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Module - 7 Petrochemical Lecture - 4 Synthesis Gas and its Derivatives: Hydrogen, CO, Methanol, Formaldehyde, Methanol to Olefin Technology

We are discussing the module 7 of the organic chemical technology. And in the lecture 1, lecture 2 and lecture 3, we discuss about the overview of the petro chemical industry. Then we discuss about the naphtha and gas cracking, which is the heart of the petro chemical plant, and then we discuss about the recovery of C 4 C 5 gases form FCC. Today, we will be discussing about the synthesis gas and its derivatives, hydrogen and ammonia, carbon dioxide, methanol, formaldehyde, methanol to olefin technology. Although that technology we discussing in the more detail, I will discuss in the propylene. So, these are the some of the very important feed stock for the chemical industry. And if you remember when we discuss about the structure of the chemical, chemical industry and the, so that was the in the first stage that was the, the petro chemical industry, the hydrogen ammonia synthesis gas they become very important feed stock.

And, because of it is part in daily complex, because if you see this one of the large integrated, you can say the fertilizer complex although in this another unit of RCO of the manufacture some other petro chemical. And similarly, in case of the Gujarat state and fertilizer, because they are making the synthesis gas and that synthesis, they are using for production of large number of the chemical like the, they are making the corporate; they are making the melamine; they are making; they are making some other dimethyl formaldehyde. So, these are the some of the petrochemical which are getting importance. And, because of that reason the synthesis gas that has become one of the very important feed stock in the chemical industry.

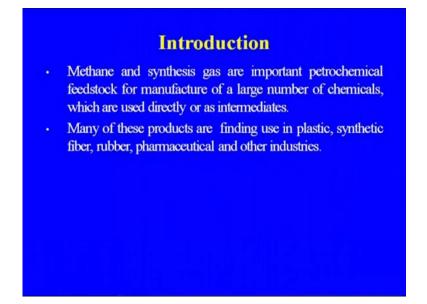
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Coverage of Lecture

- Introduction
- Emerging Technologies in Utilization of Synthesis Gas and Methane for Production of Petrochemicals
- · Synthesis Gas Requirements for Major World Scale
- Ammonia, Hydrogen, CO₂
- Methanol, Formaldehyde
- · Acetic acid
- · Dimethyl formamide
- Acetylene

So, the coverage of the lecture will be introduction emerging technology in utilization of the gas, synthesis gas and methane for production of petrochemical. Synthesis gas required for major world scale plant, ammonia, hydrogen C O 2 then methanol, formaldehyde, acetic acid, dimethyl formamide, acetylene.

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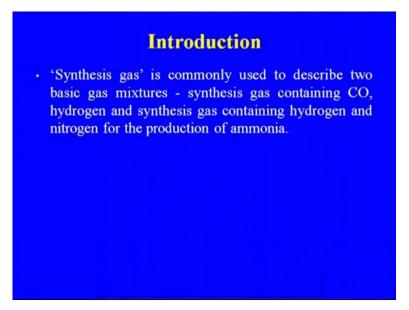


As I told you methane and synthesis gas are important petrochemical feed stock for manufacture of a large number of chemicals, which I used directly are as an intermediate. Although synthesis gas mostly we call it the both C O C O N S 2 and hydrogen, nitrogen,

because when you are making the synthesis gas then hydrogen separated and that is going to the ammonia plant. So, the both the synthesis gas, they are very important and that is why while discussing the coverage of lecture I told you that will be also discussing about the hydrogen and the ammonia.

So, in case of the many of these products are finding use in the plastic, synthetic, fiber, rubber, pharmaceutical industry and other industry. And one of the very important product from the synthesis gas that was the methane oil and methane oil to formaldehyde. And then other uses of the methane oil in more production of MTV in the production of now the methane oil to olefin technology, which is find the avoid application and the acceptability in the petrochemical industry. So, these are the some of the major factor why the synthesis gas that is very important petrochemical feed stock.

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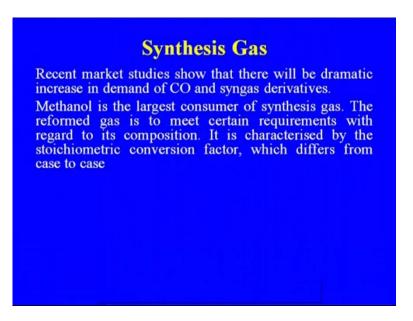
Synthesis gas, as I told you is commonly used to describe 2 basic mixtures - synthesis gas containing C O 2 and hydrogen, which I first produce in the process while going for the different processes, which again you will be discussing in the later stage in the first slide. And the synthesis gas containing hydrogen and nitrogen, which we are using for the production of the ammonia. Petrochemical derivatives based on the synthesis gas and carbon monoxide have experienced steady growth due to large scale utilization of the methanol and development of the carbonylation process for acetic acid oxo synthesis for detergents, plasticizers, and alcohols.

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Synthesis Gas

 Petrochemical derivatives based on synthesis gas and carbon monoxide have experienced steady growth due to large scale utilisation of methanol and development of carbonylation process for acetic acid and oxo synthesis process for detergents, plasticizers, and alcohols.

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Recent market study show that there will be dramatic increase in the demand of C O and syngas derivatives. Methanol as I told you the largest consumer of the synthesis gas. The reformed gas is to meet the certain requirements with regard to its composition. It is characterized by the stoichiometric conversion factor, which differs from case to case, because different plant there will be require in different amount of the synthesis gas. One of the before starting the synthesis gas, because here we are also discussing the methane, because that methane part of the synthesis gas and natural gas that you are using for

making of the synthesis gas. So, the some of the working technology for the more and more utilization of the methane, methane.

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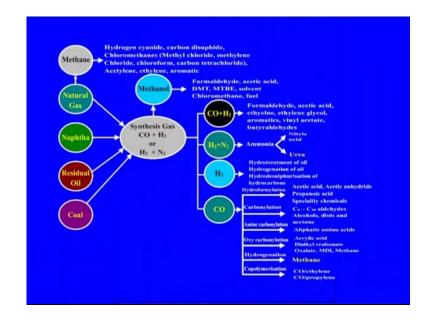
Emerging Technologies in Utilization of Synthesis Gas and Methane for Production of Petrochemicals

- Oxidative coupling of methane to yield ethane and ethylene,
- Methanol to Olefin technology (MTO).
- Fischer-Tropsch synthesis is being studied in great detail world over and it is promising to be a future technology for manufacture of olefins from synthesis gas.
- CO that can be separated from synthesis gas either by cryogenic or by pressure swing adsorption is a promising feedstock for production of variety of products.

The oxidatic coupling of the methane to yield ethane and ethylene. So that is one of the then the methane oil to olefin technology, these are the, because the methane oil that will formed the synthesis gas from the methane to synthesis gas, and synthesis gas to methane oil and methane and methane and methane oil to olefin, the propylene. Fischer Tropsch synthesis is being studied in the great detail world over and it is promising to be a future technology for manufacture of olefins from the synthesis gas. So, this is another area which is wide scope of the methane and methane to methane oil technology that is there. C O that can be separated from the synthesis gas either by cryogenic or by pressure swing absorption is a promising feed stock for production of variety of products.

These are the some of the, you see the product profile of synthesis gas and one of the major product that you are getting methane oil. Natural gas and natural gas to methane and methane to again we are producing large some of the product is the hydrogen cyanide, that is one of the coroneted methane's. The various compounds we are getting carbon dichloromethane that we getting after carbon disulfide that is also one of the very important feed stock for the manufacture this.

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Then the other compounds that is the Estelline from the methane, that you can produce and the ethylene aromatics, because there is technology available from synthesis gas to aromatic also another important outlet for synthesis gas. And these are the some of the raw material, you see the raw material methane, natural gas, naphtha, residual oil, coal even biomass that can be also use for production of the synthesis gas which we discuss in detail and the module 1 while discussing the raw material.

So, the another for the methane oil, I was discussing that is the formaldehyde tradition of the major outlet acetic acid, DMT in the DMT we are using the methane oil MTB methyl ethyl that we are using the methanol then the chloromethane fuel, because again, again there is lot of discussion, why not use methanol as a blend and the gasoline. Another synthesis gas which was telling the, that will go to the methanol, methanol to permel dehydrate acetic acid. Ethylene; ethylene glycal, aromatics phenyl, acetate and then the betyl dehydrate.

Then the synthesis gas which I was telling from the hydrogen and nitrogen. This will be the ammonia and ammonia as you know one of the major outlet is as a nitrogenous fertilizer in the form of urea. Another use of the nitric ethane, apart from that ammonia is finding wide use in some of the technology now which is being used in petrochemical industry. And one of the major out application is the deformation of the acyclic fiber where we are making the aclo nitrate and in the preparation aclo nitrate we are using ammonia.

And other acrylic process are there where you are using ammonia as a feed stock in the preparation large number of the chemicals. Then the C O as I told you C O is also one of the very important and not the only C O. Now, the lot of the work that is why not utilize that C O 2 C O 2 and then the C O 2. It is because normally what is happing in the refinery we are producing huge amount of hydrogen. And in that hydrogen C O 2 that is aware why not utilize that C O 2 for making some of the useful petrochemical. So, the, because some of the chemicals we can adopt from the, and the already lot of the work is going on to make it the come economical at the commercial level.

So, the C O I was telling about the C O carbon monoxide that is the hydro formation reaction, carbonation reaction, amine carbonation. Then the oxo carbonation the hydrogenation and the other and these are the long list of the products are there which we are getting from the C O. So, this may be now, you can realize the importance of synthesis gas and it is not only important from the, your fertilizer production, but also it is important equally important for the manufacture of over petrochemical also.

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	Inajoi	World Sca	lie
Product	Required H ₂ : CO	Typical world- scale capacity, TPA	Syn gas required, Nm ³ /hr.
Methanol	2:1	1,60,000- 12,75,000	48,000-1,90,000
Acetic acid	0:1	2,75,000- 5,45,000	18,000-36,000
Acetic anhydride	0:1	90,000	3500
Oxo alcohol	2:1	1,15,000- 2,75,000	12,000-25,000

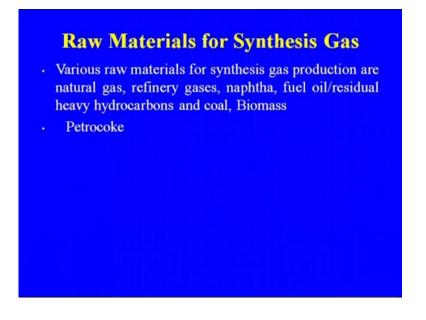
N	<u>lajor \</u>	World Sc	ale
Product	Required H ₂ : CO	Typical world- scale capacity, TPA	Syn gas required, Nm ³ /hr.
Phosgene	0:1	4,800-1,60,000	3,500-12,000
Formic acid	0:1	45,000	3,500
Methyl formate	0:1	9,000	600
Propionic acid	0:1	45,000-68,000	2,400-3,500
Methyl methacrylate	1:1	45,000	4,700
1,4-Butandiol	2:1	45,000	4,700

This is the requirement and of the hydrogen to C O, typical world scale capacity and synthesis gas requirement. Then see the already I discuss the various product, one of the methanol that is the important product then the acetic acid, acetic anhydride, oxo alcohol. Phosgene; another product which is fine we are using now it is specially in case of the making the poly carbonate, formic acid, methyl formate, propionic acid, methyl methacrylate. That is also very one of the very important product for making of the, your polymer of this and the 1 4 butandiol.

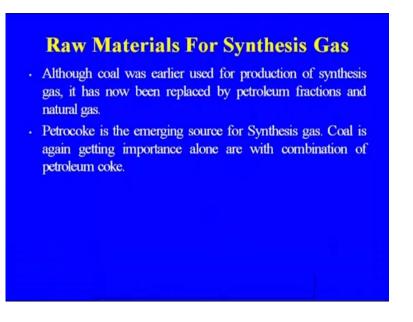
So, these are the some of the requirement of the synthesis gas typical world scale capacity and synthesis gas requirement. So, you can see the huge amount of synthesis gas that is required, and this is the reason why many of the fertilizer plant they have been ticketed there with the production of the petrochemical. You take the one of the largest fertilizer complex integrated fertilizer complex is your Gujarat state fertilizer complex at vadodhara, where they are making apart from making of the various great of the prosthetic and the nitrogenous fertilizer.

They are making melamine; they are making capro; they are making nylon like that. Then dimethyl formamaide RC at their unit they have started making dimethyl formalmyde dimethyl acetamyde that can be also one of the product. Apart from methanol, because even some of the fertilizer plant like RCL NFL they are making the methanol. So, because the methanol they are using in the process for absorption, this you too.

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So, various raw materials for synthesis gas production are natural gas, refinery gases, naphtha, fuel oil, residual heavy hydrocarbon coal, biomass. And now the petrocoke which is getting important, because the refinery they are producing and with the use of more and more heavier feed stock. Now, the already Reliance Jamnagar refinery, they are going for the petrocoke gas specification so that the petrocoke that can be utilize there.

So, these are the, and in detail we discuss about the various products, what are the various method and while discussing the, in the module 2, module 1, the raw material for organic chemical industry.

Although the coal was the earlier used for the production of synthesis gas, it has now been replaced by petroleum fractions and the natural gas. Because you see the birth of the chemical, that was through the coal road not through the petroleum road. So, petrocoke is the, another emerging source for the synthesis gas, coal is again getting, because you see the. We started the manufacture, the many chemical through the coal and again coal is getting importance along are with the combination of the petroleum coke. Because the, now the in some of the country huge amount of the coal deposit are there only the constant in case of India is the highest contain of the coal. But the China, they are going to have the coal based chemical plants.

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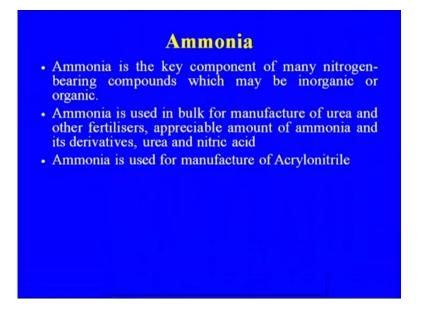


The synthesis gas and ammonia manufacture from steam reforming from the steam reforming, or the partial excedation, what are the process that you are using depending upon the feed stock? The various steps involved in the production synthesis gas are desulphurization of the natural gas or it may be naphtha or even in cases partial oxidation also, the gas has to be desulphurise before it is going to the substance stages. So, steam reforming of the natural gas and naphtha, because that is the requirement in case of the

natural gas and naphtha, desulphurization that has to be done, because the 5 different level of the sulfur that is required.

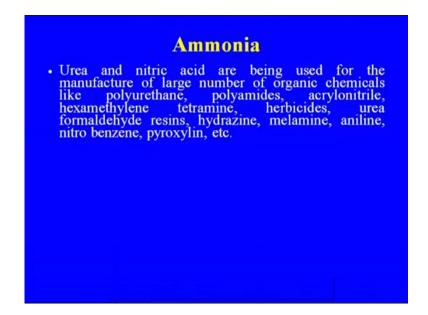
Then after the synthesis steam reforming of the natural gas then it is a safe C O shift conversion, because there we are getting a mixture of C O and H 2. And now the process actually the further, what was the process is there C O shift conversion, C O to the verification. This all the part of the ammonia manufacture, but so far the methanol is concern first 2 steps are common. C O shift conversion, C O 2 removal by absorption in K 2 C O 3 MEA or it may be methanol purification for removal of traces of C O and C O 2 by methanation or nitrogen wash, depending on because in case of the partial oxidation nitrogen is available. Because they are using the oxygen and so that nitrogen use for the removal of traces of C O and C O 2 which may poison the calculus and then refinery ammonia synthesis. Let us discuss about the ammonia.

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As you know ammonia is the key component of many nitrogen bearing compounds which may be inorganic or organic. Ammonia is used in bulk for manufacture of urea another fertilizers, appreciable amount of ammonia and its derivatives, urea and nitric acid. Ammonia is used for manufacture of acrylonitrile, which I told you that the one of the major changes in the process technology of the acrylonitrile which was earlier from the (()). Now, it is the propylene and ammonia that we are using C O process that we are using for the manufacture of acrylonitrile tight, which I has revolunised the synthetic fiber industry providing the substitute for wool.

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Urea and nitric acid has to do or being used for the manufacture of the large number of organic chemicals or so just you take the case of the urea formaldehyde another application urea is also there. And nitric acid we are finding many of the reaction also nitric acid, nitric acid along with the sulphuric acid we are using at the catalyst also.

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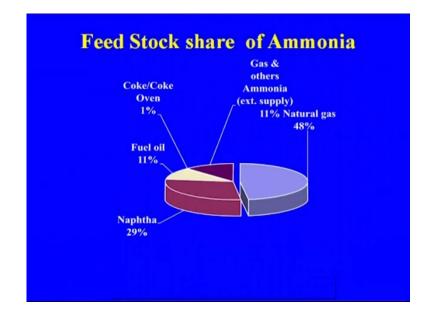
number

Ammonia • There are about 400 ammonia plants globally. • Some of the fertilizer complexes also produce large petrochemicals of like ethanolamines, acetic acid, acrylonitrile, caprolactam, Dimetyl formamideetc.

methanol,

So, they are being use for the manufacture polyurethane, polyamides, acrylonitrile, hexamethylene, tetramine, herbicides, urea of formaldehyde resins, hydrazine, melamine. Because melamine that is the product that we are manufacturing in the one of the fertilizer plant GCFC Gujarat state fertilizer complex at badorda aniline, nitro benzene, pyroxylin. In all the case, we are using the some or other form this nitric acid.

They are about more than 400 ammonia plants globally, some of the fertilizer complexes are also produce large number of the petrochemical like methanol, ethanolamine, acetic acid, acrylonitrile, caprolactam, dimethyl formamideete, and few more other.



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This is the feed stock share for the ammonia and still you see the, this is major share, because they are in naphtha. If you take the case of India the naphtha that was made available to fertilizer plant when the some of the refinery they came in the earliest stages, because the natural gas that was supply processing the pipe line the other problem were there in the supply of the natural gas and the lot of the natural gas was fare at that time in the initial stages. But slowly after coming of the petrochemical the naphtha was made available to the petrochemical complexes.

And the natural gas was apply through the pipeline by Gayle another agency that is they started and because of that reason. Now, the natural is the major feed stock for the manufacture of the ammonia And here you see the fuel oil because some of the fertilizer is NF l plant, when it was started they started all there Bijaypur plant they started with

the fuel raw material. But now they have actually change over to the, even the if coke full four the fuel oil would that was raw material again all these this some of the NF 1 are they are shifted another alternative raw material means the natural gas and the naphtha. So, this was the coke, coke plant that is also we discussed about, when the discussing the coal, chemical ammonia that you are getting from the process so that, that is being used for the making of the fertilizer.

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Deserves	Reaction	Descent and distant
Process steps	Keacuon	Process condition
Desulphuris	$\mathrm{C_2H_5SH} + \mathrm{H_2} {\rightarrow} \mathrm{H_2S} + \mathrm{C_2H_6}$	Al-Co-Mo
ation: 1st	$C_6H_5SH + H_2 \rightarrow H_2S +$	Al-Ni-Mo
Stage	C_6H_6	Catalyst
2 nd Stage	$C_4H_4SH + 3H_2 \rightarrow H_2S +$	350-400 °C
	C_4H_9	Zinc oxide absorbent
	$CS_2+4H_2 \rightarrow 2H_2S + CH_4$	200-500 °C
	$\text{COS} + \text{H}_2 \rightarrow \text{H}_2\text{S} + \text{CO}$	
	$CH_3SC_2H_5 + H_2 \rightarrow H_2S +$	
	$CH_4 + C_2H_4$	
	$H_2S + ZnO \rightarrow ZnS + H_2O$	

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	ess Steps in I thesis Gas an	Production of d Ammonia
Process steps	Reaction	Process condition
Steam reforming two stage	$\begin{array}{c} C_{n}H_{m}+1/4(4n-m)H_{2}O \rightarrow 1/8(4n+m)\\ CH_{4}+1/8(4n-m)CO_{2}\\ CH_{4}+H_{2}O \rightarrow CO + \\ 3H_{2}\\ CO+H_{2}O \rightarrow CO_{2}+H_{2} \end{array}$	Nickel catalyst 800 °C
CO-shift conversion	$\rm CO+H_2O \rightarrow \rm CO_2+H_2$	Magnetite crystals stabilised using chromium oxide. Low temperature shift catalyst copper oxide supported or zinc oxide and alumina.

These are the some of the reactions in the desulphurization we are having the 2 stage desulphurization. And these are the some of the series of reaction that is taking place in the removal of the sulfur compound, even the absorption phenomena is also taking place. So, these are the some of the reaction that is taking place in the desulphurization. Then the steam reforming in 2 stage steam reforming is there. Next process the C O shift conversion, where the C O is converted to C O 2, because this is the requirement we need for the urea manufacture C O 2.

So ammonia and C O 2, so that is why in the fertilizer plant, because if you are interested in the methanol that only up to the C O and H 2. That is the shift synthesis gas which I am making that will go for the ammonias methanol synthesis. But if are interested in fertilizer, then further some of the steps which I am discussing that will required one of the step, step is C O shift conversion means the conversion of C O 2 C O 2 C O 2.

Then the, how to remove, because the synthesis gas which is being which is to be use for ammonia manufacture that has to separated from C O 2. And that C O 2 we are removing by absorb various absorbent that you are using and the potassium carbonate that was the earlier absorbent that was used very commonly in case in the fertilizer. But now that has been depressed with the some ethanol amine and the methanol also that is being used. So, this is the reaction that is taking place and the, your regeneration contains regeneration is also there.

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Carbon Monoxide

- Carbon monoxide is one of the constituent of synthesis gas which is produced by steam reforming of natural gas, naphtha, partial oxidation of heavy hydrocarbons and coal gasification and major portion of CO is used in world in the form of gas mixtures containing hydrogen.
- However, carbon monoxide in purified form is used in the manufacture of phosgene, acrylates, diisocyanates, bisphenol-A & polycarbonate, methyl methacrylate, pivalic acid, adipic acid, propionic acid, formamide, acetic acid, formic acid, oxo alcohols, polyketones, etc.

Then one further step is there, because in case of the ammonia synthesis the catalyst poisoning that may be there. So, in order to avoided catalyst poisoning the thesis you to which is remaining that is the removed methanation when you are having the steam reforming process or by nitrogen when you are having the this partial oxidation process. This is the final ammonia synthesis process.

Carbon monoxide as I told you is the one of the constituent of the synthesis gas which is produced by steam reforming of natural gas, naphtha, partial oxidation of heavy hydrocarbon and coal gasification and major portion of C O is used in the world in the form of gas mixtures containing hydrogen. And so which is discuss the various products which we are getting from C O and H 2.

However, the carbon monoxide in purified form is used in the manufacture of this. Already we discussed about the various product that like phosgene, acrylates, diisocuanates, bisphenol where we are using the phosgene a poly carbonate again the raw material bisphenol is raw material of poly carbonate, methyl methacrylate. Then the adipic acid, propionic acid, formamide, dimethyl formamide, acetic acid, formic acid, oxo alcohols. And the large amount of the list of the petrochemical are there which can be derived from the synthesis gas or the CO. Now let us discuss about the methanol.

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Methanol

Methanol was first obtained by Robert Boylein in the year 1661 through rectification of crude wood vinegar over milk of lime and was named *adiaphorous spiritus liglorum*.

The term methyl was introduced in chemistry in 1835. Methanol is

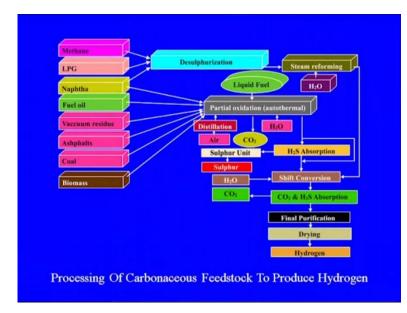
one of the largest volume chemicals produced in the world.

Methanol consumption can be separated into three end use categories – chemical feedstock, methyl fuels, and miscellaneous uses.

About 71% of the current global consumption of methanol is in the production of formaldehyde, acetic acid, methyl methacrylate, and dimethyl terephthalate.

You see the methanol was first obtained by Robert Boylein in the 1661 that through the rectification of the crude wood vinegar over milk of lime and was named adiaphorous

spiritus liglorum that was the name that time given. The term methyl was introduced in chemistry in 1835; methanol is one of the largest volume chemical produced in the world. Methanol consumption can be separated into 3 used categories chemical feed stock, methyl fuels, and the miscellaneous usage. About 71 percent of the current globe global production of the methanol is in the preparation of the formaldehyde, acetic acid, methyl methaacrylate, and dimethyl terephthalate. Although the, now the dimethyl terephthalately are not making, because that that has been replaced by terephthalate, but earlier when another major outlet of the methanol that was for the manufacture of your MTV.



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This is the processes which I was telling the various raw material even for synthesis gas or the methanol, when you are talking it may methane LPG naphtha, fuel oil, vacuum residual. And then the ashphaltis, coal, biomass, these are all the product depending upon the feed stock, we can go either for reforming estimate forming are the partial actually. In generally, what is happening in case of the naphtha or the natural gas? We are having or for the lighter H C. We are having the steam reforming for heavier feed stock are even in case of the coal or the biomass which discussed earlier that the gasification part that we are using.

So, partial oxidation the process that we are using, so the, what is happing the, we are getting from the air partial oxidation the gases. Then it is going for the steam reforming

steam reforming to as I as I told you the before here also this steam H 2 S removal is there, before it is going to here desulphurization process then it will go this steam reform. In case of the partial oxidation, again the gases that will for the removal of the H 2 S. And then the shift conversion C O 2, H 2 S observation final propagation and the hydrogen that you are getting which will go for the manufacture of the ammonia. If you are interested for the, then the some of the process that will be eliminated that is the removal of the C O 2, another thing directly C O N H 2 that will go for the, that I will discuss in the next slide.

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	Hydrogen
	rogen is used in various processes in Refinery and etrochemical complexes
Hyd	lrogen producing technology :
	Thermal
	Electrochemical
	Biological
Hyd	rogen recovery technologies :
	Membrane
	Adsorption
	Cryogenic

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Product	Uses
DMT/ Polyethylene	Polyester fiber and film,
terephthalate	Adhesives, Wire coating, Textile sizing, Herbicides
Methyl methacrylate	Cast sheet, surface coating,
(MMA)	molding resins, oil additives

So, let us discuss before discussing the final hydrogen, hydrogen is used in the various process in the refinery and the petrochemical complexes. Hydrogen producing technology; thermal, electrochemical, biological, hydrogen recovery technology, membrane, adsorption, cryogenic, separation all these process that the technology are available. So, the product profile I was discussing about the methanol.

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Product	Uses
MTBE	Oxygenate
Mono methanol	Naphthyl-n-methyl carbamate,
amine	monoethyl hydrazine,
	Monomethylamine nitrate

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DimethylDimethyl acetamide, DimamineDimethyl hydrazine, 2,4-Jacetic saltMethylPaint remover	
acetic salt	
Methyl Paint remover	Dichlorophenoxy
acetate	
Dimethyl Solvent, Flavoring, Dyes, aniline	Fragrance

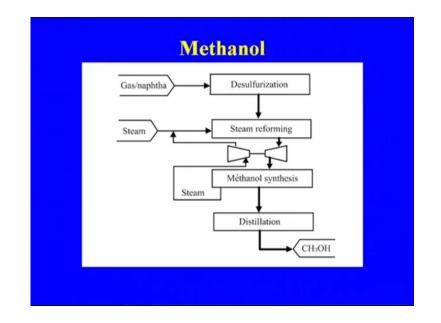
So, these are the product profile of your methanol DMT, polyethylene terephthalate, polyester fiber film, adhesive, wire coating, textile sizing, herbicides. Methyl

methacrylate; that is the sheet very, that is the, we are calling the methyl polymethyl surface coating, molding resins, oil additives. MTB and the MEA, MTB; we already discussed the importance of the MTB and the oxygenate, how we are making while discussing the recovery of the C 4 C 5 from the petroleum and the petrochemical complex. So, monomethylamine; that is another very important that is also a very good solvent, apart from and the absorbent that we also we are using.

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Product	Uses
Acetic acid	Vinyl acetate, Acetic anhydride,
	Chloroacetic acid, Ethyl acetate, Butyl
	acetate, Isopropyl acetate, Acetyl chloride,
	Acetanilide
Formalde-	Phenolic resins, Pentaerythritol, Trioxane,
hyde	1,4-butanediol, Formaldehyde,
	sulphoxylate, Tetraoxane, Resorcinol resin
Methyl	Quaternary amines, Methyl cellulose, Butyl
halides	rubber, Tri-methanol propene

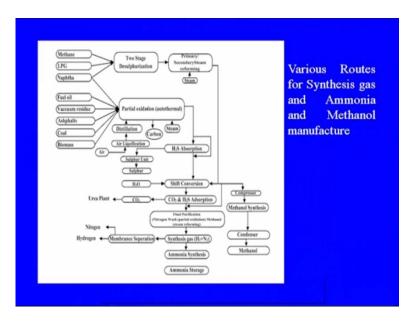
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These are the some of the other products that we are getting from the MEA, then dimethyl amine, dimethyl acctamide, dimethyl formamide, dimethyl hydrazine. So, the many of the, some of the actually you see the fertilizer plant. They are making some of the immense also, methyl acetate, paint remover. Dimethyl aniline; that you are these are all the products we are getting from the methanol.

Then the acetic acid formaldehyde and formaldehyde that you know one of the major outlet for the formaldehyde that has been the thermo the all the phenolic resins that you are getting the phenol formaldehyde, which we called the, and the pantaerythritol. That is the, you are using in making of the explosive trioxane 1 4 butanediol, formaldehyde, sulphoxylate, tetraoxane, and resorcinol resin.

So, this is the brief about the summary of the process which you are I discussed earlier also the, what we are doing the gas naphtha, steam, that is after the, it is going the gas and naphtha after vaporizing desulfurization process. And then it will go to the steam reforming an from the steam reforming then this synthesis gas which you are getting that will go for the methanol synthesis and methanol synthesis to distillation.



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This is the process detail about the various raw material and already I discussed this process, but here actually the synthesis are hydrogen are depending upon the requirement as you are interested for. Because this after this, your shift conversion directly the synthesis gas from here that will go for the methanol or it will go to the synthesis gas, it

will go for the synthesis gas manufacture for the manufacture of the ammonia. So, this is the and the various raw material and the I discussed this process. These are the some of the units which are making the methanol in India. And you see the number of the fertilizer plant, because the synthesis gas manufacturing already there, so they are making the methanol also.

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Consumptie Capacity Fo			
Units	Location	Capacity (Tpa)	Share (%)
Gujarat Narmada Valley Fertilisers Ltd.	Gujarat	238100	51.11
Deepak Fertilisers & Petrochemicals Ltd.	Maharashtr a	100000	21.46

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Profile Of Mer Consumpti Capacity Fo	on Pa	ttern in In	dia
Units	Location	Capacity (Tpa)	Share (%)
Rashtriya Chemicals & Fertilisers Ltd.	Mahara- shtra	72600	15.58
Assam Petrochemicals Ltd.	Assam	33000	7.11
National Fertilisers Ltd.	Punjab	22110	4.74
Total		465810	100.00

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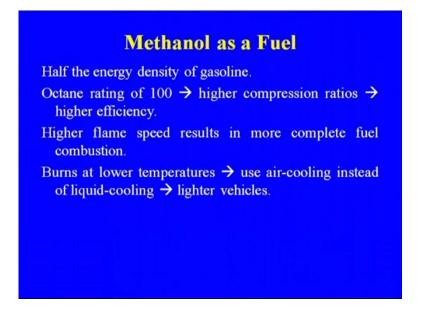
Users	Share (%)	Growth Rate (%)
Formaldehyde	48	7
Pharmaceuticals	21	8.5
Oxygenates	9	-
Acetic Acid	5	4

So, one of the major produces is Gujarat, Narmada valley fertilizer, Deepak fertilizers, RCF Rashtriya chemicals and fertilizers, Assam petrochemical that was the one of the very old unit that was started utilizing the natural there, national fertilizer Panipat Bhatinda, they are making the methanol plant is there. Methanol, because they are in host use of the methanol is also there of the absorption of this C O 2. This is the, if you see the uses of the, your methanol maximum is the formaldehyde other users are less.

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Methanol Consumption Pattern And Growth			
Users	Share (%)	Growth Rate (%)	
Alkyl Amines	4	9	
Dimethyl Sulphate	3	8	
Agrochemicals	3	5	
Chloromethanes	4	8	
Solvents/Others	3	8	
Total	100	6	

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This is the methanol consumption growth, dimethyl sulphate, agrochemicals, chloromethanes, solvent end products, which you are getting from this. Methanol as a fuel, because already I discussed about the importance of the oxygenates while in the module 6. But you see the methanol as a fuel half the energy density of the gasoline octane rating of 100 higher compression ratios, higher efficiency, higher flame speed results in more complete fuel combustion, burns at lower temperature use air cooling instead of liquid cooling higher lighter vehicle.

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Methanol Process Technology

From the early 1800s until 1920s, the ditillation of wood to make wood alcohol was the source of Methanol. The most common industrially favored method for the production of methanol was first developed by BASF in 1923 in Germany from synthesis gas utilising high pressure process using zinc-chromic oxide catalyst.

Methanol Process Technology

However, due to high capital and compression energy costs compounded by poor catalyst activity, high-pressure process was rendered obsolete when ICI in the year 1966 introduced a lowpressure version of the process at 5-10 MPa and 210-270 °C, with a new copper-zinc oxide based catalyst of high selectivity and stability.

So, some of the, these are the some of the advantage of the methanol while methanol that is being prefer as, as oxygenate in the fuel. You see the, we are having the, for the technology which you have level first the, from the early 18 until 1920, the distillation wood to make wood alcohol was the source of methanol. The most common industrially favored method for the production of the methanol was first developed by BASF in 1923 in Germany from synthesis gas utilizing high, high pressure process using. So, again there has been development in the methanol technology, high pressure, medium pressure and low pressure technology.

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Methanol Process Technology

- The advantages of low-pressure technology as compared with high-pressure routes to methanol
- Lower capital costs due to increased process material efficiency and exclusive use of turbine driven centrifugal compressors.

However, due to high capital and compression energy costs compounded by the poor catalyst activity, high pressure process was rendered obsolete when ICI in the year 1966 introduced the low pressure version of the process with a new copper zinc oxide based catalyst of high selectivity and stability. This was the actually change in the process technology from earlier BASF technology to ICI low pressure technology.

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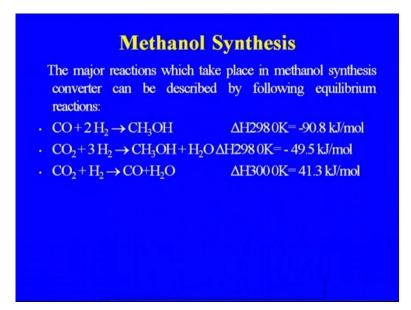
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Process Steps Involved In The Production Of Methanol Are:

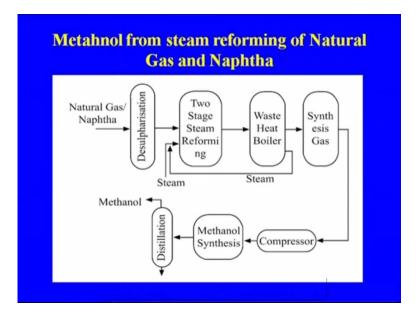
- Production of synthesis gas using steam reforming or partial oxidation.
- · Synthesis of methanol by
- High-pressure process (25 30 MPa)
- Medium pressure (10-25 MPa) process
- Low-pressure process (5-10 MPa).

The advantage of the low pressure technology as compared with high pressure technology to methanol. The lower capital cost due to increased process material efficiency and exclusive use of turbine driven centrifugal compressors. Lower capital cost, lower maintenance cost, improved reliability. Process step in the already I have discussed production of the synthesis gas using or the partial oxidation. So, first step is production of the synthesis gas and after the synthesis gas production. Then it will go for the methanol synthesis, and these are the 3 process which I discussed the high pressure, medium pressure, and the low pressure technology.

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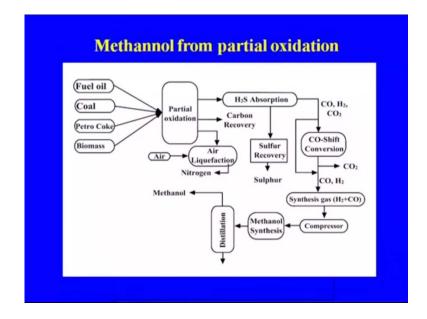


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These are the some of the reaction that is taking place during the methanol synthesis. This is the separate process I am discussing about the, here natural gas that is going to desulfurization then steam reforming waste heat boiler, because this is the high temperature operation. So, it always the reformers are having the steam waste heat boiler, synthesis gas, synthesis gas to compressor, compressor to methanol synthesis and then the finally, distillation we are getting methanol. So this is the process flow diagram for the methanol that was the actually from various raw material, how we are getting the synthesis gas I discussed in detail in the previous few slides.

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This is also the same if you are having the heavier feed stock fuel oil, coal, petrocoke and the biomass. Then the partial oxidation process there and it will also go for the H 2 S absorption, because normally in case of the partial oxidation always fine carbons are also produce. So, the carbon recovery section, air liquefaction, because the air that will be required for the partial oxidation, this is oxygen it is going the direction like that.

So, here air liquefaction nitrogen then the finally, C O shift conversion that will be when you are using for the ammonia for methanol that will C O shift conversion, that will be not required. Because it is directly going to the synthesis gas and the compressor methanol synthesis, but if you are interested then the C O shift conversion will be there for in case of the fertilizer plant. Now, let us discuss another very important product of

the synthesis gas which you are getting from methanol is the basic raw material that is formaldehyde.

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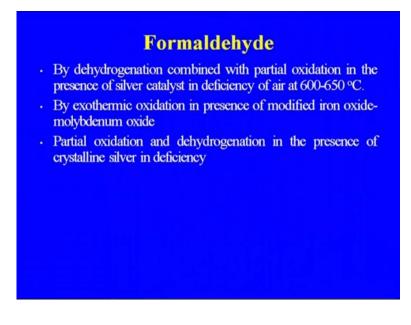
Formaldehyde

Some major intermediates derived from formaldehyde are chelating agents, acetal resins, 1,4-butanediol, polyols, methylene diisocynate.

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

Formaldehyde is commercially available as aqua solution with concentration ranging from 30 to 56 percent weight formaldehyde. It is also, sold in solid form as paraformaldehyde or trioxane. The production formaldehyde in India has been growing at a fairly constant rate during the last 10 years. Some of the major intermediates derived from formaldehyde are chelating agents, acetyl resins, 1 4 butanediol, polyols, methylene diisocynate. It is also used for the manufacture of wide variety of the chemical, including scalant, herbicides, fertilizers, coating, and pharmaceutical.

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Product Profile Of Formaldehyde

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

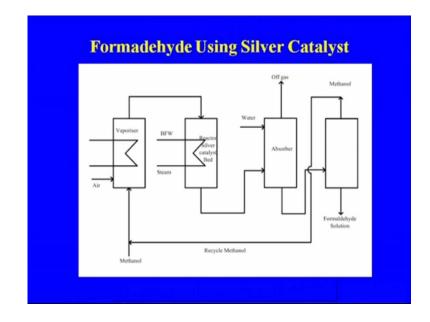
By dehydrogenation combined with the partial oxidation in the presence of silver catalyst is the process, we are using for the making of the formaldehyde from the methanol. By exothermic oxidation in presence of the modified iron oxidemolybdenum catalyst, partial oxidation and dehydrogenation in the presence of crystalline silver catalyst. Because the molybdenum and silver catalyst both the catalyst and that has been used in the process. These are the some of the various product for formaldehyde as I told you the one of the major outlet for the formaldehyde, that is the thermosetting resin, phenol formaldehyde and urea formaldehyde and melamine formaldehyde. These all the 3 major thermosetting resin are finding application in the (()) specially the phenol formaldehyde that we are using in case of the, all the back light which you called commercial name back light and the electrical switch in other thing.

Melamine for the kitchen ware there was the changes in the use pattern of the kitchen utensil from the stencil steel to the melamine wares in the kitchen. So for the melamine and I told you the Gujarat state fertilizer they are making the melamine, because there also they are making the synthesis gas they having the fertilizer plant. So, the melamine is also one of the very valuable product there. Hexamethylene tetramine, plastic and pharmaceutical 14 butadiol, methylene diisocynate, disinfectant, biocide, preservative, because now we see the always we complain at formaldehyde is there that is being used as a preservative. So that is the good amount of the that is formaldehyde that we are using as a preservative producing as an corrosion inhibitor, polyaceta resin, para formaldehyde and pentaerythritol that is the explosive PTN.

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

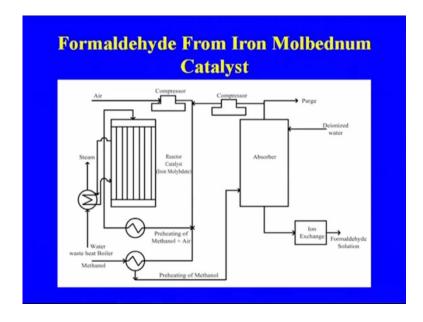
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So, these are the compression of the silver catalyst and they are iron then the molybdenum, these are the various process licensor. So, both the catalyst that is being used and so these are process licensor for the silver catalyst for a iron molybdenum. The degussa process, formox process, fisher adler process, these are the some of the process where we are using the iron molybdenum catalyst. This is the process using the silver catalyst the air and the raw material that is going to the reactor.

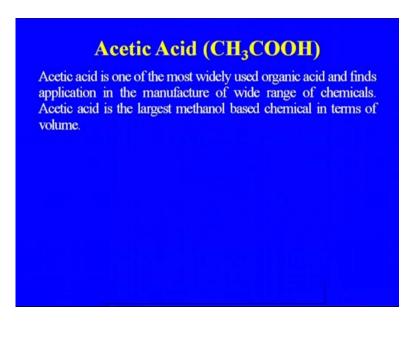
And from the reactor absorber is there of gasses that you are taking finally, the formaldehyde is the main reactor that is there this is the vaporizer we are having. And then the, because the methanol from here it is going. So, vaporizer and after the vaporization, it is going to the reactor where you are having the silver catalyst from the silver catalyst you are going the absorber. And from the absorber you are getting here formaldehyde and the feed stock is separated and it is recycle to this system. So, this is the process we are using in manufacture of the formaldehyde.

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This is the process we are using in case of the molybdenum catalyst here also the methanol that is going to the main reactor. And after the reaction the methanol the formaldehyde that is going for the separation. And you are getting finally, the formaldehyde, there and these are the compressor that is found where here is compression then it is going to the system. So this is the process when you are using the formaldehyde from the iron molybdenum catalyst, another important outlet.

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Produ- c t	Consu mptio n 2002 ('000 tonnes	Gro	Growt	sumption frowth ercent)	Capa- city 2002 ('000 tonnes)	Annou- nced Capacity due by 2012 ('000	Cha Need 20 2002	acity inge led by 12 after ncemen
)	1997 - 2002	2002 - 2007	2007- 2012		tonnes)	('000 tonnes	percer t
Acetic Acid	8,302	3.9	3.4	2.5	9,559	994	1,785	19

And use of the synthesis gas is the acetic acid which is one of the most widely used organic acid. And finds application in the manufacture wide range of chemicals acetic acid is the largest methanol based chemical in terms of the volume. Because the both the process that we are using the acetic acid from the methanol root or it may be the from the ethanol root also we are making acetic acid. So, these are the consumption and the consumption growth global consumption growth of the acetic acid.

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Acetic Acid In India		
Company	Installed capacity	
	(TPA)	
Indian Organics Chemicals Ltd.	15,000	
Somaiya Chemicals Itd.	15,000	
Somaiya organics	20,000	
Andhra Sugars Ltd.	1,000	
Ashok Organic Industries	30,000	
EID Parry (I) Ltd.	10,000	
Gujarat Narmada Valley Fertiliser	50,000	
Corp. Ltd.		

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Acetic Acid In India		
Company	Installed capacity	
	(TPA)	
Kanoria Chemicals & Industries	6,000	
Laxmi Organic Ltd.	9,500	
Trichy Distilleries	12,000	
Vam Organics	1,15,500	
Ashok Alcochem Ltd.	5,400	
Dhampur Sugar mills	7,300	
Pentokey Ltd.	7,000	
Polychem Ltd.	7,500	
Trident alcochem	6,000	

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Manufacturer		
Name of the companies	Percent Share	
Jubilant Organosys Ltd.	22	
Ashok Organics Itd.	17	
IOCL	9	
Gujarat Narmada Valley Fertiliser Corp. Ltd.	9	
Others	43	

These are the some of the major companies which are making the acetic acid that is in Indian organic chemicals limited, Somaiya chemicals. This all companies which are seeing here these are all based on the alcohol based companies are there except the Gujarat Narmada valley fertilizer. All others are making from the ethanol which is from the molesis. These are other companies Kanoria chemicals, Laxmi organic, Trichy distilleries, Vam organics, Ashok alcochem, Dhampur sugar. These are all based on the ethanol root not from the methanol root. This is the market share of the acetic acid manufacturer. So, jubilant is one of the major producer of the acetic acid. Again as I told you this is from the, not the methanol root, it is from the ethanol root they are making.

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Product	Uses
Monochloro acetic acid	CMC manufacture, adhesives, thickeners for drilling muds, food industry, pharmaceuticals, textiles, 2,4- D(insecticides)
Ethyl acetate, n-butyl acetate, isopropyl acetate	Coatings, adhesives, inks and cosmetics
Vinegar	Food Preservative
Vinyl acetate	Polyvinyl acetate, polyvinyl chloride, paints, Adhesives, and coatings

These are the some of the major usage of the acetic acid monochloro acetic acid, ethyl acetate n butyl acetate, isopropyl acetate, vinegar, vinyl acetate, and so the vinyl acetate polyvinyl acetate, because that was the name earlier to the jubilant organizer that was the vam organic. So, vinyl acetate; one more the, making so that was going to the polyvinyl acetate. And you see the polyvinyl that has a very wide application polyvinyl, chloride paints, adhesive and coating. So, these are the some of the major outlet for the vinyl acetate and why the importance of the vinyl acetate is there. Cellulose acetate that will be discussing while discussing the synthetic fiber in the manufacture of some of the irons we are using the acetic acid.

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Uses
Fibers, plastic film
Pharmaceuticals, intermediates, cellulose acetate
Pharmaceutical, dyes intermediate, Rubber accelerator, Peroxide stabilizers
Special Oxidants
Polyester fiber, packaging, photographic films, magnetic tape sectors

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Chloromethanes (Methyl Chloride, Methylene Dichloride, Chloroform, Carbon Tetrachloride)

Chlorinated methanes, which include methyl chloride, methylene dichloride, chloroform and carbon tetrachloride, are important derivatives of methane and find wide application as solvents and as intermediate products. Product profile of Chloromethanes is given in table.

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Product	Uses
Methyl	Refrigerant, butyl rubber, silicones,
chloride	solvent, tetramethyl lead, intermediates
Methylene	Solvent, Intermediates, Photographic
dichloride	film, Degreasing solvents, Aerosol,
	Propellants

Acetanilide that we are making from the peracetic acid and the terephthalic acid and DMT. So, there we are using this acetic acid. Another one of the major outlet, we are for the methane as I told you that the chloromethanes, methyl chloride, methylene dichloride, chloroform, carbon tetrachloride. And Gujarat heavy chemicals, which is also making the soda as they are have been where they are making the chloromethane.

Similarly, the cyanide and chemicals they are using the methane, they are making the cyanide chemicals, so number of the cyanide chemicalsa they are making. This is the chloromethane, product profile, methyl chloride, methyl, methylene dichloride that you are getting into various usage of this product up there. Refrigerant, and the rubber, butyl rubber, silicones solvent, tetramethyl lead, intermediates, solvent intermediates about the methyl dichloride.

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Product	Uses
Chloroform	Chlorodifluoromethane,
	(Refrigerants), Propellants,
	Pharmaceuticals
Carbon tetra	Dichloro difluoro methane,
hloride	Trichlorofluoro methane, Solvent,
	Fire extinguishers

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Process Technology

There are two major routes for the manufacture of chloromethane

- · Direct chlorination of methane.
- · Through methanol route

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Process Technology

Direct Chlorination of Methane : Chlorination of methane (natural gas) is carried out at around 400-450 °C during which following reaction takes place:
CH₄ + Cl₂ CH₃Cl + HCl (Methyl chloride)
CH₃Cl + Cl₂ CH₂Cl₂ + HCl (Methylene Dichloride)
CH₂Cl₂ + Cl₂ CHCl₃ + HCl (Chloroform)
CHCl₃ + Cl₂ CCl₄ + HCl

Chloroform, carbon tetra chloride, so these are the various application of the chloroform to various very important chemicals that we are making similarly, carbon tetrachloride also. There are 2 roots for making of the chloromethane; one is the direct chlorination of methane and through the methanol both the process that can be a methane is cheaper and normally. And some of the plant they are making the direct chlorination of the methane . This is the process technology And if you see the chlorination of methane during the process, all the 4 3 which compound major compounds which I was telling the methyl chloride, methylene chloride, chloroform and carbon tetra chloride they are form during the process.

One of the very important product in case of the synthesis gas outlet means this where we are using the synthesis gas that is dimethyl formaldehyde. And some of the fertilizer plant like your, this RCF and the GCF, see they have started making dimethyl formaldehyde which is one of the widely used solvent in the manufacture of acrylic fiber. Because with the coming of the dimethyl formamide, in case of the acrylic fiber where we are using the wet spinning, it has been possible to go for the dispinning of the acrylic fiber. So, this was only with the availability of the dimethyl formamide and at the sometime dimethyl formamide also, we are using as a solvent in the while discussing this C 4 chemicals. We discussed dimethyl formamide also, that bring you the distraction of this some of the petrochemical.

Dimethyl Formamide [HCON(CH₃)₂]

• Dimethyl formamide is one of widely used solvents in the manufacture of acrylic fiber. Because of its high dielectric constant, aprotic nature, wide liquid range and low volatility, it is frequently used for chemical reactions. Other applications require high dissolving power.

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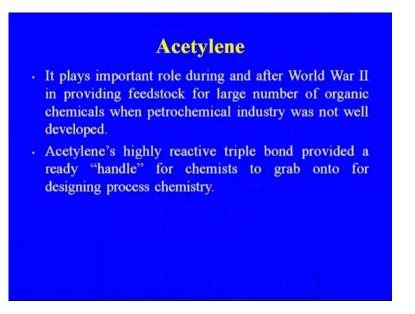


So, because of its high dielectric constant aprotic nature, wide liquid range and low volatility, it is frequently used for chemical reactions other application required high dissolving power. Because of the, we are we are using for this spinning process. This is the 2 step process. The process involves carbonization of the methanol to methyl formate using basic catalyst and reaction of methyl formate with dimethylamine. So, these are the, this day 2 step process which we are using for making of the dimethyl formatide. Another while discussing synthetic gas, we should not forget acetylene, because

acetylene is not only made by the, your this calcium carbohydrate, but also the acetylene can be made from the methane root.

And so, this is the, and the acetylene the importance of the acetylene the, because they most of the mini of the large number of chemicals which we are making to the petrochemical root phosphate from the acetylene. That is why the importance of the acetylene in the chemical industry still there. And one of the unit by and chemicals fertilizer, they are making; they are using the extreme forces for making of the phenyl chloride and the PBC.

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Acetylene; highly reactive triple bond provided a ready handle for chemists to grab onto for designing the process chemistry. So, the most many of the chemical which we are making through the ethylene was earlier the root that was not followed.

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Acetylene

Safety issues involved with handling of large volumes of acetylene and its expense are big problem with adoption of acetylene based processes. The process of acetylene requires much energy and is very expensive. of attractive petrochemical feedstock acetylene is still being used for manufacture of chemicals.

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Various Routes For Acetylene Are:

- Calcium Carbide Route : Calcium carbide is produced by reacting lime with coke at temperature 2,000-2,100 °C in an electric furnace.
- · Wet process and Dry process.
- Dry process is preferred as in case of calcium hydroxide, which is produced during the process (is produced in the form of dry calcium hydrate).
- $CaC_2 + 2H_2OC_2H_2 + Ca(OH)_2$

- Acetylene from Cracking of Hydrocarbons: Cracking of hydrocarbons such as methane, ethane, propane, butane, ethylene, and natural gas can make acetylene.
- $2 \text{ CH}_4 \text{ C}_2 \text{H}_2 + 3 \text{ H}_2$
- $\cdot \quad C_2H_4 \quad C_2H_2 + H_2$
- $\cdot \ C_4 H_{10} \ C_2 H_2 + C_2 H_4 + 2 \ H_2$

One of the problem in case of the safety issues involved with handling of large volumes of acetylene. And it is expensive are big problem with adoption of the acetylene based processes. The process of acetylene requires much energy and is very expensive of attractive petrochemical feed stock acetylene is still being used for manufacture of chemical. This is the 2 process we are having in case of the calcium carbide route process and the dry process that we are making the acetylene. Another route is the cracking of the hydrocarbon means the methane, ethane, propane, because during the process of cracking in the natural gas also they we are having we are getting the acetylene. And one of the petrochemical they are recovering the acetylene also, this is the reaction that is taking place during the cracking.

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Product Profile Of Acetylene

Acetaldehyde :

$$\begin{split} & \text{HC} = \text{CH} + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CHO} \\ & \text{Acrylonitrile}: \\ & \text{HC} = \text{CH} + \text{HCN} - ---- \text{HC} = \text{CH} = \text{CH2} = \text{CHCN} \\ & \text{Chlorinated solvents}: \\ & \text{HC} = \text{CH} + 2\text{Cl}_2 - --- \text{CH}_2\text{Cl}_2\text{CHCl}_2 - --- \text{CHCI} = \text{CCl}_2 + \\ & \text{HCI} \\ & \text{CHCI} = \text{CCl}_2 + \text{Cl}_2 - --- \text{CH}_2\text{Cl}_2\text{CCl}_3 - --- \text{CCl}_2 = \text{CCl}_2 \\ & + \text{HCI} \end{split}$$

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Product Profile Of Acetylene

Vinyl acetate :

HC=CH + CH_3COOH ----CH_2 = CHOOCCH_3

Chloreprene

HC=CH + CH_3COOH ----CH_2 = CHOOCCH_3

CH_2 = CHOOCCH_3 + Cl_2 ---CH_2 = CCICH=CH_2

Vinyl Chloride and Vinylidene Chloride

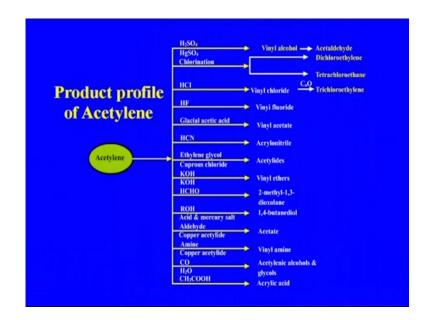
HC=CH + HCl -----CH_2 = CHCl

CH_2 = CHCl + Cl_2 ---CH_2 = CHCl

CH_2 = CHCl + Cl_2 ---CH_2 = CCI_2
```

These are the some of the products which we are getting from the acetylene and the, this was the reason why the importance of the acetylene is there was there in the during initial stage of the development of the chemical industry, when there was no petrochemical. So, acetaldehyde is the reaction that is my acrylonitrile, again acrylic fiber that was through acrylonitrile root made from the acetylene, chlorinated solvents. Vinyl acetate, vinyl chloride, and vinylidene chloride, vinyl chloride as I told you that has been used for the manufacture of the, your polyvinyl chloride, so that was the root available.

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So, this is the so, we are saying that the, this is a long list of the already I have discuss the various issues of the acetylene. So, this is about the synthesis gas and the importance in the chemical industry for the making of the large number of the petrochemical, and the reason why the, now the many of the fertilizer. So, apart from manufacturing the fertilizer, they have gone by the manufacture of the some of the very valuated product. And one of the major product, which was there that was the manufacture of the by the Gujarat state fertilizer chemicals and the fertilizer and chemicals, where they are using the ammonia. At the same time ammonia sulphate is also bi product, although now we are taking about the ammonia free (()) process.

Second development in case of synthesis gas that was the use of the huge amount of the methanol in the market and so that was the use of the methanol that also led to the. Because the fertilizer why the fertilizer come from the methanol and methanol formamide. So, this is all about the synthesis gas and its derivatives. In the next lecture, we will be discussing about the ethylene and its derivatives. Already, we have discussed the naphtha cracker; in detail we will be discussing, what are the other sources of the ethylene, and then the, what are the various products from the ethylene? Because the ethylene that is called the king of the chemicals and so the, a large number of the petrochemicals we are manufacturing on the ethylene.