ABS and SAN resins, Acrylonitrile, Butadiene, styrene plastics, protective

So, these are the some of the other important nitrobenzene. As I told you the nitrobenzene that being used for the manufacture of the aniline- dyes and intermediates, rubber chemical, drugs and pharmaceuticals, photographic chemicals, iso-cyanate. BHC that is being used as a pesticides. Ethyl benzene that is one of the very important derivative of the benzene which is going for the manufacture of the styrene. And so, if you see the styrene that is the polystyrene, SBR, ABS, acrylonitrile, butadiene, styrene, polymer resin, SAN resin, acrylonitrile, butadiene styrene, plastic, protective.

So, these are the some of the outlets. Then, the toluene you see that they are having the less use of toluene normally. But, one of the major usage is the manufacture of the benzoic acid where, the benzoic acid toluene to benzoic acid and benzoic acid to caprolactam the truth is existing. But, mostly what we doing, we are going for the disproportionation of the dealcalization of the toluene for getting the more valuated product benzene and the xylene.

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Gasoline	Motor gasoline
Benzoic Acid	Caprolactam, pharmaceuticals and flavors, phthalates, terephthalic acid.
	Phenol, sodium benzoate - food preservatives.
p-cresol	Di-tert-butyl-p-cresol (antioxidants)
Solvents	

This is the about the benzoic acid. Then, the phenol sodium benzoate that is the one of the very important preservative we are making from the benzoic acid that is the sodium benzoate. Para-cresol solvents, these are some of the outlet.

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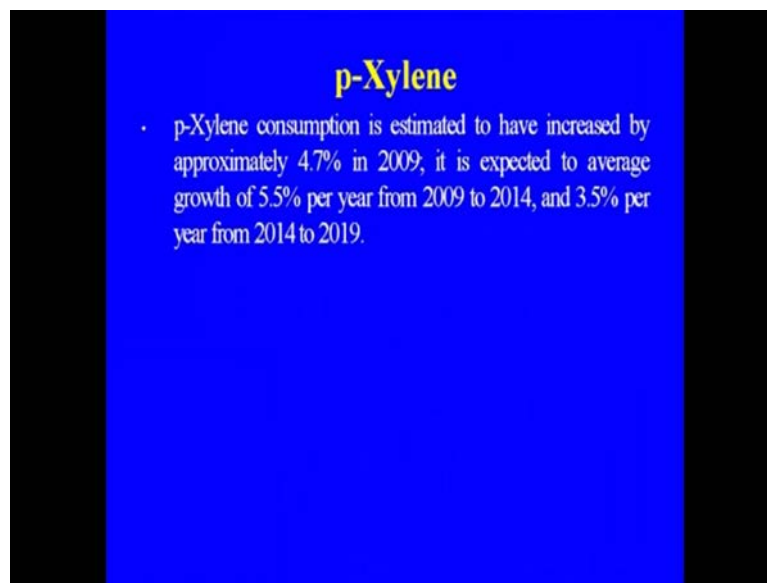
Gasoline	Motor gasoline	
Nitro toluene	Toluene diisocyanate	Polyurethane (Rigid foam, flexible foam, surface coatings)
	Trinitro-toluene	Explosives

Of course, that the TNT which I told you, that is the very important product trinitrotoluene. Nitro toluene that is going for the toluene diisocyanate which is used for the polyurethane rigid foam, flexible foam, surface coating. Trinitrotoluene: As I told you that is one of the very important explosive because your toluene that was available there from the coke over plant

also. But, with the coming of your catalytic reforming more and more toluene is available. So, the explosive that may be the one of the very important derivatives from the toluene which has been used. But, although the product of the other explosive that has been also developed.

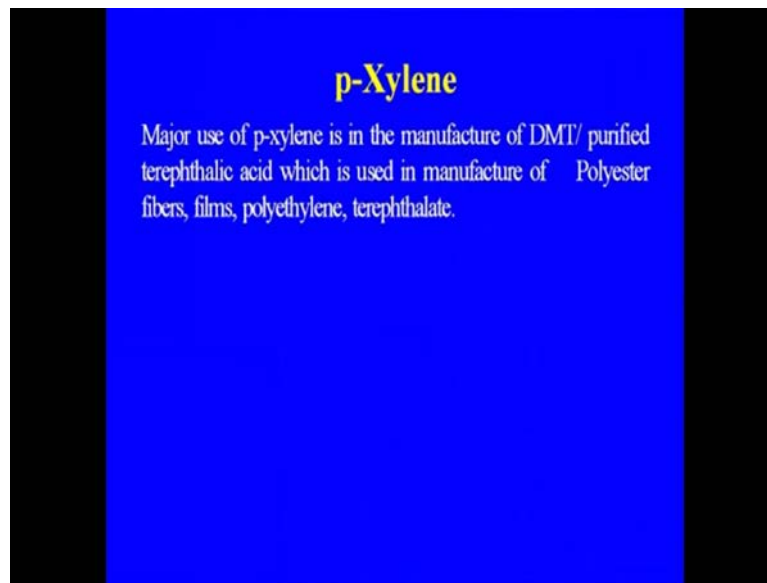
So, another important product of the benzene this aromatic group is the para-xylene. Para-xylene that is used for the manufacture of the polyester means the first para-xylene to DMT or the refined terephthalic acid.

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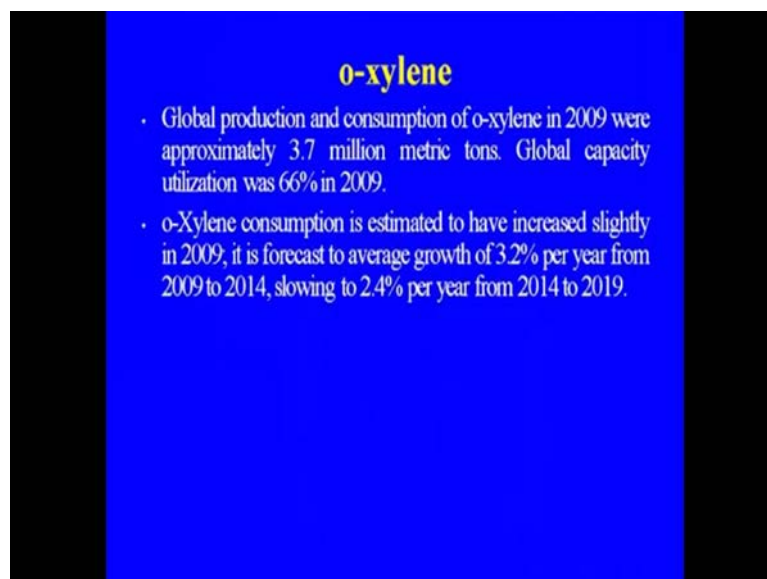
So, the consumption of the para-xylene estimated to have increased by approximately 4.7 percent in 2009, it is expected to average growth of 5.5 percent per year from 2009 to 2014 and 3.5 percent per year from 2014 to 2019 this is per as the market analysis of SLA. So, major use of the para-xylene as I discussed earlier also this in the manufacture of the DMT purified terephthalic acid which is used in the manufacture of polyester fibers films and the polyethylene terephthalate, polyethylene terephthalate.

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So, this is one of the major outlets for the para-xylene. So, this is the integral part of the any DMT acid plant where we are making the polyester. Another important product which you are getting from the catalytic reforming and when you are doing the para-xylene manufactures so, ortho xylene that is the bi product of the para-xylene plant. And so, now the para ortho xylene major portion of the ortho xylene that is going for the manufacture of the ethyl.

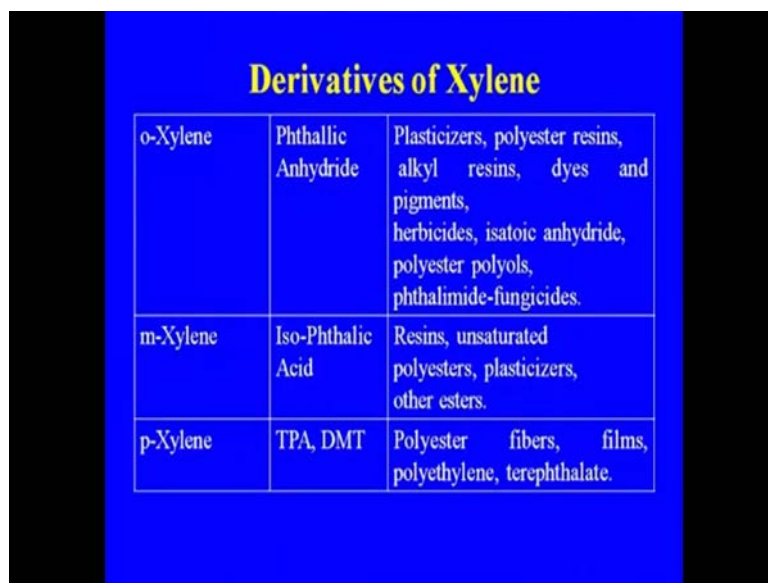
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So, the global production consumption of the ortho xylene 2009 was approximately 3.7 million metric tons. Global capacity utilization was 66 percent. Ortho xylene consumption is

estimated to have increase slightly in 2009 and it is forecast to average growth of 3.2 percent per year from 2009 to 2014. So, this is how the requirement of the ortho xylene that is increasing and especially for the manufacture of the ethylic.

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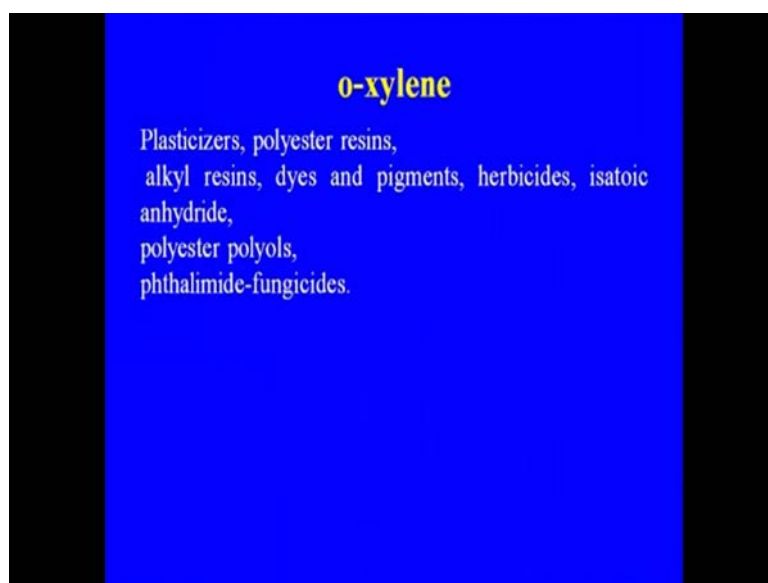


o-Xylene	Phthalic Anhydride	Plasticizers, polyester resins, alkyl resins, dyes and pigments, herbicides, isatoic anhydride, polyester polyols, phthalimide-fungicides.
m-Xylene	Iso-Phthalic Acid	Resins, unsaturated polyesters, plasticizers, other esters.
p-Xylene	TPA, DMT	Polyester fibers, films, polyethylene, terephthalate.

So, these are the some of the major derivative of the ortho xylene. That is the phthalic anhydride which is being used. Plasticizer one of the major use of the phthalic anhydride as plasticizer, polyester resin, alkyl resins, dyes and pigments, herbicides and the some other polyester polyols.

So, these are the some of the. So, as far the meta-xylene is concerned, one of the major derivatives is the iso-phthalic acid which is being used for the resins, unsaturated polyesters and then, the plasticizers and other esters para-xylene all you have to discuss.

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And so, this is as I told you the ortho xylene plasticizer, polyester resin, alkyl resins, dyes and pigments, herbicide, isatoic anhydride, polyester polyols and phthalimide fungicides that has been used.

Another, actually the aromatic route is naphthalene which was the earlier route for making of the ethyl anhydride because this was obtained from the coke oven plant. And so, the major use of the naphthalene apart from the other uses insecticide, naphtha and mouth balls another usage that was the one of the important source of the ethyl anhydride.

So, before coming of the para-xylene plant most of the ethyl anhydride that was been manufactured from the naphthalene route. So, these are the some of the surface actually present synthetic, staining agents, dyes, rubber chemicals, solvents, agriculture usage. So, these are some of the usage of the naphthalene.

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Product	Consumption 2002 (⁰⁰⁰ tonnes)	Consumption Growth (in%)	
		1997- 2002	2007- 2012
Benzene	33,278	3.5	2.8
Toluene	16,688	1.9	2.4
Ethyl benzene	25,130	4.2	2.7
Styrene	22,188	3.9	2.7

So, this is about the world aromatic petrochemicals scenario consumption figure of the benzene, toluene and xylene and the changing scenario from 1996 to 2002 and 2007 to 2012. Consumption growth that will be in percentage 3.5 for benzene, from 3.5 to 3.8, 1.9 to 2.4, ethyl benzene 4.2 to 2.7 and then, the styrene 3.9 to 2.7.

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Product	Consumption 2002 (⁰⁰⁰ tonnes)	Consumption Growth (in%)		
		1997- 2002	2002- 2007	2007- 2012
Mixed Xylenes	29,187	5.7	5.1	4.1
Xylene	3,050	3.4	4.5	2.7
p-Xylene	18,701	6.2	5.8	4.6

Similarly mixed xylenes, xylene, para-xylene, these are the some of the consumption figure and the growth consumption growth during the period 1997 to 2002 and 2002 to 2007 and 2007 to 2011.

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Product	Consumption 2002 (⁰⁰⁰ tonnes)	Consumption Growth (in%)		
		1997- 2002	2002- 2007	2007- 2012
Cumene	9,214	5.8	4.7	2.6
Phenol	7,166	5.2	4.4	1.7
Caprolactam	3,746	6.1	3.1	3.3
Phthalic Anhydride	3,488	3.5	4.1	2.5
TDI	1,383	3.9	4.1	3.7

This is about the cumene, phenol, caprolactam, phthalic anhydride and toluene diisocyanate. So, these are the some of the figures from where you can get an idea of how importance is the aromatic compounds which are being used in some their form in our daily life.

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Product	Consumption 2002 (⁰⁰⁰ tonnes)	Consumption Growth (in%)		
		1997- 2002	2002- 2007	2007- 2012
Terephthalic Acid	24,822	8.2	5.9	5.0
Dimethyl Terephthalate	3,747	-3.7	1.5	0.5
TDI	1,383	3.9	4.1	3.7

This is about the terephthalic acid and the dimethyl terephthalic. So, here also if you see the consumption that is the growth rate another earlier, it was the terephthalic acid. Huge growth was there in case of terephthalic slightly that has gone down but, the requirement that is increasing.

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Present Capacity and Production Scenario of Benzene, Toluene, and Xylenes in India (2009-10)

Product	Present capacity ('000 tonnes)	Production ('000 tonnes)
Benzene	1158	823
Toluene	281	137
o-Xylene	474	358
p-Xylene	2296	2223
Mixed xylene	165	55
Total	4374	3595

This is the present capacity and production scenario of the benzene, toluene and xylene in India. So, this is the figure. You can here, you can see the benzene production toluene is less and the more ortho xylene and para-xylene is there because the para-xylene requirement that is going in the major portion around 70 percent more than 70 that is going to for your terephthalic or the DMT.

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Installed & Production Capacity Major Intermediate ('000 MTPA) 2009-10 in India

Chemicals	Installed Capacity	Production
Acetone	46.0	44.3
Aniline	48.7	39.4
Benzene	1158	823
Nitrobenzene	54.0	12.3
o-Nitrotoluene	10.0	13.8
o-xylene	474	358
p-xylene	2296	2223
Phenol	74.0	71.6
Phthalic anhydride	298	232

This is the installed capacity production capacity of the major intermediate where, the aromatics are involved. Acetone, I have given because we are getting as a bi product from the

cumene plant while making the phenol aniline, benzene, nitro benzene, ortho nitro toluene, ortho xylene, para-xylene, phenol, phthalic anhydride.

So, this is the installed capacity of the various aromatic products we are getting. And this is the production figure this indeed is multiplied by 1000 metric ton per annum. So, this is the about the install and production capacity of the major intermediate during 2009 to 10.

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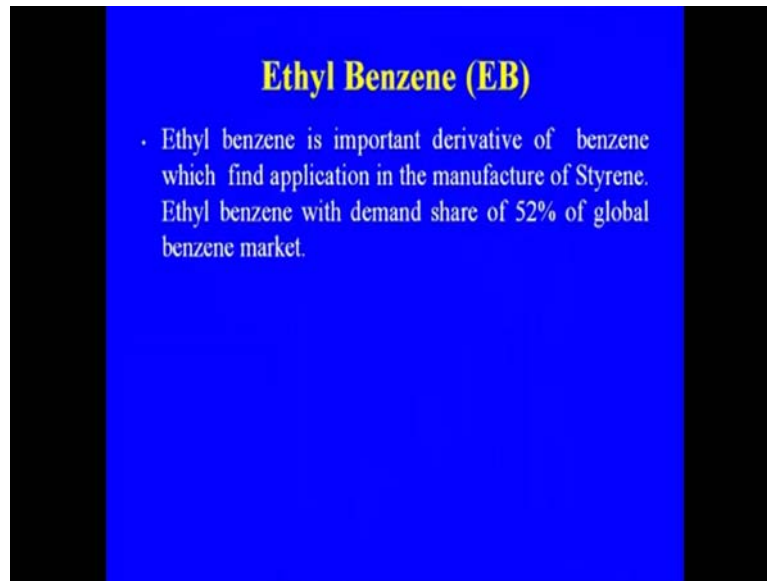
Product	Installed Capacity	Production
Aromatics		
Benzene	1158	823
Toluene	281	123
Mixed xylene	165	55
o-Xylene	474	358
p-Xylene	2296	2223
Linear Alkyl benzene	497	464
Phenol	74	71.59

This is the again installed capacity and production of the various aromatics major aromatics during the 2009 to 10 about the benzene, toluene, mixed xylene, ortho xylene and one of the another important product linear alkyl benzene and the phenol. So, these are the install capacity and this is the production figure and so your utilize capacity utilization that may be.

So, let us now discuss some of the important derivatives of the benzene in more detail in this series that will be the first that will be the ethyl benzene, because ethyl benzene you see the that is being used for the manufacture of the styrene and during the world war 1 and 2 that was the huge requirement of the styrene butadiene rubber at that time.

So, the even before coming of the petrochemical also, the styrene that was as you see in case of the synthetic chemical apparently they started making styrene butadiene rubber long back during the 60s. So, this is the importance of the ethyl benzene.

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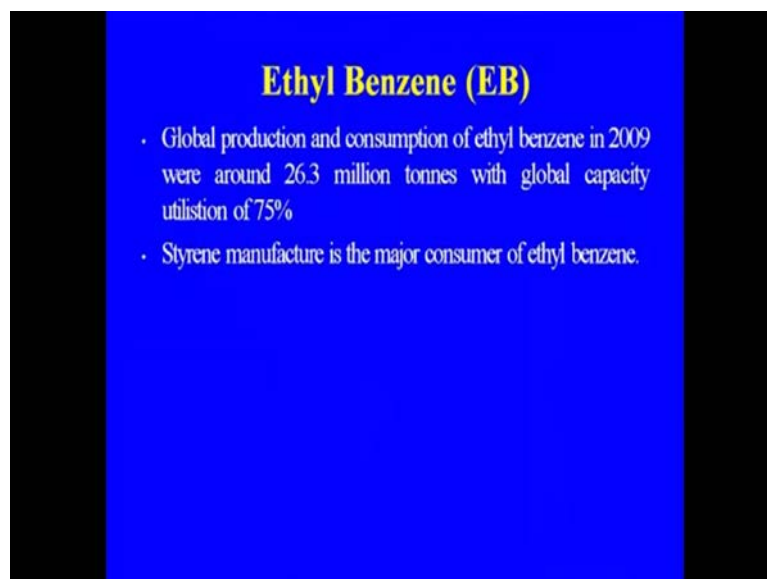


Ethyl Benzene (EB)

- Ethyl benzene is important derivative of benzene which find application in the manufacture of Styrene. Ethyl benzene with demand share of 52% of global benzene market.

So, ethyl benzene important derivative of the benzene which find application in the manufacture of the styrene. Ethyl benzene with the demand share of more than 52 percent of the global benzene market, where we are calculating the benzene with the ethylene. And ethylene that was coming through the molasses route at the time in the earlier stages when the styrene manufactured that was started.

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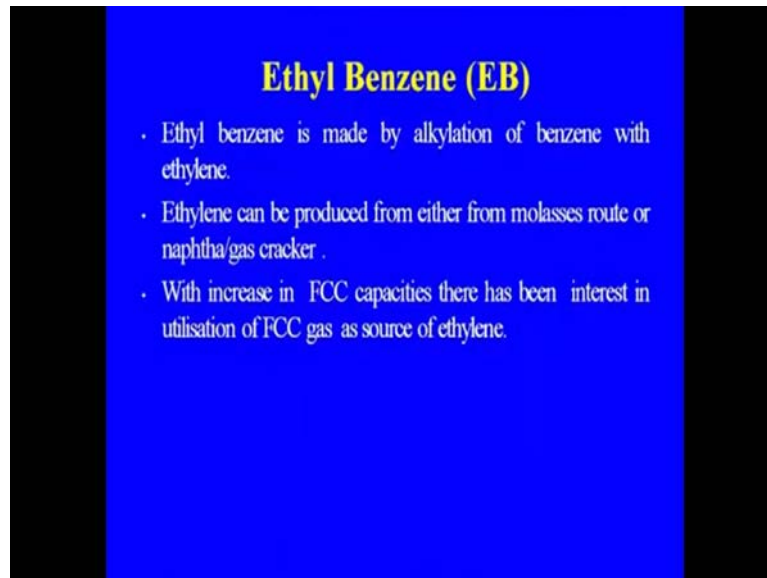
Ethyl Benzene (EB)

- Global production and consumption of ethyl benzene in 2009 were around 26.3 million tonnes with global capacity utilisation of 75%
- Styrene manufacture is the major consumer of ethyl benzene.

Global production consumption of the ethyl benzene 2009 where they around 26.3 million tones with the global capacity utilization of 75 percent. Styrene manufacture is the major

consumer of the ethyl benzene. Let us discuss now, what are the routes for the making of the ethyl benzene? Ethyl benzene, as you say the ethyl and benzene so, that is made by the alkylation of benzene and ethylene.

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Ethyl Benzene (EB)

- Ethyl benzene is made by alkylation of benzene with ethylene.
- Ethylene can be produced from either from molasses route or naphtha/gas cracker .
- With increase in FCC capacities there has been interest in utilisation of FCC gas as source of ethylene.

And so, again here also the same calculus about the hydrofluoric acid and now to the solid acid calculus. So, these are the some of the development that has taken place. So, ethylene because we need the benzene and ethylene. So, ethylene can be produce from either molasses route or the naphtha and the gas cracker.

But with increase in the FCC and because more and more we are going to operate on the propylene mode. So, there has been intense in the utilization of the FCC gases where, the ethylene that may vary from 8 to 12 percent. A source of ethylene and direct taking ethylene for the alkylation the processes are now available.

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Ethyl Benzene (EB)

- The conventional alkylation catalysts are metal chlorides(BF_3 , AlCl_3 , etc) and mineral acids(HF , H_2SO_4).
- Catalyst used for alkylation are,
 - ZSM-5 for vapor-phase
 - MCM-22 for liquid phase

Ethyl benzene technologies

- Catalytic Distillation technology
- UOPEB One process
- Mobil/Badger EBMax Process

The conventional as I told you in case of the alkylation catalysts where the metal chlorides and the mineral acid, hydro fluoric acid and H_2SO_4 . Catalysts used for alkylation are ZSM 5 for vapor phase, MCM 22 for liquid phase. The calculus use already I discuss, the ethyl benzene some of the technology which are available for the manufacture of the ethyl benzene that is the catalytic distillation then, the UOPEB 1 process, mobile badger EB max process. These are the 3 major process licensor for what is applying the process for the ethyl benzene technology. Now, let us discuss the first process that is the catalytic distillation technology because this is one of the major developments that has taken place.

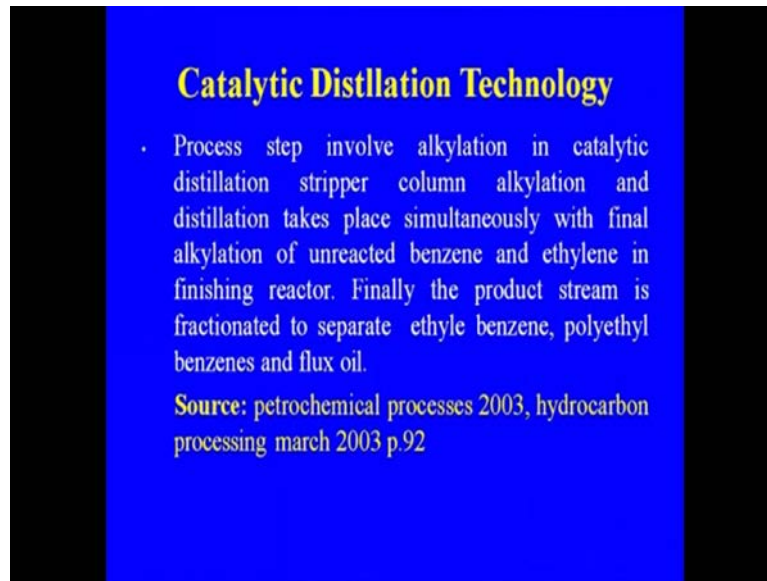
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Catalytic Distillation Technology

- The process consists of alkylation of benzene with ethylene using proprietry zeolite alkylation catalyst in a fixed bed catalytic distillation technology. This process is capable of handling a wide range in ethylene composition ranging from 10-100%.

The process consists of the alkylation of the benzene with ethylene using a property zeolite alkylation catalyst in a fixed bed catalytic distillation technology where, both the reaction and slight separation that is also taking place. This process is capable of handling a wide range in ethylene composition ranging from 10 to 100 percent because in case of the dilute steam of the ethylene that can be also use in this process.

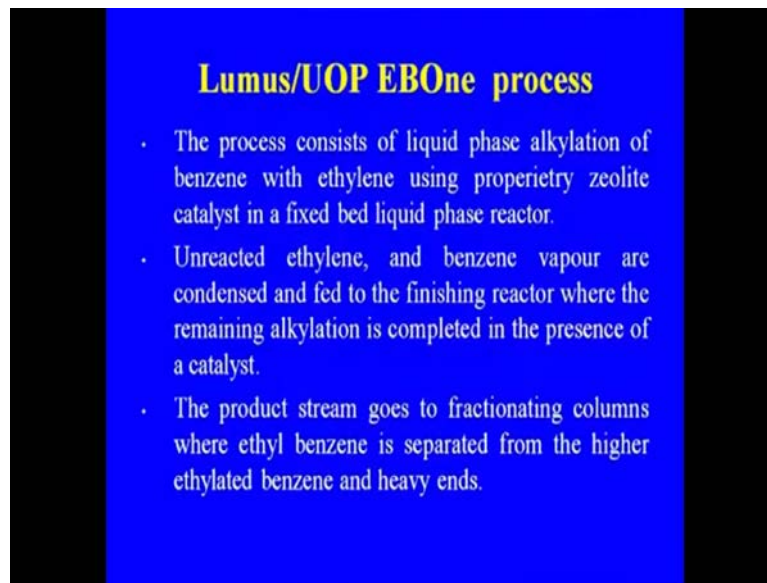
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So, process step involved in case of the catalytic distillation technology is the first is the major unit the catalytic distillation stripper column where alkylation distillation takes place simultaneously with the final alkylation of the unreacted benzene and ethylene in the finishing reactor where the remaining benzene and ethylene alkylation that is completed. Finally, the product steam is fractionated to separate ethyl benzene and the poly ethyl benzene which is also formed during process which is recycled to the trans-allocation section and to the flux oil.

So, these are some of the bi product the poly ethyl benzene and the flux oil. So, poly ethyl benzene that is again converted that is being recycled but, the flux oil that is the waste we are getting from the ethyl benzene plant.

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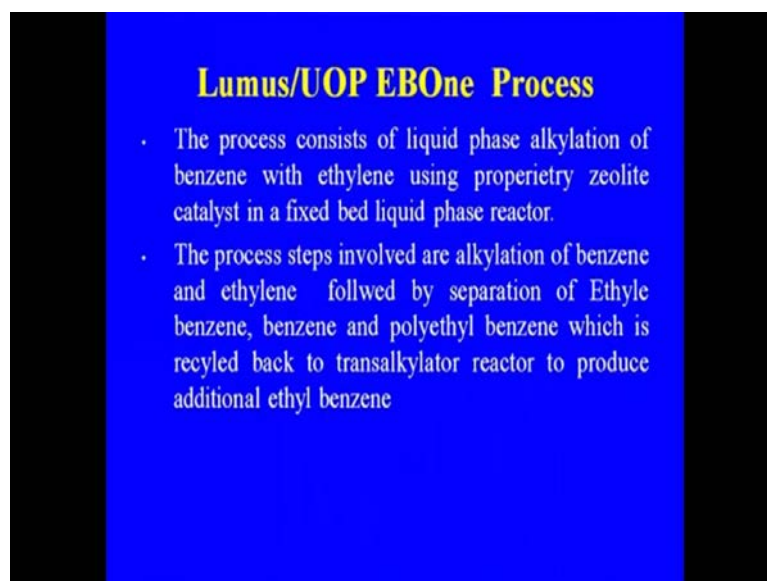


Lumus/UOP EBOne process

- The process consists of liquid phase alkylation of benzene with ethylene using proprietry zeolite catalyst in a fixed bed liquid phase reactor.
- Unreacted ethylene, and benzene vapour are condensed and fed to the finishing reactor where the remaining alkylaton is completed in the presence of a catalyst.
- The product stream goes to fractionating columns where ethyl benzene is separated from the higher ethylated benzene and heavy ends.

Another process that is the lumus UOP EB1 process: The process consists of liquid phase alkylation of benzene with ethylene using proprietry zeolite catalyst in a fixed bed liquid phase reactor. So, this is the process by lumus and UOP unreacted ethylene and benzene vapors are condensed and fed to the finishing reactor where the remaining alkylation is competed in the presence of the catalyst. So, here also 2 reactors are there and so, the finishing reactor that is complete reaction. The product stream goes to the fractionating columns where ethyl benzene is separated from the higher ethylated benzene and heavy ends.

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Lumus/UOP EBOne Process

- The process consists of liquid phase alkylation of benzene with ethylene using proprietry zeolite catalyst in a fixed bed liquid phase reactor.
- The process steps involved are alkylation of benzene and ethylene follwed by separation of Ethyle benzene, benzene and polyethyl benzene which is recyled back to transalkylator reactor to produce additional ethyl benzene

The process steps involved are as I told you the benzene and ethylene followed by separation of ethyl benzene and the polyethyl benzene which is a here also the bi product and which is recycle back to transalkylator reactor, this is the finishing stage reactor to produce the additional ethyl benzene.

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Liquid Phase Alkylation Of Benzene With Ethylene Using MCM-22 Catalyst

This process alkylation of ethylene takes place in a liquid filled alkylator reactor containing multiple fixed beds of MOBIL MCM-22 catalyst

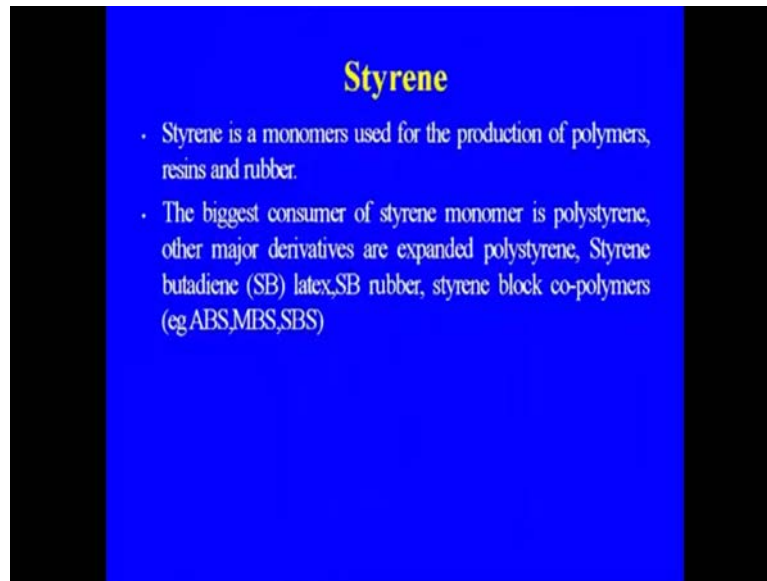
During alkylation Ethyl benzene and small quantity of polyethylbenzenes are formed which is converted to ethyl benzene using trans-alkylation catalyst.

$$\text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$$

Another process, the liquid phase alkylation of benzene with the ethylene using MCM-22 catalyst: This process alkylation of ethylene takes place is a liquid field alkylator reactor containing multiple fixed beds of mobile MCM 20 catalyst. Here also the alkylation ethyl benzene and small quantity of polyethylene benzene are formed which is converted to ethyl benzene using trans-alkylation catalyst.

So, this is the reaction which is taking place here the alkylation reaction. Now, this was the process for making of because any styrene plant that will be the combination of the ethyl benzene and then, the styrene manufacture.

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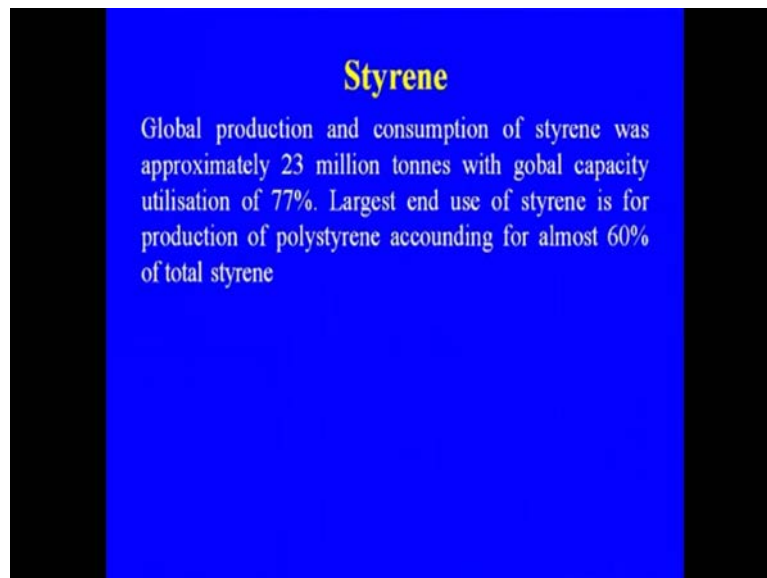


Styrene

- Styrene is a monomers used for the production of polymers, resins and rubber.
- The biggest consumer of styrene monomer is polystyrene, other major derivatives are expanded polystyrene, Styrene butadiene (SB) latex,SB rubber, styrene block co-polymers (eg.ABS,MBS,SBS)

So, in case of the styrene is a monomer used for the production of the polymer, resins and rubber. And the biggest consumer of the styrene monomer is the polystyrene. Other major derivatives are expanded polystyrene, styrene butadiene, latex, styrene butadiene rubber, styrene block co-polymers with the combination of the acrylonitrile ABS, MBS or the SBS.

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Styrene

Global production and consumption of styrene was approximately 23 million tonnes with global capacity utilisation of 77%. Largest end use of styrene is for production of polystyrene accounting for almost 60% of total styrene

So, styrene is a global production and consumption of styrene was approximately 23 million tones with the global capacity utilization of 77 percent. Largest end use of the styrene is for the production of the poly styrene accounting for almost 60 percent of the total styrene.

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Styrene

Styrene is made by catalytic dehydrogenation of ethyl benzene

$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \longrightarrow \text{C}_6\text{H}_5\text{CH}=\text{CH}_2 + \text{H}_2$$

Styrene plant consists of two major units. The process involves:

- Production of ethylene either from molasses route or by naphtha/natural gas cracking.
- Production of ethyl benzene
- Dehydrogenation of ethyl benzene.

So, the process of making styrene that is the styrene made by the catalytic dehydrogenation of the ethyl benzene. So, this is the process that we are using. Styrene plant consists of the 2 major unit's: Production of the ethylene either from molasses route or by naphtha natural gas cracking, production of ethyl benzene and then, the dehydrogenation of the ethyl benzene to styrene.

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Process For Styrene Manufacturing

Lumus/UOP EB One Process: In this process first alkylating benzene with ethylene followed by dehydrogenating the EB to form styrene.

The polyethylbenzene formed during alkylation is fed to another reactor for transalkylating with benzene.

$$\text{C}_6\text{H}_6 + \text{C}_2\text{H}_4 \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$$
$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + \text{C}_6\text{H}_6 \longrightarrow 2\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$$
$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + \text{C}_6\text{H}_6 \longrightarrow 2\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$$

This is the lumus UOP EB process. In this process first the alkylating benzene with the ethyl benzene followed by dehydrogenation of the ethyl benzene to form styrene. So, the poly ethyl

benzene which is formed during the alkylation is fed to another reactor where the transalkylating alkylation reaction is taking. So, these are some of the reaction that is taking place in case of your styrene manufacture. First it will be the ethyl benzene and some of the higher polyethylene benzene that will be converted to again ethyl benzene. So, this is the dehydrogenation process that is taking place. Finally, ethyl benzene that was during the manufacture of the ethyl benzene.

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Process For Styrene Manufacturing

Ethyl benzene and recycled ethyl benzene are then dehydrogenated to styrene in the presence of steam at high temperature (550-68°C) under vacuum in a multistage reactor

$$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 \longrightarrow \text{C}_6\text{H}_5\text{CH}=\text{CH}_2 + \text{H}_2$$

$$\text{H}_2 + 1/2\text{O}_2 \longrightarrow \text{H}_2\text{O}$$

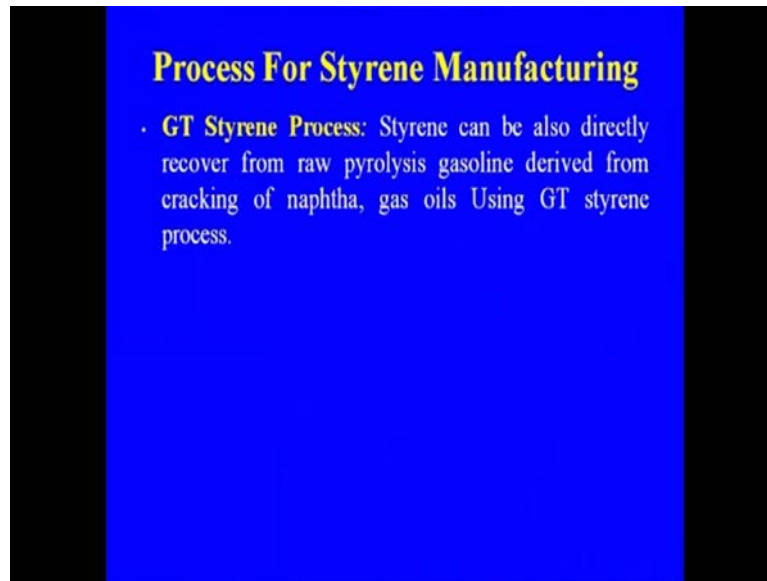
Toluene is formed during the process which is recovered

$$\text{C}_6\text{H}_5\text{CHCH}_2 + \text{H}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}_3$$

$$\text{C}_6\text{H}_5\text{CHCH}_2 \longrightarrow \text{C}_6\text{H}_5\text{CH}_3 + \text{C}$$

Ethyl benzene and recycled ethyl benzene are then dehydrogenated to styrene in the present of the steam at a pressure temperature of 550 to 568 degree centigrade under vacuum in a multistage reactor. So, this is the reaction that is taking place. But, toluene is formed in the process which is recovered.

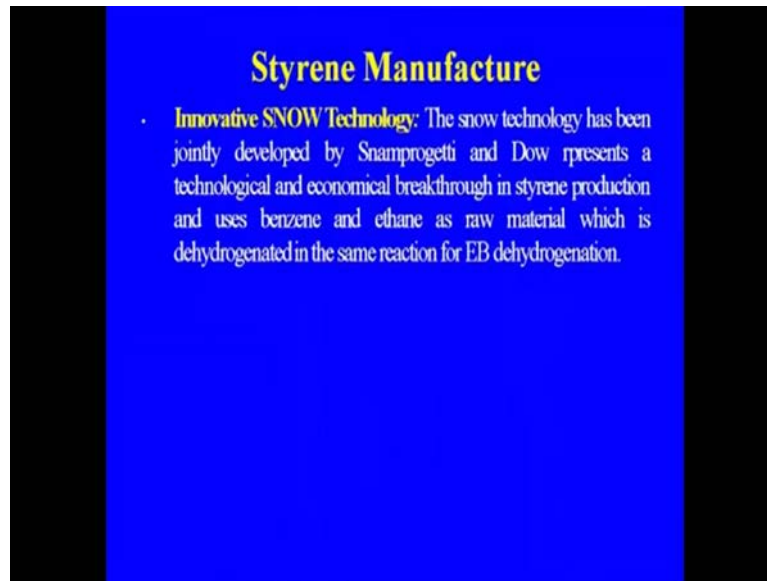
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Another process technology for manufacture of the styrene is the GT styrene. Styrene can be also directly recovered from the raw pyrolysis gasoline derived from the carking of naphtha, gas oil using the GT styrene process. Here, what is happening in case of the as I told you, during the manufacture of the aromatics along with the other ceat is the para-xylene, ortho xylene, ethyl benzene is also there.

That ethyl benzene that is separated and that can be used for making of the styrene as I discussed, I told you that even the ethylene part, that the ethylene which is available from the FCC gases that can be also used. So, here directly ethyl benzene because from the pyrolysis gasoline that can be separated. This is another very new development in case of the styrene technology that the innovative snow technology. The snow technology has been jointly developed by Snamprogeti and Dow represents a technological and economical breakthrough in the styrene production and uses benzene and ethane as raw material which is dehydrogenation in the same reactor for ethyl benzene. Because dehydrogenation of the ethane to ethylene that will be there and so that will be used for the ethyl benzene manufacture.

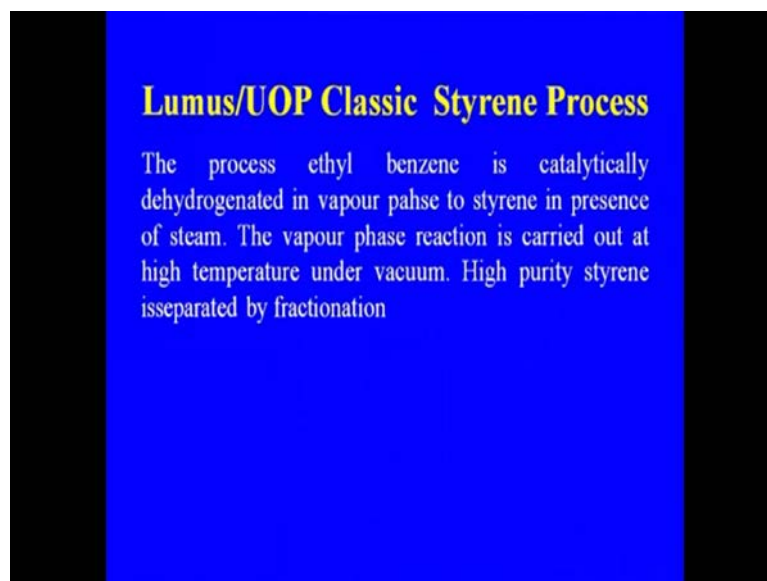
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Styrene Manufacture

- **Innovative SNOW Technology:** The snow technology has been jointly developed by Snamprogetti and Dow represents a technological and economical breakthrough in styrene production and uses benzene and ethane as raw material which is dehydrogenated in the same reaction for EB dehydrogenation.

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Lumus/UOP Classic Styrene Process

The process ethyl benzene is catalytically dehydrogenated in vapour phase to styrene in presence of steam. The vapour phase reaction is carried out at high temperature under vacuum. High purity styrene is separated by fractionation

Lumus UOP classic styrene process: The process ethyl benzene is catalytically dehydrogenated in vapour phase to styrene in presence of the steam. The vapor phase reaction is carried out at high temp under vacuum. High purity styrene separated by fractionation. Now, this was about the ethyl benzene, the styrene which is one of the very important derivatives because huge amount of the styrene that is going for the making of the polyester. Another important product that has been in case of the benzene is the cumene to methanol to cumene to phenol.

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Cumene

Cumene is made by alkylating benzene with propylene using zeolite catalyst.

Following three major processes are available

- Catalytic Distillation Technology
- Liquid phase Q-max Process
- Cumene by Mobil Badger Process

So, cumene is made by alkylating benzene with the propylene. And this was only actually this process why the cumene process came into that replaced the other process because the propylene that is available from the cracker plant benzene is available from the aromatic plant. So, the raw material definitely that is much economical than the conventional raw material which was use for making of the phenol that was from the chloro benzene route or some other routes are also there. So, the cumene is made by alkylating benzene with propylene using zeolite catalyst. Following are the 3 major processes available: Catalytic distillation technology, liquid phase Q-max process, cumene by mobil badger process.

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Primary Alkylation And Transalkylation Chemistry For Cumene Production

The diagram illustrates the chemical reactions for cumene production:

- Alkylation:** Benzene reacts with propylene to form cumene.
- Transalkylation:** Two reactions are shown where a diisopropylbenzene (DIPB) isomer reacts with benzene to produce cumene and another DIPB isomer. The first reaction shows 1,2-DIPB reacting to form 1-cumene and 1,3-DIPB. The second reaction shows 1,3-DIPB reacting to form 2-cumene and 1,2-DIPB.

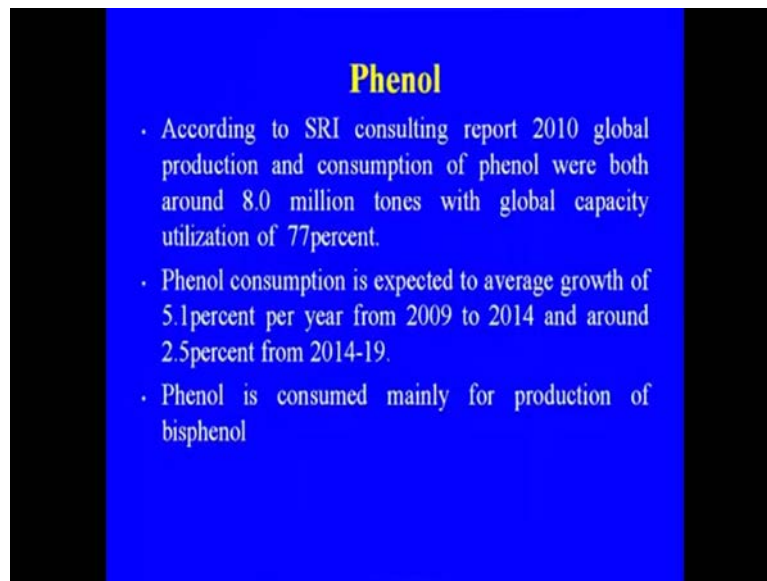
Sources: Degnan T.F., Morris C. S., Venkat C. R. 2011. Alkylation of aromatics with ethylene and propylene: recent developments in commercial processes Applied Catalysis A: General Vol 221, P 283–294

These are the some of the reactions that is taking place in case of the benzene, propylene and then, you are getting the cumene. During the cumene manufacture we are also getting and some which are some of the DIPB plus benzene to cumene. And similarly, the other side reaction also taking place. But, finally, we are getting the cumene.

So, this is the process where the propylene and the benzene along with the fresh benzene that is going to the sires of the reactor the alkylkating reactor, the trans alkylation reactor, depropanizer and then, the benzene column, cumene column and the poly isopropyl benzene column. So, that is the finally, here the cumene is separated and so that cumene will go for the making of the phenol.

So, this was the importance of the cumene and now, the phenol process making of the phenol this all through the cumene process. So, while making of the cumene to phenol we are getting acetone. One of the very important product as a bi-product.

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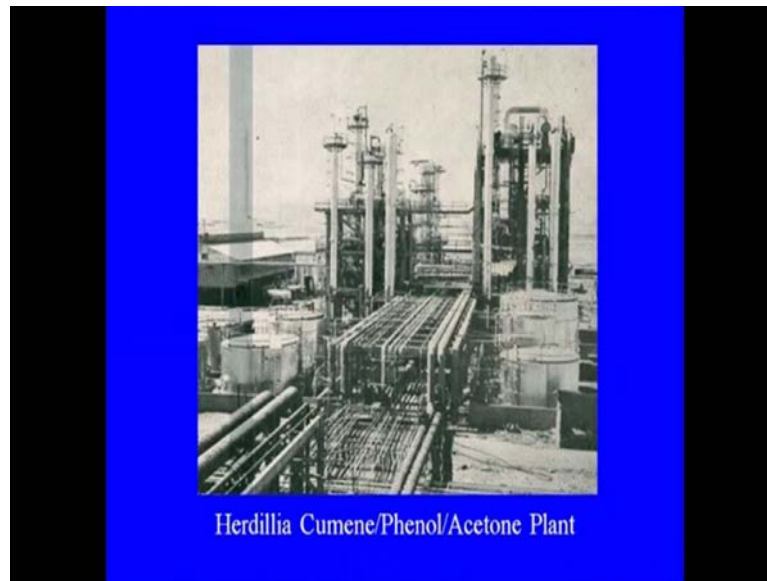


Phenol

- According to SRI consulting report 2010 global production and consumption of phenol were both around 8.0 million tons with global capacity utilization of 77percent.
- Phenol consumption is expected to average growth of 5.1percent per year from 2009 to 2014 and around 2.5percent from 2014-19.
- Phenol is consumed mainly for production of bisphenol

So, according to SRI consulting report 2010 global production and consumption of phenol were both around 8.0 million tons with global capacity utilization of 77 percent. Phenol consumption is expected to average growth of 5.1 percent per year from 2009 to 2014 and around 2.5 percent from 2014 to 19. Phenol is consumed mainly for the production. One of the major use of although the phenol other uses are also there. One of the major outlets that has been manufacture of bisphenol which is being used for making of the poly carbon.

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This is the cumene a phenol acetone plant of the hedrilla chemical. This is also one of the large integrated petrochemical complex where they are making a large number of the petrochemicals and this is one of their very important product.

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Phenol from Cumene

Phenol from cumene is a two step process with the first step being the production of cumene hydroperoxide and the second step is the decomposition of the cumene hydroperoxide to phenol and acetone.

Temperature : 180-200 °C

Pressure : 3.5-4.0 MPa

Catalyst :Metal catalyst, Aluminium chloride, Bentonites, Silica aluminate

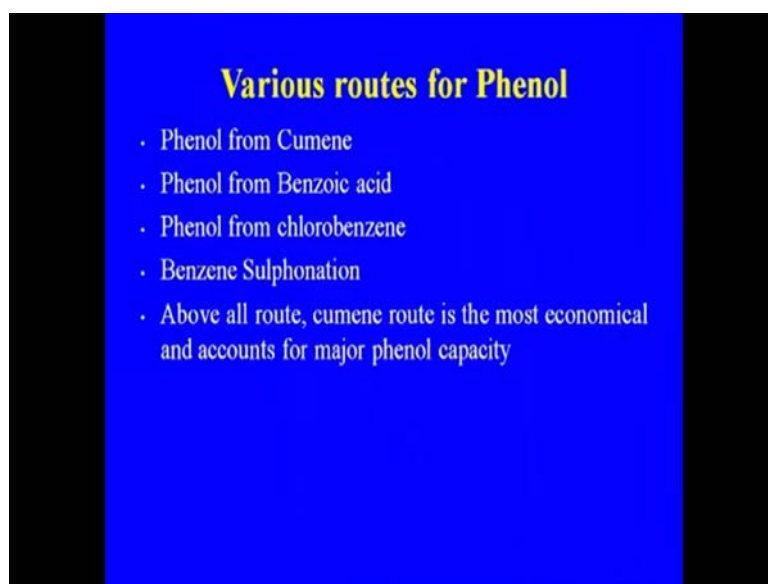
Phenol from cumene: Because as I told you now all the phenols that have taken place with the cumene process. So, cumene phenol from cumene is a 2 step process with the first step being the production of cumene hydro peroxide and the second step is the decomposition of the cumene hydro peroxide to phenol and acetone.

So, this is as I told you that, there is the acetone that is the bi product during the manufacture of the phenol. So, temperature around 180 to 200 degree centigrade. This is the pressure catalyst, metal catalyst and aluminum chloride, bentonites, silica aluminates. So, the various routes for the phenol other route are as I told you the other routes are there and earlier the phenol was made by these benzoic acid route or the chloro benzene route or the benzene sulphonation route. But, now most of the phenol the cumene process that has been most attractive process because of the availability of the benzene from the catalytic reforming process and propylene for the cracker plant or from the dehydrogenation of the propylene.

But, these other routes are because benzoic acid again from butadiene to benzoic acid. So, they from the benzoic acid to phenol or from the chloro benzene. Again in case of the chloro benzene, you are taking the benzene so that has to be chlorinated. So, involvement of the chlorine is there.

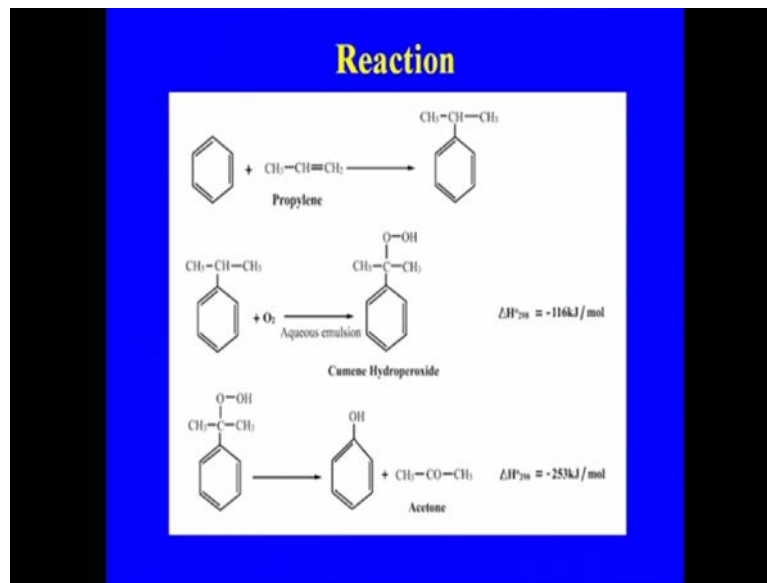
So, because of all those reason now it is the more prefer route for the making of the phenol is the cumene route. Another route that was the benzene sulphonation, where again the handling of the sulfuric acid is there.

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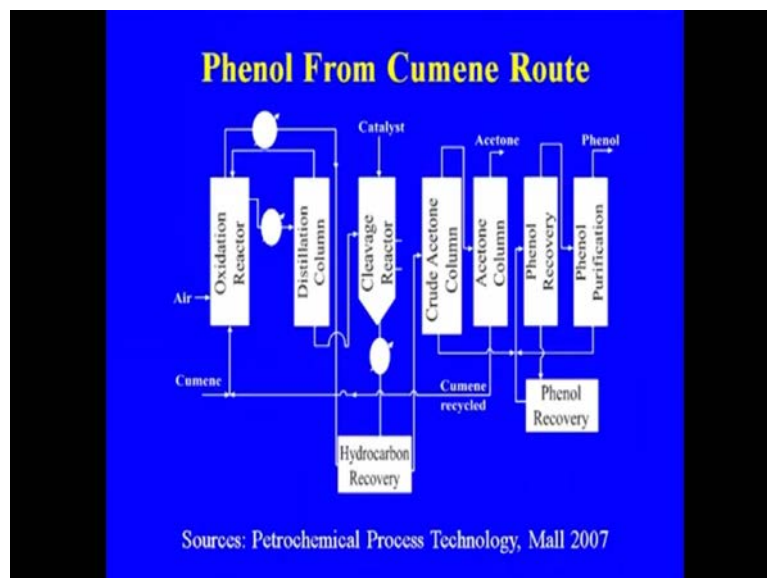
Above all route, the cumene route is the most economical and account for major phenol capacity.

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This is the reaction that is taking place in case of your phenol manufacture. Benzene, propylene that is reacted and you are getting the cumene hydroperoxide and from the cumene hydroperoxide your finally, getting the phenol and the acetone as the bi product. So, this is the oxygen of aqua solution. The cumene hydro peroxide is formed and from the cumene hydro peroxide phenol process that you are having. So, this is the process that has being used for the manufacture of phenol.

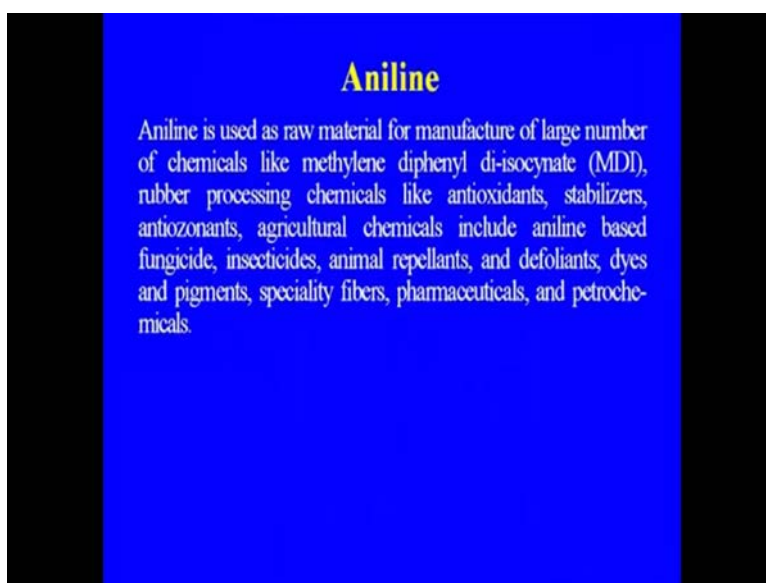
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This is your phenol from the cumene process. So, the cumene will go to oxidation tower, distillation tower. Then, the cleavage reactor catalyst you are riding here, crude acetone column and then, it will go to the acetone column where the separation of the acetone that will take place and from the screw distillation bottom product that will go to the phenol purification section where the phenol finally, will be getting the phenol here.

Here at the bottom again this will join to the phenol recovery section. Then, final distillation that was separates the phenol. So, this is the you see the first will be the any phenol manufacture any that will have the cumene manufacturing part then, from the cumene to phenol recovery means the finally, you are getting the phenol here and the acetone that will be the bi product of the cumene process. Now, let us discuss another very important product of the benzene that is the aniline which is being used in huge amount as a di-intermediates.

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So, aniline as used as a raw material from manufacture of the large number of the chemical like methyl diphenyl di-isocyanate MDI, rubber processing chemicals like antioxidants, stabilizers, anitozonants, agriculture chemicals include aniline based fungicide, insecticide, animal repellants and defoliants; dyes and pigments, specialty fibers for the fiber then, the pharmaceuticals and the petrochemicals.

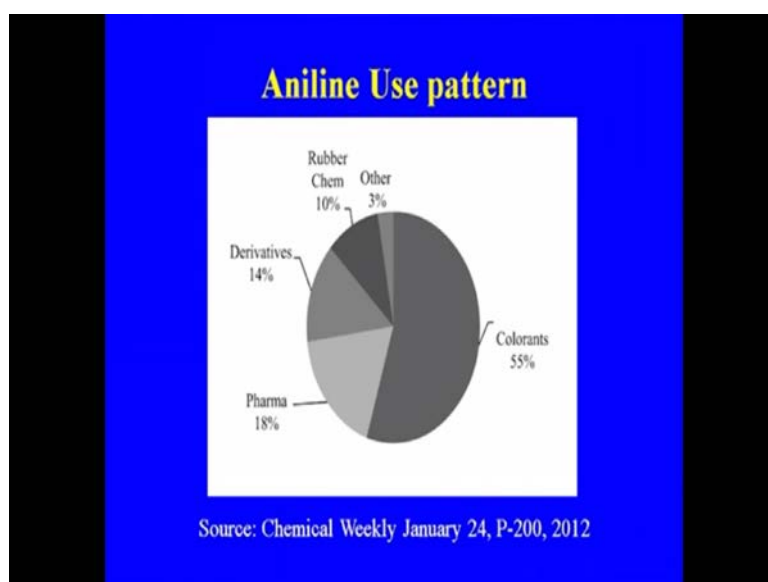
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Aniline

A large number of aniline derivatives are used in large variety of dyes. A major portion of aniline is used in the manufacture of rigid polyurethane

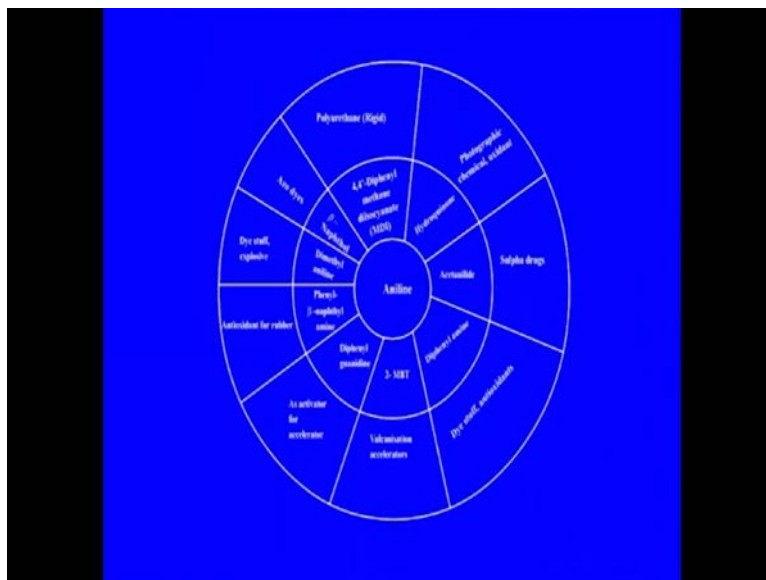
But as I told you the last of the aniline derivatives are used in the large variety of the dye because now the wide variety of the dyes depending upon the type of your textile that has been developed. And so, the aniline that has been providing basic intermediate for making number of the dye. A major portion of the aniline used in the manufacture of the rigid polyurethane also.

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This is you see the major portion of the aniline that is going as the colorants manufacture of your dyes. So, rest of the other used the pharmaceutical and the other derivatives rubber chemicals. But, major portion that is going as the colorants.

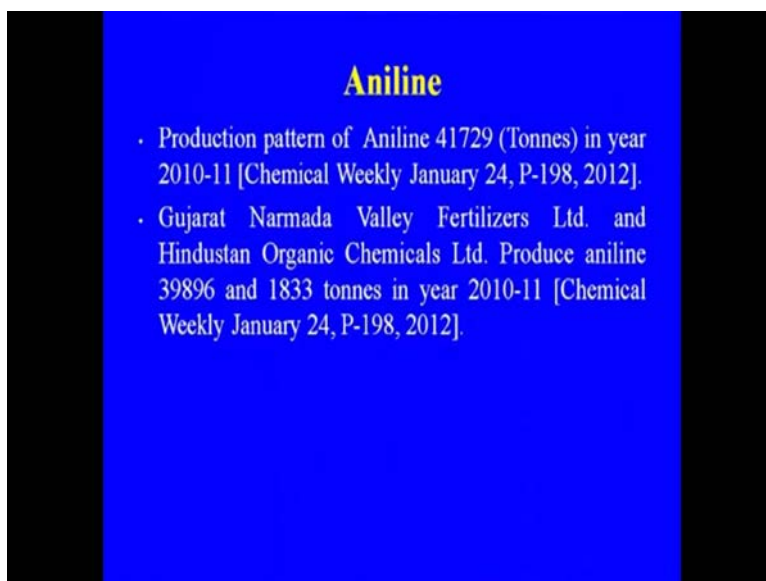
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These are the major uses of the aniline if you see the aniline to hydro cumene acetenyle then, the diphenyl amine, 2 MB2 to diphenyl ingredient, diphenyl naphthyl amine, veta naphtha already is one of the very important intermediate which are using in the dye industry.

So, this is for making of the eso dyes. Although there is ban on the use of eso dye. But, these are the some of the again the dimethyl amine is also going for your dye stuff and the explosive. So, these are a large number of the products are there which are 2 MB2 that is going for the vulcanizing and the accelerator as activator for accelerator dye phenol. So, these are some of the major outlet of the aniline. And even as you see before coming of the aromatic plant the route was for making the benzene aniline again it was through the coke oven plant, aromatic oven the coke oven plant.

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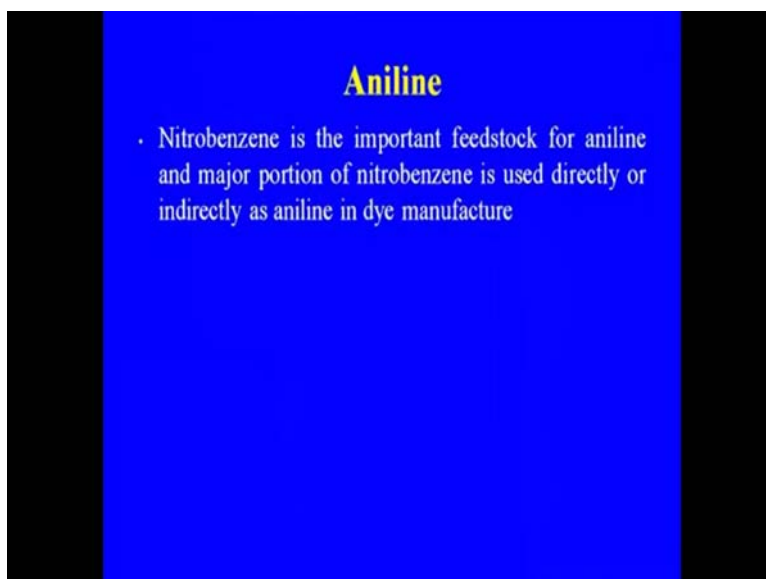


Aniline

- Production pattern of Aniline 41729 (Tonnes) in year 2010-11 [Chemical Weekly January 24, P-198, 2012].
- Gujarat Narmada Valley Fertilizers Ltd. and Hindustan Organic Chemicals Ltd. Produce aniline 39896 and 1833 tonnes in year 2010-11 [Chemical Weekly January 24, P-198, 2012].

So, this is the production pattern of the aniline in the year 2010 and 11, this is in India. Gujarat Narmada valley fertilizers GNVFC that is Hindustan organic, they are the major producer of the aniline. GNVFC is the one of the large integrated petrochemical complex where they are making also the fertilizer and at the same time many of the petrochemicals. Now, they have two divisions: One is the fertilizer division and other is the chemical division.

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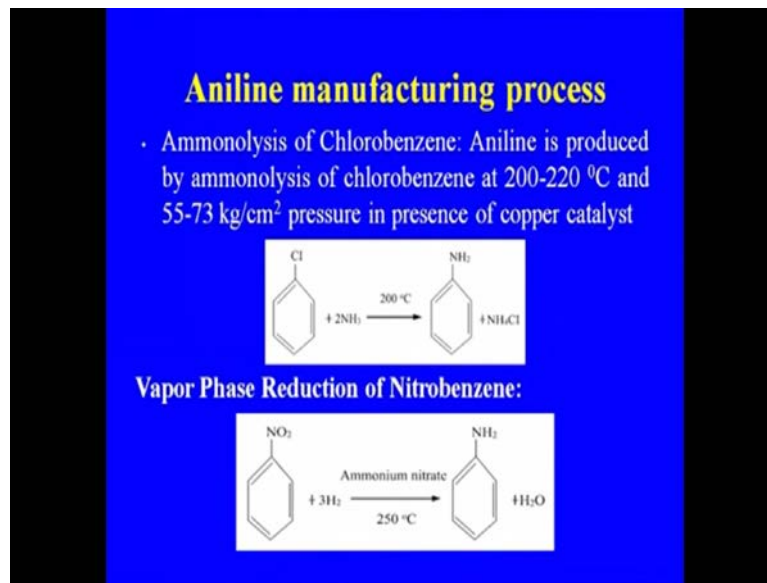


Aniline

- Nitrobenzene is the important feedstock for aniline and major portion of nitrobenzene is used directly or indirectly as aniline in dye manufacture

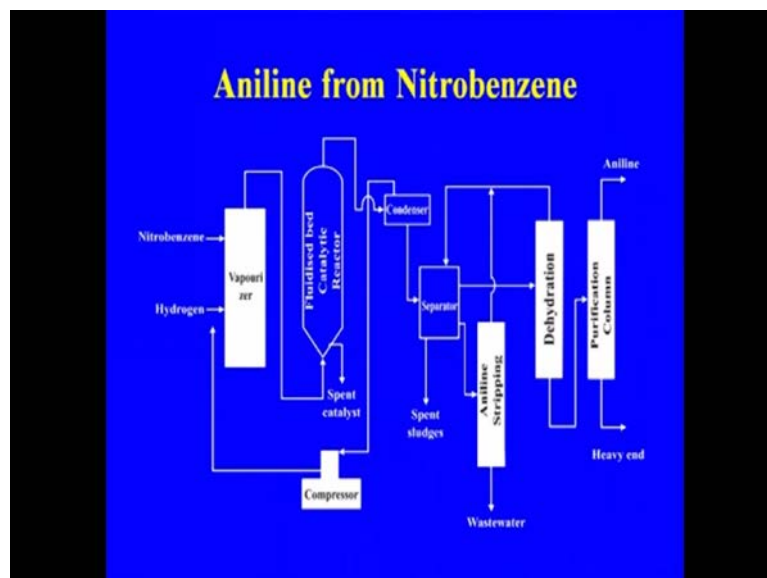
So, aniline nitro benzene is the important feed stock for the aniline and the major portion of the nitro benzene is used directly or indirectly as aniline in dye manufacture.

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This is the reaction in the manufacture of aniline. Ammonolysis of chlorobenzene: Aniline produced by ammonolysis of the chlorobenzene at 200 to 220 degree centigrade and the other vapor phase reduction of the nitro benzene. So, this is from the nitro benzene route, this is from the chloro benzene routes. So, both the routes were earlier used for making of and the still that is being used for making of the aniline that the, either through the chloro benzene or from the nitro benzene route.

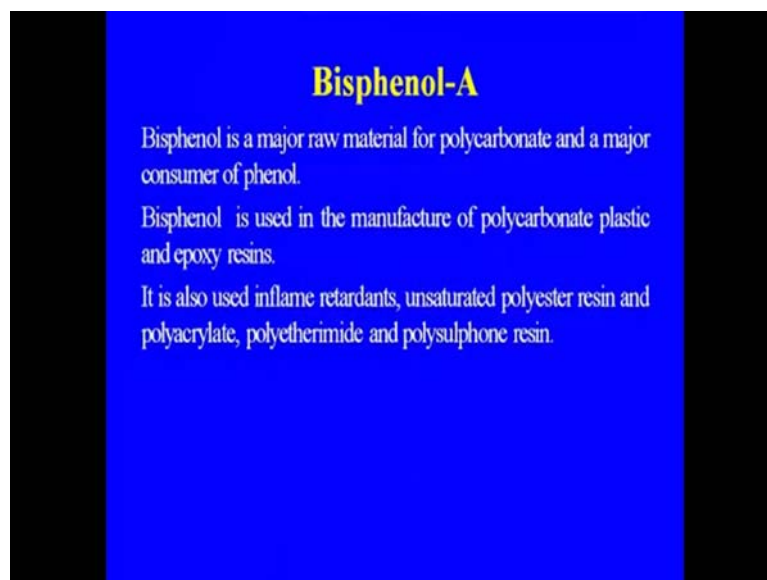
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This is the method for the aniline manufacture nitro benzene hydrogen that going to be vaporizer from the vaporizer to your. This is the catalytic reactor come distillation column where the reaction is taking place and then finally, it is going for the after the separation of the calculus, it is going to separation of the aniline and the heavy aniline.

So, this is the process that we are using for the making of the aniline from the nitro benzene route. Now, let us discuss about the bisphenol which is one of the important derivative I told you earlier also because this is the major raw material for poly carbonate and major consumer of the phenol because the phenol and the phosphene that you are using here that is going for the making of the bisphenol. And so, the bisphenol and now we are saying your polycarbonate.

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And the bisphenol is used for the manufacture of the poly carbonate plastic and epoxy resins. It is also used in as the inflame retardants, unsaturated polyester resin and polyacrylate, polyethrimide and the polysulphone resins. One of the major outlets is for the bisphenol that is the poly carbonate, optical glasses and the many because that is having very high stain. So, that is being used for poly carbonate, even the CD another and the electronics industry also lot of the uses of the poly carbonate is there.

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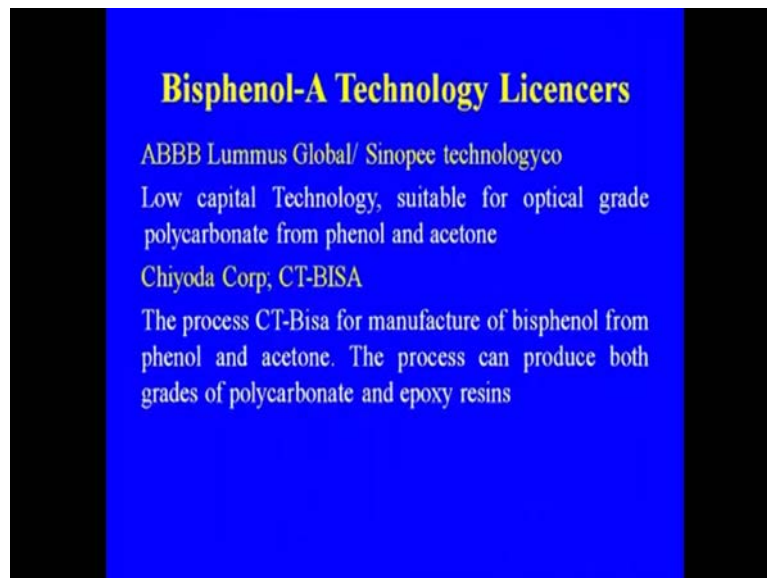


Bisphenol-A :Process Technology

- Condensation of phenol with carbonyl compounds.
- Condensation of phenol with alkenyl phenol.
- Condensation of phenol with ethylene and acetylenes.
- Condensation of phenol with alkyl benzene.

So, technology: The condensation of the phenol with the carbonyl component compounds, condensation of phenol with the alkenyl phenol, condensation of phenol with the ethylene and acetylenes, condensation of phenol with the alkyl benzene. These are the some of the routes available.

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Bisphenol-A Technology Licencers

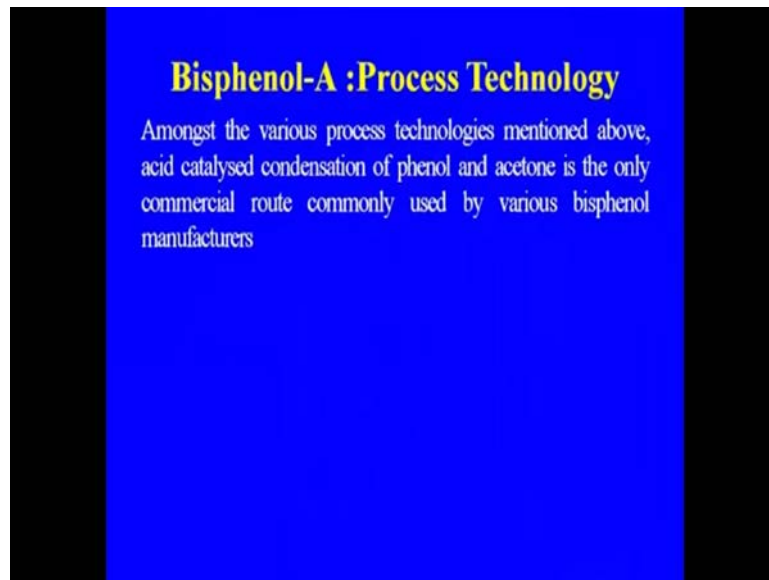
ABBB Lummus Global/ Sinopee technologyco
Low capital Technology, suitable for optical grade polycarbonate from phenol and acetone

Chiyoda Corp, CT-BISA
The process CT-Bisa for manufacture of bisphenol from phenol and acetone. The process can produce both grades of polycarbonate and epoxy resins

But, actually the major process which we are using for the making of the bisphenol is the either way ABBS lummus global, sinopee technology or with the chiyoda corporation CT-BISA. This is some of the advantage low capital technology suitable for optical grade poly

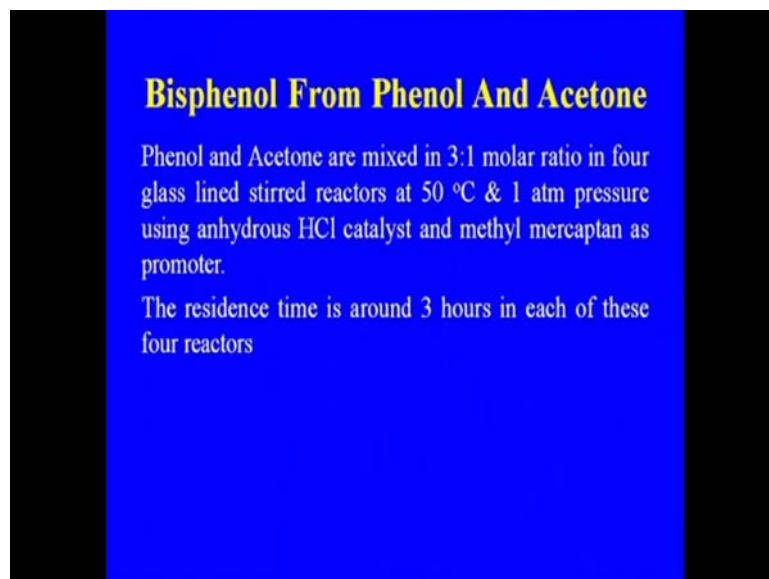
carbonate from phenol and acetone because the huge application of the poly carbonate is for making optical glasses. So, another process for the manufacture of the bisphenol, phenol and acetone. The process can produce both grades of the poly carbonate and epoxy resins. Let us discuss the process technology in case of the bisphenol.

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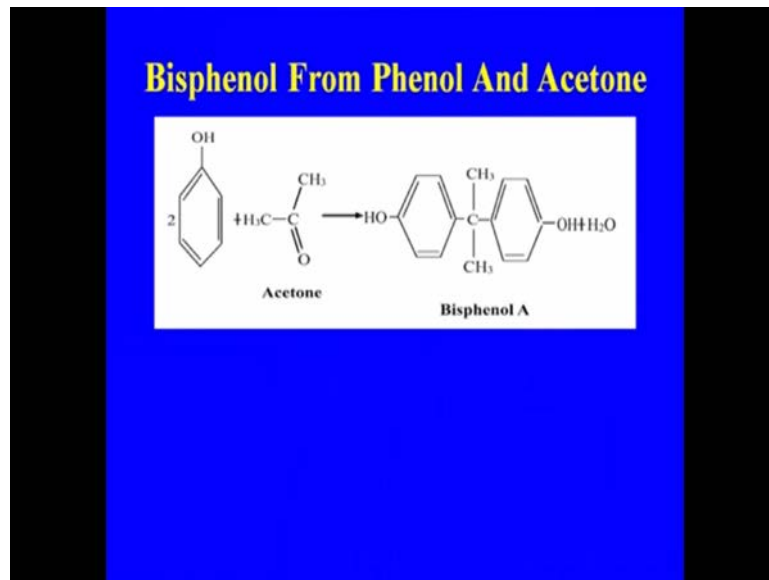
Amongst the various process technology mentioned above, acid catalyzed condensation of the phenol and acetone is only commercial route commonly used for the various bisphenol manufactures.

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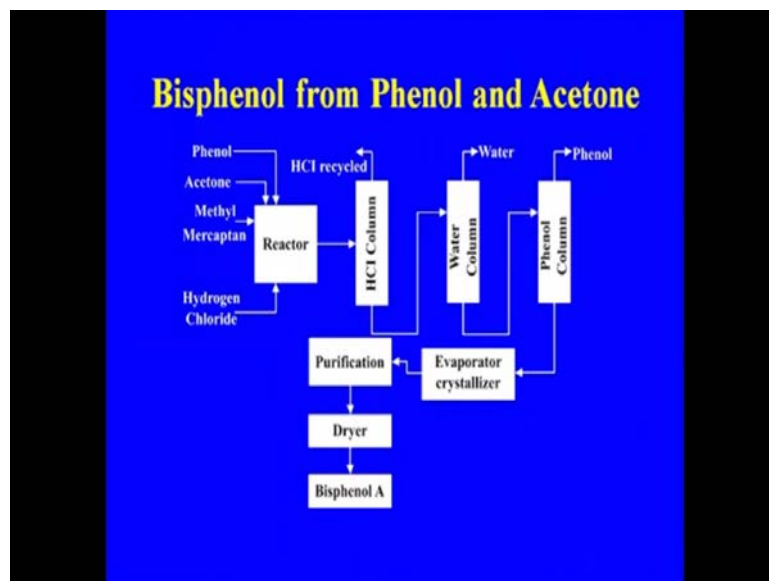
So, this is the phenol and acetone are mixed in the 3 percent, 3 isto 1 molar ratio in 4 glass lined stirred reactors at 50 degree centigrade and 1 atmosphere pressure using anhydrous HCL catalyst and methyl mercaptan as promoter. The residence time is around 3 hours in each of these four reactors.

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This is the reaction that is taking place during the manufacture of the bisphenol.

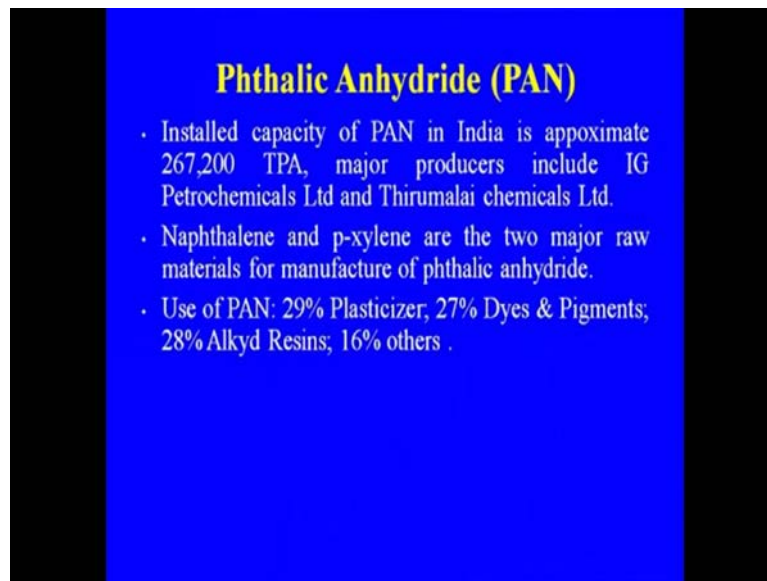
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This is the process flow diagram for the manufacture of the bisphenol from the phenol and acetone route. So, that is the phenol acetone methyl mercaptan hydrogen chloride that is

going to the reactor from the reactor the product the product steam is going for the separation of the HCL. Another impure is present. So, that is your water, phenol. And then, after the phenol recovery the heavier end that is going to the evaporation crystallizer purification dryer and the finally, you are getting the bisphenol. So, this is the process technology for the manufacture of the bisphenol. Now, let us discuss one of another very important aromatic compound which is finding large application in the paint industry.

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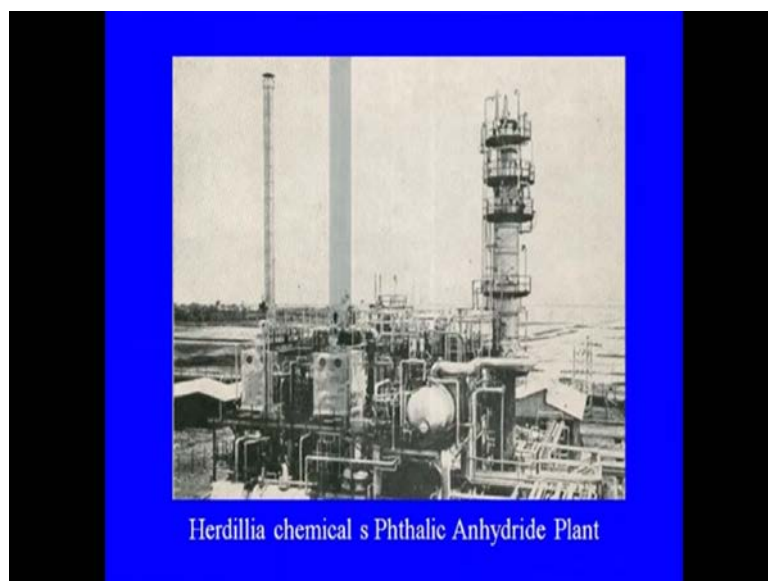


Phthalic Anhydride (PAN)

- Installed capacity of PAN in India is approximate 267,200 TPA, major producers include IG Petrochemicals Ltd and Thirumalai chemicals Ltd.
- Naphthalene and p-xylene are the two major raw materials for manufacture of phthalic anhydride.
- Use of PAN: 29% Plasticizer, 27% Dyes & Pigments, 28% Alkyd Resins, 16% others .

So, the installed capacity ethylic anhydride in India is approximately 267,200 tons per annum, major producers include the IG petrochemical limited and Thirumalai chemicals limited. Naphthalene and para-xylene, ortho xylene are the two major raw material for the manufacture of the ethylic anhydride. Use of ethylic anhydride 29 percent is plasticizer, 27 percent is dyes and pigments, 28 percent is the alkyd resins and 16 percent is others.

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This again is the ethylic anhydride plant of the herdillia chemicals. So, the process earlier as I told you, the naphthalene route that was the only the raw material that was naphthene available from the coke oven plant. So, that was being used for the manufacture of the ethylic anhydride.

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Manufacturing Processes Of Pan

Naphthalene Route: Phthalic anhydride is produced by oxidation of naphthalene in the gas phase using vanadium pentoxide catalyst supported on silica or silicon carbide promoted with various other metal oxides, e.g. titanium oxide (wire) in either a fixed bed multiple reactors or fluidized bed reactor

c1ccc2ccccc2c1.O=O>>O=C1OC(=O)c2ccccc12.CO.O $\Delta H_{298K}^{\circ} = -1790 \text{ kJ/mol}$

So, ethylic anhydride produce by oxidation of the naphthalene in the gas phase using vanadium pentoxide catalyst supported on silica or the silicon carbide promoted with the various other metals oxides like titanium oxide in either a fixed bed multiple reactors or the

fluidized bed reactor. But, now all the ethylic anhydride we are making from the ortho xylene routes.

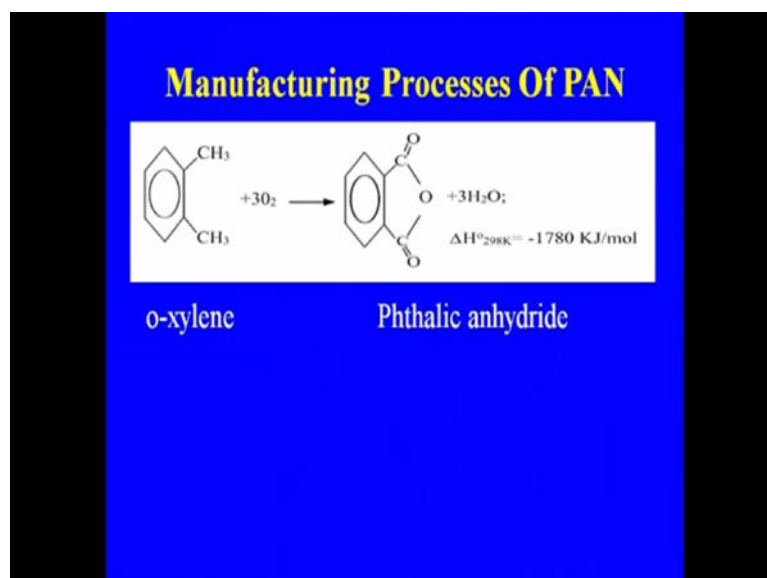
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Manufacturing Processes Of PAN

- **Phthalic Anhydride from o-xylene:** Production of phthalic anhydride from o-xylene is similar to naphthalene route. Catalytic oxidation of o-xylene is done either in fixed bed catalytic reactor having multi tube or fluidised bed reactor in the presence of vanadium pentoxide and titanium oxide catalyst.

So, production of the ethylic anhydride from ortho xylene is similar to the naphthalene route. But, here we are using the ortho xylene and so the catalytic oxidation ortho xylene is done either in the fixed bed catalytic reactor or having multi tube or the fluidized bed reactor. Now, the fluidized bed reactor is more common in the presence of the vanadium pentoxide and the titanium oxide catalyst.

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So, this is the reaction that is taking place during the manufacture of ethylic anhydride, oxidation of the ortho xylene to the ethylic anhydride. So, this was the about the various aromatic petrochemical that we are manufacturing, there uses and application and because you the aromatics are equally important. In the next module, modules 8 we will be discussing about the polymer industry, because the polymer means the plastic elastomere or the synthetic fiber, in which these aromatics are also findings wide application for the making of the various feedstock.

So, the next few lectures will be about 8 lectures are in module 7, where will be discussing about the different type of the starting on the poly olefins to the PVC and then, the poly styrene manufacture and then, the manufacture of the synthetic fiber, caprolactam, nylon 66 and the terephthalic acid. And also, will be discussing in that part the viscos ion and the acetate ion, which are also one of the important segment of the synthetic fiber industry. So, this will be the next 8 lecture will be on the polymer elastomer and synthetic fiber in the module 8. And after that the last module will be on the pesticides and dygene intermediate.