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# Module - 7 Petrochemical Lecture - 6 Propylene, Propylene Oxide and Isopropanol

We are discussing the module seminar for any chemical technology course, and today we will be discussing about the Propylene, Propylene Oxide, Propylene Glycol, Isopropanol and acrylonitrile and some other derivatives. Although acrylonitrile again I will be discussing in detail, while discussing the acrylic fiber and it is monomer. But some just brief account of this acrylonitrile, I will be discussing.

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# **Coverage of Lecture**

- Introduction
- · Product Profile Of Propylene
- · Sources Of Propylene
- · Emerging FCC Based Propylene Technologies
- · Commercial Propylene Technology
- · Propylene Oxide, Propylene Glycol And Polyols
- Isopropanol
- · Acrylonitrile
- · Acrylic Acid

This will be the coverage of the lecture introduction, product profile of the propylene, sources of propylene, emerging technology for the propylene, manufacture, commercial propylene technologies, propylene oxide, propylene glycol, and polyols isopropanol, acrylonitrile. So, this will be the coverage in very brief acrylic acid also discuss.

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### Introduction

Propylene often referred as the crown prince of petrochemicals is superficially similar to ethylene but there are many differences both in production and uses.

Propylene - propylene is often referred as the crown prince of petrochemical and is superficially similar to ethylene, but there are many differences both in the production and uses. You see the propylene that has become one of the very important product for the automobile sector, where we are using the propylene there, and so the importance of the propylene that is increasing, with the increase in the population with the increase in the automobile.

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### Introduction

Propylene is used in many of the world's largest and fastest growing synthetic materials and thermoplastics. The demand of propylene has increased rapidly during the last twenty years and is primarily driven by polypropylene demand So, propylene is used in many of the world's largest and fastest growing synthetic materials and thermoplastics. One of the as I told you the propylene of the polypropylene, that is one of the major outlet where the major portion the propylene. That we are using the demand of propylene has increased rapidly during the last 20 years and is primarily driven by the polypropylene demand. Because, the it is not confined to the only the automobile sector, we are also making the in the poly in the synthetic fiber. As well as the huge amount of polypropylene, is also that is the hospital for making the syringe and other disposable material, which has replaced practically all the glass which, we are using they are in case of the hospitals.

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### Introduction

Refinery grade propylene is consumed mainly for production of cumene and isopropyl alcohol. Chemical grade propylene mostly goes into oxo alcohol, propylene oxide and acrylonitrile.

Refinery grade propylene is consumed mainly for the production cumene and isopropyl alcohol. This is one the major outlet because cumene that is the raw material for phenol and so the during the process also acetone buy product that we are getting. Because, the conventional process of the propanol manufacture that has taken place because of the availability of the propylene from the refine refinery.

Isopropyl alcohol if you see the history of the petro chemical. This was the first petro chemical need from the refinery during the initial stage even the propylene, that was actually discovered in the FCC gases. So, that propylene that was recovered and that propylene, that was used for the isopropanol, so sometimes it is called the first petro chemical also.

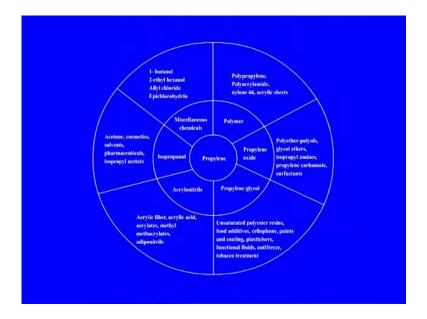
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### Introduction

Refinery grade propylene is consumed mainly for production of cumene and isopropyl alcohol. Chemical grade propylene mostly goes into oxo alcohol, propylene oxide and acrylonitrile.

Chemical grade propylene mostly goes into oxo alcohols, propylene oxide and acrylonitrile and then another important outlet for the this polypropylene, this propylene has been in the manufacture of acrylonitrile. Because the conventional process during the acetylene, that has been replaced with the propylene using propylene and ammonia process. So, that is one of the another development, that has taken place and now you are seeing the acrylic fiber which is very important part of the synthetic fiber industry. And completely it has actually, the if you see the changes in the old industry, because this is the acrylic fiber which we are using.

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These are the various uses of the so broad product which you are getting from the propylene and that is polymer, so polypropylene, poly acrylonite nylon, 66 acrylic acid, the where you are using the propylene propylene oxide. This is having the load of the other uses poly ether, polyols glycol ethers, isopropyl amines. Similarly propylene glycol and polyester resin where the use of the propylene glycol is there and here in the during the manufacture of propylene glycol both the mb mpgs dpg and and tpg mono di entrile propylene glycol.

That is made it is just similar to the ethylene glycol manufacture, which we are having in the case of the ethylene from the ethylene derivatives. There we already discussed about the product profile of the and how the mpg dg and how, we are controlling them and another important, which I told you that the acrylonitrile, because acrylonitrile that is one of the major acrylic fiber, that we are making and then the acrylic acid. That we are making from the end that acrylic acid, that is going for the acrylic methyl, methyl acrylites and that adiponitrile lot of the uses.

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| Product   | Uses  |
|-----------|---|
| Chemicals | 1 butanol, 2-ethyl hexanol, Allyl chloride, |
|           | Epichlorohydrin                             |
| Polymer   | Polypropylene,, Polyacrylamide, nylon       |
|           | 66, acrylic sheets                          |
| Propylene | Polyether-polyols, glycol ethers,           |
| oxide     | isopropyl amines, propylene carbamate,      |
|           | surfactants                                 |

Isopropanol that is another very important product on the propylene, which is for the acetone, cosmetic, solvent pharmaceuticals industry and the isopropyl acetate miscellaneous chemical also we are having from the propylene. So, this is the you can just see the this is the chemical utilization one of the major utilization, as I told you that

is in the automobile sector, where the propylene the form of the polypropylene. That is going this, what that is the major your uses of the poly the propylene is there.

These are let us discuss about the slightly more that, the chemical. These are the some of the chemicals 1 butanol 2 ethyl hexnol, allyl chloride, epichlorohydrin. Polymer polypropylene, polyacrylamide nylon 66, acrylic sheet that we are making. Propylene oxide polyether-polyols, glycol ethers, polyols that we are using in case of the polyethylene isopropyl amines, propylene carbamate and surfactant industries.

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| Product             | Uses   |  |
|---------------------|--|--|
| Propylene<br>glycol | Unsaturated polyester resins, food additives, cellophane, paints and coating, plasticisers, functional fluids, antifreeze, tobacco treatment |  |
| Acrylonitrile       | Acrylic fiber, acrylic acid, acrylates, methyl methacrylates, adiponitrile   |  |
| Isopropanol         | Acetone, cosmetics, solvents, pharmaceuticals, isopropyl acetate   |  |
| Polyols             | Polyurethane and Polyester   |  |

That is the propylene glycol all the three glycols and unsaturated polyester resins food additives, Cellophane paints and coatings plasticizers functional fluid antifreeze and tobacco treatment that we are using acrylonitrile as I told you this. Acrylic fiber, acrylic acid, acrylates, methyl methacrylates, adiponitrile. Adiponitrile which is going for the manufacture of nylon 66. Isopropanol acetone, cosmetics, solvents, polyols that is polyurethane i told you and the polyester. What are the let us, discuss the what are the sources of the propylene as i told you, the first majors who serve the propylene, before coming of the petrochemicals that was the FCC.

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## **Sources of Propylene**

- Steam crackers.
- Catalytic Cracking
- Propylene from FCC light ends
- Propane dehydrogenation
- Metathesis.
- Methanol to olefin technology

So, this steam crackers now, it has become the major source of the propylene catalytic cracking is the now what we are doing in case of this steam crackers also. The now the catalyzed of level where you can do the catalytic cracking of the of only this steam cracking. So, that the modes selective production of the or the just equal 1 list 1 proportion of the propylene, that may be there.

Propylene from the FCC light ends and that is the one of the very important source in case of the FCC and most of the refinery. They are recovering this propylene from the FCC and some of the refinery like Jamnagar. The propylene from the FCC, that is one of the very important product there. Another actually the development that is there in case of beyond purpose propylene, that has been the as per the requirements of propane dehydrogenation. As in case of the ethylene, it may be ethylene and ethane for ethylene. Similarly here you can go for the dehydrogenation of propane you can produce propane, because the propane is the available from the natural gas from the LPG.

So, this is the how the propane, that can be utilized for the production of the propane, another source is the metathesis that is also one of the important development in case of the propylene manufacture.

Then the last methanol to olefin technology, that has come in a big way and lot of the research that has done on this technology. And now that has been commercialized also in some of the country and the because of the availability of the natural gas and especially

with the coming of the shell gas are in the future. It may be the gas sided problem of the natural gas that will be available, that can be converted to methanol.

And methanol to olefin means mostly it is the propylene technology sometimes methanol to propylene propylene or sometimes it is also called the methanol to plastic technology means the from the propylene. Again we are going for the polypropylene. Improved FCC technology as I tell you the initially the technology, which was available the catalyst, which was available in case of the FCC. The yield of the propylene that was.

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# Improved FCC Technologies

Improved FCC technologies can effectively maximize propylene yield from traditional FCC feed stocks and selected naphtha. While FCC operates typically produce less than 6 wt% propylene, specialized fluidized catalytic processes can further raise propylene yields as high as 20 % or more from FCC feedstocks

So, improved FCC technology can effectively maximize the propylene yield, from the traditional FCC feed stock and selected naphtha. While FCC operates the typically, produce less than 6 percent that was the in the initially state in the FCC. That was being operated more in the gasoline mould than the propylene, because it was only after the major uses when the when the uses of the propylene, that was increased. Now, the refinery they have just started to operate the FCC, in the both the gasoline and the propylene mode depending upon the requirement.

So, specialized fluidized catalytic processes can further raise propylene yield as high as 20 % or even higher. One of the development that has been increased of the because normally if you are increasing this in ferity you can go for the more propylene yield, because only the choice the choice has to be there whether you going to operate your FCC on the gasoline mode or the propylene mode. So, the in this the development in

case of the FCC to meet the demand of the propylene, that in the deep catalytic cracking which is commercially.

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 Deep catalytic cracking is commercially proven fluid catalytic process to selectively crack a wide variety of hydrocarbon feedstocks into light olefins-particularly propylene and isobutylene. Other specialised technologies are also there which produces higher propylene.

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| Technologies              |                 |  |  |
|---------------------------|-----------------|--|--|
| Process                   | Propylene yield |  |  |
| Deep catalytic cracking   | 14-23           |  |  |
| Catalytic Pyrolysis       | 18-24           |  |  |
| High severity FCC         | 17-25           |  |  |
| Indmax                    | 17-25           |  |  |
| Maxofin                   | 17-25           |  |  |
| PetroFCC                  | 15-25           |  |  |
| Select component cracking | 20-25           |  |  |

Proven fluid catalytic process to selectively crack, a wide variety of hydrocarbon feedstock into light olefins particularly, the propylene and isobutylene. Other specialized already we discussed about the recovery of the c 4 c 5 gases from FCC and the cracker. So, the propylene and isobutylene, these are the 2 very important product of the refinery, that it may be the isobutylene as I told you earlier we started with looking the mtb and

mtb there it has been made, but still isobutylene that can be a major raw material, for this synthetic rubber industry. Other specialized technologies are also there which produces higher propylene, apart from the this deep catalytic cracking.

These are the some of the development that has taken place in case of FCC, that is the deep catalytic cracking. Other I told you the catalytic pyrolysis high severity FCC indmax technology, that has been developed by Indian oil corporation. Maxofin, that is the petro FCC select component. So, if see the propylene yielding these processes. That is quite high around 40 to you can say the 25 percent in some of the cases, select component cracking means the catalyst will be searched at the production of the, it will more selective towards the propylene.

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| Propylene FCC |                  |                    |  |  |
|---------------|------------------|--------------------|--|--|
| Wt% on feed   | Conventional FCC | High propylene FCC |  |  |
| Dry gas       | 1.5-3            | 3-9                |  |  |
| Ethyene       | 0.5-1.5          | 3-7                |  |  |
| LPG           | 16-22            | 32-44              |  |  |
| Propylene     | 4-7              | 12-22              |  |  |
| Butenes       | 4-8              | 8-14               |  |  |
| gasoline      | 47-53            | 30-40              |  |  |

The yields of the conventional or say high propylene FCC, this is the again 1 figure I am giving the composition of the gases, which are getting here you see the butanes gasoline yield. Because, you will have figure operating FCC in the propylene mode definitely that is on the cost of the gasoline. So, as I told you the depending upon the situation, depending upon the requirement you can operate the FCC either on the gasoline mode or the propylene mode, because the propylene is more valuated, product than the gasoline.

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| Products           | Yield weight (percent) |
|--------------------|------------------------|
| Dry gas (including |                        |
| ethylene)          | 12.7                   |
| Propane            | 6.5                    |
| Propylene          | 21.0                   |
| Butene             | 35.8                   |

So, this is the you see the percentage of the FCC and beyond propylene that may be there, in case of the this 12 to 25, 20 percent propylene. That may be there butanes will also be in the quantity. Gasoline yield, that will go down 47 to 53 here it is only 30 to 40 percent. This is the composition of the typical FCC in case operating the gasoline mode here you see the propylene is 21 percent propane, is also the that you can separate and then the propane that can be used for the dehydrogenation of the propane to propylene.

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| Olefin conversion<br>technology | Methanol to propylene (MTP) Technology             |
|---------------------------------|--|
| UOP/Hydro MTO<br>Process        | C <sub>4</sub> hydrogenation and Meta-4<br>Process |
| Propylur Process                | Olefin Ultra ™                                     |
| UOP Oleflex Process             | KBR's MAXOFIN-3 Technology                         |
| Superflex Process               |  |

These are the some of the commercial propylene technology UOP hydro MTO process propylur process, UOP oleflex process, superflex process, olefin conversion technology.

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# **Olefin Convers Ion Technology**

This process involves production of propylene from ethylene and 2-butenes in a fixed bed metathesis reactor containing proprietary catalyst, which promotes reaction of ethylene and 2-butene to form propylene and simultaneously isomerises 1-butene to 2-butene.

Licensor, ABB Lumus Global

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#### **UOP Oleflex Process**

This process produces polymer grade propylene from propane and the process consist of a reactor, catalyst regeneration section and product separation and fractionation section. The process uses platinum catalyst (DeH-12 catalyst).

This process involves production of propylene from ethylene and 2 butenes, which I was telling at the that is in case of the metathesis also, that you are doing ethylene and 2 butenes in a fixed bed metathesis reactor. That is the process, we called metathesis reactor containing proprietary catalyst, which promotes reaction of ethylene 2 butene to

form propylene and simultaneously, isomerizes 1 butene to 2 butene. So, that will be again available, so the licensor ABS lumus global.

UOP oleflex process, this process produces polymer grade propylene from propane and the process consist of a reactor, catalyst regeneration section and product separation and the final fractionation of the product. So, that to separate the propylene the process uses platinum catalyst and this is the catalyst, the commercial name of the catalyst. These are all the proprietary catalyst, that is been used in all the process.

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## **UOP/Hydro MTO Process**

This process converts crude methanol (produced from synthesis gas using natural gas) to ethylene and propylene and can be operated either a maximum ethylene or a maximum propylene production mode using MTO-100 silicoaluminophosphate synthetic molecular sieve based catalyst. The process utilises fluidised bed reactor and regenerator.

Lincesor: UOPLLC and Hydro Norway

UOP hydro MTO process, this process converts crude methanol produced from the synthesis gas. Using natural gas to ethylene and propylene and can be operated either a maximum ethylene or a maximum propylene production mode. Using MTO 100 silico alumino phosphate synthetic molecular sieve based catalyst, again this is the property. the process utilizes fluidised bed reactor and regenerator. So, this is the UOP hydro ethanol to methanol process. So, the choice is that depends upon the whether you are interested in the ethylene and the propylene. So, that can be operated in the both. The mode or it may be 1 is to 1, then c 4 hydrogenation already discussed this process involve the production of polymer again.

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# C<sub>4</sub> Hydrogenation and Meta-4 Process

This process involves production of polymer grade propylene plus an isobutylene rich stream or MTBE by upgrading low value  $C_4$  stream pyrolysis  $C_4$  cuts or butene rich cut.

Propylene plus isobutylene rich stream or MTBE by upgrading the low c4 stream pyrolysis c4 cuts or butene rich cut this already I discussed.

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# Olefin Ultra: TM

A new ultra high activity ZSM-5 additive that provides the highest activity has been developed by Davision Catalysts.

Olefin ultra TM a new ultra high activity ZSM 5 additive, that provides the highest activity has been developed by Davision catalysts division. Because, this one of the largest catalyst manufacturing unit in the world of continuous development, that is going on the various catalyst, whether it may be the formal catalyst, whether they are FCC catalyst or for the increasing the yield of the propylene. This is the KBRs maxofin

process again, this is the KBR is one of the the another leading licensor of the petroleum and petrochemical processes.

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#### KBR's MAXOFIN

This process is based on fluidised bed cracking of gas oils and residue feeds using ZSM catalyst and proprietary MAXOFIN-3 catalyst additive. The process gives 15% or higher propylene yield from gas oil.

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# Catalytic Dehydrogenation of Paraffins

Catalytic dehydrogenation of light paraffins is of increasing importance because of the growing demand of olefins such as propylene and isobutene and n-butenes.

Propane dehydrogenation accounts for 2 percent of the total world propylene production

This process is based on fluidised bed cracking of gas oils and residue feeds using ZSM zsm catalyst and proprietary maxofin 3 catalyst additive. The process gives 15 percent higher propylene yield from gas oil, here you see the instead of the raw material, we are using the gas oil. So, the definitely the advantage in case of the at the gas oil is there and.

So, 15 percent higher propylene yield will be there. Catalytic dehydrogenation can be paraffin, if this is one of the what we call the on purpose propylene.

So, catalytic dehydrogenation of light paraffin is of increasing importance. Because, of the growing demand of the olefins such as propylene and isobutene and n butane, the propane dehydrogenation account for, 2 percent of the total world propylene production. This is the same catalytic dehydrogenation take place the condition for the dehydrogenation the paraffin.

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# Catalytic Dehydrogenation of Paraffins

Catalytic dehydrogenation takes place at high temperature (650  $^{0}$ C) using platinum based or chromium-alumina or Fe, Cr/Al<sub>2</sub>O<sub>3</sub> as catalyst.

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# Methanol to Olefin(Propylene) Technology

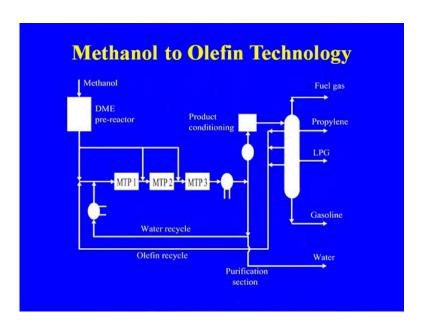
This process produces propylene from natural gas via methanol by converting methanol to dimethyl ether in adiabatic reactor using high activity, high selectivity catalyst.

DME is converted to Propylene

The catalytic dehydrogenation takes place at high temperature using platinum based or the chrominum alumina or the Fe chromium alumina as catalyst. So, where is combination that is there, then already I discussed about the methanol to olefin technology the UOP process.

The process produces propylene from natural gas via methanol by converting methanol to dimethyl. This is another process development of methanol to dimethyl ether, dimethyl ether as such it can be used in the fuel stream. So, the lot of the interest now there is for the manufacture dimethyl ether and and dimethyl ether is converted to again into propylene in this process. So, this is a technology process technology that is available.

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This is the process methanol to olefin technology, where methanol and dimethyl ether pre-reactor and different reactors are there from the different reactors. The product which we will be getting that including the fractionating common including fractionation of the product and then the duplication section and this is the gasoline propylene LPG. So, this is the final product from this, you are getting during the from the methanol to olefin technology.

So, here the raw material methanol actually as I told you, the methanol will way from the synthesis and the raw material. That may be the because while interest in methanol is because of the coming of the huge amount of the natural gas that is available. In a

various country at the same time there is no interest also for the classification of the coal. So, coal to this is the reason, why china they have gone because there coal quality is good. So, methanol to polypropylene that is they call it a methanol to plastic technology means the olefin and that olefin, that will go for the making of the polypropylene.

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# Catalytic Dehydrogenation of Paraffins

- · Oleflex (UOP).
- · Catofin (ABB Lumus).
- · FBD-4 (Snamprogetti SPA).
- · Star (Phillips Petroleum Company).

These are the some of the commercial catalytic dehydrogenation of the paraffins, oleflex, catofin, fbd-4 and star phillips process. So, these are the major dehydrogenation of the paraffins, because they are directly the paraffins propane, that you are getting from the because in the final also, we are making the LPG to propane, that can be separated that propane. That can be utilized or propane or the butane, that can be utilized for the there it may be the butylenes here it is a propane. So, that this you see the reason, why the importance of the catalytic dehydrogenation is there and more and more units are coming. Because, the on purpose propylene which are producing without going for the catalytic naptha cracking or the cracking process you can produce the propylene.

Methanol to olefin technology which the, we discussed earlier this process produces propylene from natural gas via methanol by converting methanol to dimethyl ether in adiabatic reactor, using high activity high selectivity catalyst.

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# Methanol To Olefin(propylene) Technology

This process produces propylene from natural gas via methanol by converting methanol to dimethyl ether in adiabatic reactor using high activity, high selectivity catalyst.

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# Methanol To Olefin(propylene) Technology

The methanol, water, DME stream is then feed to series of MTP reactor where steam is added. The product stream is first processed for removal of traces of water, CO<sub>2</sub> and DME, followed by further processing for yielding polymer grade propylene.

The methanol water dimethyl ether stream is then feed to series of methyl the methanol to propylene reactor, which I showed you in that diagram that this series of reactors are there. If you see the, these are the series of the reactor where the conversion is taking place and the finally, the it is going for the separation.

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# Methanol To Olefin(propylene) Technology

The methanol, water, DME stream is then feed to series of MTP reactor where steam is added. The product stream is first processed for removal of traces of water,  $\rm CO_2$  and DME, followed by further processing for yielding polymer grade propylene.

So, the finally, at the product stream is first processed for removal of traces of water CO2 and DME followed by further processing, for yielding the polymer grade propylene.

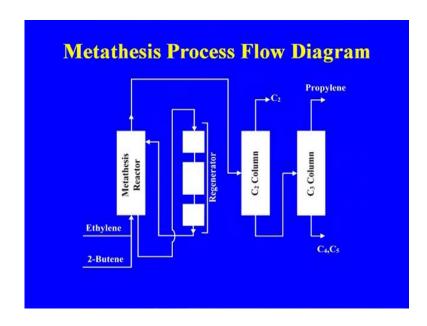
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### Metathesis

- The ethylene and butenes can be process in metathesis unit to produce additional propylene
- The C4s to C8s can be converted to light olefins through inter conversion processes to light olefins or by recycling these hydrocarbons to FCC( Kapur et al., 2009]

Metathesis already we discussed about the ethylene and butene can be process in metathesis unit. To produce the additional propylene and C4 to C8 can be converted to light olefins through, inter conversion process to light olefins or by recycling, these hydrocarbons to FCC.

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This is The flow diagram for metathesis reactor, that is the ethylene and to butene that is going to the metathesis reactor and the regenerator. And the finally, and this is the propylene column, this is the ethylene column, where the ethylene fraction, that will be C2 fraction, that will be separated. And the that will be because this will be the more heavier. So, this will go to another column where the propylene that would be separated with the C4 and C5. So, this the process in case of the metathesis that we are using.

Now let us this was all about the various pro routes for getting the propylene. Because, you see the propylene as I told you that was called the crown prince means, but now it has called the cooling part, when you compare with the ethylene. So, the now the lot of the interest there has been. So, these are the technology, which has developed. Now that is available some of the the technology they are being operated also, already some of the they have gone for the multiplication of the catalyst also, they are operating the the FCC and the propylene mode also.

So, that the more and more propylene is available further. So, these are the 3 major products propylene oxides, propylene glycols and polyols, which we are making from the other uses are also. The other products are also the, but this is one of the it is just like in case of the ethylene. It was the ethylene oxide, ethylene glycol. So, an or polyols, this is the important from the polyethylene point of view and.

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# Propylene Oxide, Propylene Glycol and Polyols

Propylene oxide, propylene glycols and polyols are important derivatives of propylene propylene oxide is used for the manufacture of propylene glycol and polyols. Major consumption of propytlene oxide is manufacture of polyurethane and polyester resins.

So, this The propylene oxide, propylene glycols and polyols are important derivatives of propylene propylene oxide is used for the manufacture of propylene glycol and polyols. Because, the starting materials, because here the same from the propylene to propylene oxide the process we are using just the similar to the the ethylene oxide process. Major consumption of the polyethylene and the propylene oxide is manufacture of polyurethane and polyester resins. Propylene glycol which I told you that the we are making from the propylene oxide.

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# Propylene Oxide , Propylene Glycol And Polyols

Propylene glycol find major application in the manufacture of unsaturated polyester resins, food additives, pharmaceuticals and personal care, tobacco humectants, cellophane, paints and coatings. Polyols major use is in the manufacture of polyurethane.

So, the propylene glycol find major application in the manufacture of unsaturated polyester resins, food additives, pharmaceutical, personal care, tobacco humectants, cellophane, paints and coatings. Another important product which I was telling the polyols major uses the manufacture of the polyurethane.

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### **Propylene Oxide**

- There are two major processes for the manufacture of propylene oxide
- · Propylene chlorohydrin process
- · Propylene oxidation process using peroxides.

Propylene oxides, there are 2 major process for the manufacture of propylene oxide, one is the propylene chlorohydrins process. Another is just like it is the propylene chlorohydrins process that was in case of propylene oxide real oxide this in process we problem, this the same that is the chlorine handling is there corrosion problem is there. So, the with the development of the propylene oxide, now the most most of the propylene oxide, that has been made through the this process, the propylene oxide and also it has enhance the actually the production, because the more and more propylene that is available from the refinery and the cracker plant. So, this was let us discuss although, this is the only the old method, the propylene chlorohydrins route not being used, but this process was the starting process. So, I thought to discuss this process.

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# **Propylene Oxide**

Propylene Chlorohydrin Route:

The chlorohydrination process consists of formation of propylene chlorohydrin by the reaction between hypochlorous acid and propylene.

The propylene chlorohydrin is epoxidised to propylene oxide by a 10% solution of milk of lime or NaOH.

So, the chlorohydrins process consists of formation of propylene chlorohydrins by the reaction between the hypochlorous acid and the propylene. The propylene chlorohydrins is epoxidised to propylene oxide by a 10% solution of milk of lime or NaOH.

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# Propylene Oxide From Propylene Chlorohydrin

Process steps

- Propylene hypochlorination
- Neutralisation
- Dehydrochlorination
- · Purification

The process steps in the propylene chlorohydrins process is propylene hypo chlorination neutralization dehydrochlorination and then the purification. These are the major steps involved and in the chlorohydrins process.

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Reactions

• Cl_2 + H_2O ------ HOCl + HCl

• CH_3-CH=CH_2 + HOCl ------ CH_3CH OH

• -CH_2Cl \Delta = -225 kJ/mol

• Propylene chlorohydrin

2CH<sub>3</sub>CHOH-CH<sub>2</sub>CI + Ca(OH)<sub>2</sub> Or NaOH ----> 2CH<sub>3</sub>CH-CH<sub>2</sub> + CaCl<sub>2</sub> Or NaCI + 2H<sub>2</sub>O

\Delta = 5 kJ/mol
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This is the reaction, that is taking place in case of the chlorohydrins process again here, this same problem of the generation of the calcium chloride or NaCl there. So, and the involvement of the Hcl is also there, so the chlorine and the Hcl. So, they are highly atmosphere, because of that is an how this process has been replaced with the propylene oxidation route. So, let us discuss now the propylene oxidation route.

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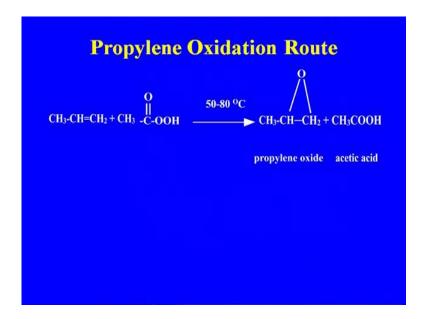
# **Propylene Oxidation Route**

In this process, propylene and peracetic acid (in ethyl acetate) which is produced by oxidation of acetaldehyde are reacted in a series of three specially designed reactors at 50-80 °C and 90-120 MPa pressure.

So, propylene in this process, propylene and peracetic acid in ethyl acetate, which is produced by oxidation of acetaldehyde reacted in a. So, this is the peracetic acid from the

acetaldehyde route in a discuss while peracetic acid also one of the product. That you are getting from the acetaldehyde are reacted in a series of 3 specially, designed reactor at 50 to 80 degree centigrade and 90 to 120 mega Pascal pressure .

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This is the a reaction that is taking place in case of the propane and the reaction you see, this is the propylene oxide that you are getting and this is the by product that you are getting here. That is the acetic acid and the during the manufacture the propylene oxide.

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# **Propylene Oxidation Route**

The reaction products are fed to the stripper where a mixture of propylene and propylene oxide are obtained as top product while mixture of ethyl acetate and acetic acid is obtained as bottom product.

Both mixtures are fed to two separate columns where separation of propylene oxide, ethyl acetate, acetic acid, and heavy end takes place. The reaction products in from the reactor in case of the propylene di, propylene oxidation is fed to the stripper where a mixture of propylene. And propylene oxide are obtained as top product while mixture of ethyl ethyl acetate and acetic acid is obtained as bottom product. Both mixture was then fed to the 2 separator separate columns, where separation of propylene oxide, ethyl acetate acetic acid and heavy end takes place.

So, this is the process which we are using for the manufacture of the propylene oxide from the propylene route. Another let us discuss now the another important product from the propylene that is the propylene glycol. Propylene glycol means the all the 3 propylene glycol mono propylene glycol and di propylene glycol. Because, these are all the 3 glycol that will form again as the same as, it is being done in case of the you will have to control the amount of the water in the hydrolysis.

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# **Propylene Glycol**

- Concentration Section: Concentration of glycol solution in multiple effect evaporator
- Distillation Section: Separation of MPG,DPG and TPG iseperated from MPG column.n series of distillation column where MPG is separated in first column.

Propylene glycol is made by hydrolysis of propylene oxide, the process steps involve the hydrolysis of the propylene oxide resulting in the formation of mono propylene glycol small amount of di propylene glycol and tri tri propylene glycol. So, the after the reaction as in case of the flow diagram of the MAG. Same in the concentration section, concentration of glycol solution in multi effect evaporator and after this.

That is going to the separation distillation section, where the separation of the MPG DPG mono propylene glycol, di propylene glycol. Tri propylene glycol is separated. Because, of the difference in the boiling point, from the MPG column and number of a series of

distillation column, where MPG is separated in the first column. Because, it is lighter and. So, they even the amount of the as i told the amount of the DPG and TPG that can be adjusted, during the hydrolysis process taking them. Now, your amount of the propylene to water ratio. So, that was about the glycol another important product, which we are getting from the propylene, that is the isopropanol as I told you the isopropanol. That was the first product petrochemical, because the propylene that was available from the refinery.

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### **Isopropanol**

Ever since its first commercial introduction in 1920 as one of the first petrochemicals, isopropyl alcohol has found wide use as a solvent and raw material for other chemical products like acetone, isopropyl acetate, glycerol, isopropyl and disopropyl amines, corrosion inhibitor diisopropyl ammonium nitrate, floatation agent isopropyl xanthate, isopropyl myristates etc.

Ever since its first commercial introduction in 1920 as one of the first petrochemical, isopropyl alcohol has found wide use as a solvent raw material for other chemical products. Like acetone, isopropyl acetate, glycerol, isopropyl and disopropyl amines, corrosion inhibitor, diisopropyl ammonium nitrate, flotation agent, isopropyl xanthenes, isopropyl myristate. So, these are the some of the product, that you are getting from the isopropanol.

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# **Isopropanol Process Technology**

- Two major processes
- Esterification of propylene by sulphuric acid and hydrolysis
- ·  $CH_3$ -CH= $CH_2$ + $H_2SO_4$   $\longrightarrow$   $(CH_3)_2CH$ -O- $SO_3H$   $(CH_3)_2CH$ -O- $SO_3H$ + $H_2O$   $\longrightarrow$   $CH_3$ - $CH(OH)CH_3$ +  $H_2SO_4$
- Direct catalytic hydration of propylene (vapor phase, liquid phase and mixed phase)
- ·  $CH_3$ -CH= $CH_2$ + $H_2O$   $\longrightarrow$   $CH_3$ -CHOH- $CH_3$   $\Delta$  = -51 KJ/mol

These are 2 major technology that is available for the production of the isopropanol, the etherification of propylene by sulphuric acid and hydrolysis. These are the reaction that is taking place, after the etherification and the hydrolysis part and we are getting the isopropanol, direct catalytic hydration of the propylene. So, this is because when you are handling the steps over the problem corrosion another problems are there.

So, this process that is more, it is better than the this process by sulphuric acid and hydrolysis route. Let us now, actually this was the some of the major products, another major product or way discussing only the brief summary of the acrylonitrile. Because, we are discussing the propylene part, but indeed detail of the process will be discussing again while discussing the acrylic fiber in module 8. They are the what are the monomer, that is required for the synthetic fiber industry that will be discussed in about in detail. So, the acrylonitrile was here also the, if you see these historical background of acrylonitrile any large number the chemicals, that was the actually the the alternative role means the acetylene role.

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# Acrylonitrile

 Acrylonitrile was first synthesized by Moureu in 1893 but remained practically a laboratory curiosity until the development of acrylonitrile butadiene rubber used as self sealing lining in aircraft, gasoline tank during World War II [Pujado, 1977].

Acrylonitrile was first synthesized by moureu in 1893, but remained practically a laboratory curiosity until the development of the acrylonitrile, butadiene rubber used as self sealing lining in aircraft. Aircraft gasoline tank during the world war 2. So, these were the actually the development of the nitrile the world, that was being used as the ceiling because that was having the decision. So, that was the requirement at that time for the aircraft and so that led to the development of the acrylonitrile also or the commercialization of the acrylonitrile process. But later on the more and more it was for the use of the acrylonitrile for making of the acrylic fiber.

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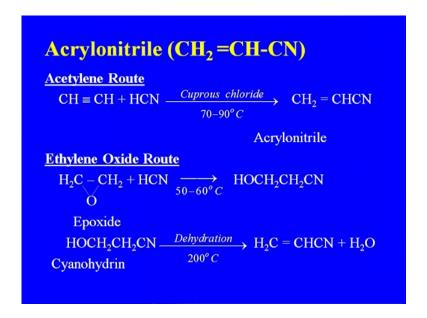
# Acrylonitrile

However, this was moderate tonnage application & its major application started with the production of acrylic and modified acrylic fiber and resin acrylonitrile (ABS) and styrene acrylonitrile (SAN) where large tonnage of acrylonitrile being used. Worldwide demand for acrylonitrile in 2002 was approximately 5 million tonnes. Demand in Asian market reached 50percent of worldwide demand and a high rate of growth is expected to continue.

So, this as I told you with the development the moderate tonnage application and it is major application, started with the production of acrylic and modified acrylic fiber, which is told you. Because, this was the change in the even the production pattern also and the resin acrylonitrile ABS resin and styrene acrylonitrile resin. So, styrene combination of the butane combination or a different resins, we are that is coming in this specialty of this, and your polymer.

So, that has led to the further development in case of the requirement of the acrylonitrile, where large tonnage of acrylonitrile being used. Worldwide demand of the acrylonitrile was approximately 5 million tones, demand in the Asian market reached 50 percent of worldwide demand and a high rate of growth is expected to continue. But one of the major development, that has been in case of the acrylonitrile, that was development of the process by amino oxidation of the propylene. Let us first discuss this some of this routes again because just i will give the brief out outline of the process and then I, as I told you we will be discussing more in the module 8 about the acrylonitrile.

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So, it is thin route was the first route, which was available because the this was the non the petroleum route. That was the formation of the acrylonitrile from the acetylene another route that is available, that is the ethylene oxide route, that is from the ethylene oxide we are making the acrylonitrile.

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Acrylonitrile (CH<sub>2</sub>=CH-CN)

Acetaldehyde Route

CH_3CHO + HCN \longrightarrow CH_3CHOHCN

CH_3CHOHCN \xrightarrow{Dehydration} CH_2 = CHCN + H_2O

Propylene Route

CH_2 = CH - CH_3 + NH_3 + 3/2 O_2 \xrightarrow{Ammoxidation} CH_2 = CHCN
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Acetaldehyde route, propylene route is also this is the one of the major breakthrough that has been the process of the acrylonitrile by ammoxidation process.

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# Acrylonitrile by Ammoxidation of Propylene

Acrylonitrile by Ammoxidation of Propylene: A typical acrylonitrile plant consists of acrylonitrile reactor section, acrylonitrile recovery section, acrylonitrile purification section and HCN purification section. Propylene, ammonia and air are fed to fluidised bed catalytic reactor where ammoxidation of propylene – a highly exothermic reaction occurs.

So, acrylonitrile by ammooxidation of the propylene a typical acrylonitrile plant consists of the acrylonitrile reactor section, acarylonitrile recovery section, acrylonitrile purification section and the HCN purification section. Because, here in the process we are getting acetone nitrile also one of the important your this by product. Propylene

ammonia and air are fed to fluidized bed catalytic reactor, where ammoxidation of the propylene that is taking place.

So, again as I told you the with flow diagram other details, there need to discussing while the discussing the acrylic fiber. So, let us come to the another important outlet for the propylene as the polyols, where the because this is finding wider application in the manufacture polyurethane.

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# **Polyols**

Polyols are made by polymerization of propylene oxide/ethylene oxide using an proprietary catalysed chain starter. The process consist of

Raw material Preparation: Preparation of chain starter and addition in reactor along with EO/PO

Reaction: Polymerisation using catalysed cahin extender Purification: Purification of raw polyol by nutralisation

So, polyols are made by polymerization of propylene oxide ethylene oxide, using an proprietary catalyst chain starter. The process consists of the raw material preparation section, the reaction section, purification section. So, raw material preparation, preparation section, preparation of the of chain starter and addition in reactor, along with the ethylene oxide and the PO. At the reaction time polymerization using catalysed chain, extender and then the purification, involve the purification the raw polyol by neutralization. Another important outlet for the propylene that has been the acrylic acid, which is used for the acrylate, that you are making from the acrylic acid. So, that is one of the very important your product of the propylene.

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## **Acrylic Acid**

Acrylic acid is a versatile chemical which find application in the manufacture of glacial acrylic acid and acrylic esters (Acacrylates and metha acrylates), polyacrylic acid which is used in manufacture of super absorbent polymers, flocculants, detergents, paper chemicals and resin.

Various acrylic esters are methyl acylate, ethyl acrylate, butyl acylate, 2-ethyl hexyl acrylate.

The acrylic acid is the versatile chemical, which find application in the manufacture of glacial. Acrylic acid and acrylic esters, acacrylates and metha acrylates polyacrylic acid which is used in the manufacture of super absorbent polymers, flocculants, detergents, paper chemicals. And resin various acrylic esters are acylate ethyl acrylate butyl acylate 2 ethyl hexyl acrylate. So, this is the about the acrylic acid these are the various process technology.

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# **Process Technology**

Various routes for making acrylic acid are

Acetylene route

Ethylene Oxide Route

Ethylene Route

Chlorination of Propianic acid

Propylene route

Formaldehyde and Acetic Acid Route

That is available for the acrylic acid, ethylene route, ethylene oxide route, ethylene route and the chlorination of the propianic acid, propylene route formaldehyde and acetic acid route. So, this was about the propylene derivatives, apart from this some of the other propylene derivatives also the. So, propylene one of the major, because the development that has taken place in the refinery the petrochemicals complexes is the catalyst development to enhance the the production of the propylene.

Either from the FCC or from the catalytic cracking which the process, we call advanced catalytic deep cracking process, that is there which is where the more propylene yield will be there. So, that part will discuss real also. So, this is the how the propylene production and the various product of the propylene their importance you have discussed in the next lecture.

That will be on the aromatic production and the aromatic various aromatics are also playing very important role in the chemical organic chemical industries, either you can say the in the it may be pesticide, it may be explosive, it may be the your... So, we will be discussing 2 lectures, one is the aromatic production and second will be on the various aromatic products, which we are making.