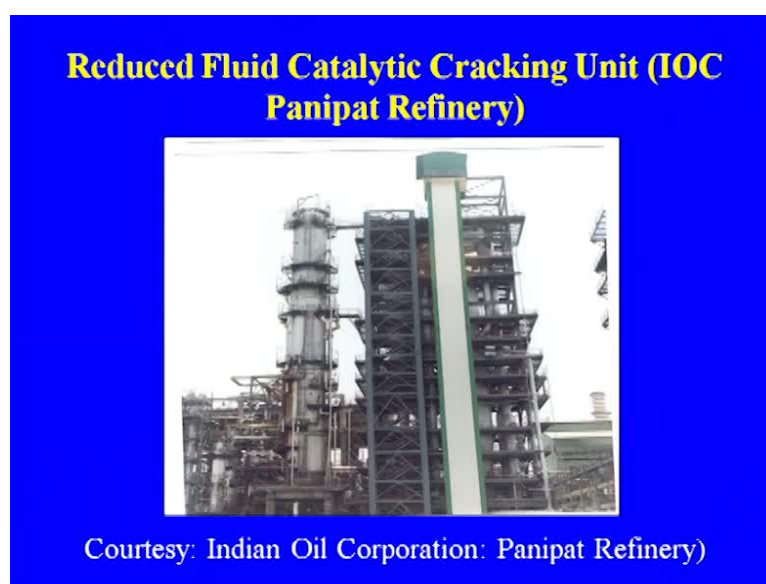


**Chemical Technology**  
**Prof. Indra D. Mall**  
**Department of Chemical Engineering**  
**Indian Institute of Technology, Roorkee**

**Module - 6**  
**Petroleum Refinery**  
**Lecture - 5**  
**Catalytic Cracking Fluid Catalytic Cracking and Hydro Cracking**

We are discussing organic chemical technology course module six and I have taken four lectures on this. And already in the last lecture, we have discuss about the thermal cracking processes. So, the today I will be discussing about the catalytic cracking. And catalytic cracking will be discussing about the fluid catalytic cracking, hydro cracking advances, which are in taken place in case of the FCC.

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And coverage this is the actually the typical, you can see the fluid catalytic cracking unit of the Panipat refinery.

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## Coverage of the Lecture Fluid Catalytic Cracking Process

- Introduction
- Feed stock
- Major land marks in the history of FCC
- Main reaction in FCC
- Process Steps
- Typical operating parameter of FCC
- FCC catalyst
- Advance catalytic Cracking processes
- Operational features of Indmax technology

The coverage of the lecture that is in two part; one is the fluid catalytic cracking process, where the brief introduction about the FCC. How the elevation of the fluid catalytic cracking from fixed bed to FCC that has taken place. Feed stock for the FCC, major land marks in the history of the FCC. Main reactions in the FCC process step. Typical operating parameter. FCC catalyst, because there is an continuous development in case of the FCC catalyst; from the now the FCC is running from the gasoline to propylene mode. So, what are the advancement that has taken to the FCC catalyst?

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## Coverage of the Lecture

- Hydrocracking
- Introduction
- Comparison of Catalytic Cracking and Hydrocracking
- Hydrotreating (Pretreat) Catalyst
- Hydrocracking Catalyst
- Single Stage and Two stage Hydrocracking Process

That will be discussing advance catalytic cracking processes, which is just two basic objective admin to increase the production of the propylene. Operational features of the indmax technology that has been developed by IOC, Indian Oil Cooperation. And the hydro cracking will be discussing about the introduction of the hydro cracking, comparison of the catalytic cracking and the hydro cracking. Why is the hydro cracking we are doing? Because they are the, it was the fluid catalytic cracking and from the fluid catalytic again the hydro cracking in many of the refinery.

Now, they have they are having both the FCC and the hydro cracking. Then the hydro cracking, because in case of the hydro catalytic both the pre treat and the cracking action that is taking place. So, the hydro treating catalytic and the hydro cracking catalyst single stage and two stage processor, they are in case of the hydro cracking. So, that will be discussing in the next two slides. Let us discuss about the history of the catalytic cracking.

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## Catalytic Cracking

- Catalytic cracking process was developed in 1920 by Eugene Houdry for upgradation of residue was commercialized latter in 1930.
- Houdry process was based on cyclic fixed bed configuration.

Catalytic cracking process were developed in 1920 by Eugene Houdry for upgradation of the residue was commercialized latter in 1930. And this was the fixed bed technology that was the cyclic fixed bed configuration. That was the original process of the catalytic cracking. Now, they with the evolution of the coming of the our development in case of the fertilization technology.

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## Catalytic Cracking

- There has been continuous upgradation in catalytic in catalytic cracking process from its incept of fixed bed technology to latter fluid bed Catalytic Cracking (FCC).
- Fluid Catalytic Cracking is now major secondary conversion process in Petroleum refinery since 1942.

Now, most of the units they are having the fluid bed catalytic cracking. There has been continuous upgradation in the catalytic cracking processes from its incept of the fixed bed technology to latter fluid bed catalytic cracking. Fluid catalytic cracking is now major secondary conversion process in petroleum refinery since 1942. That was the time in the UOP introduced that fluid catalytic cracking process. Global demand why is the catalytic?

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## Catalytic Cracking

- Global Demand for clean fuels has driven the need for increased diesel yield which has prompted an increase in the implementation of new hydrocrackers.
- Design of new hydrocracking units are challenged by the difficult feeds from heavy sour crudes and residum upgrading units

Global demand for clean fuels has driven the need for increase diesel yield, which has prompted an increase in the implementation of new hydrocrackers. That is the about the why the hydro crackers are design of new hydro cracking units are challenged by the difficult feed stock from heavy sour crudes and residum upgrading units.

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### **Fluid Catalytic Cracking**

- Fluid catalytic cracking is now major secondary conversion process in Petroleum refinery since 1942.
- There are more than 400 FCC units in world.

Now, let us come to the fluid catalytic cracking, then I will be discussing about the hydro cracking. Fluid catalytic cracking is now major secondary conversion process in the refinery since 1942. There are more than 400 FCC units in world. Now you cannot imagine a refinery without FCC. The process provides around 50 percent of all transportation fuel and 35 percent of the total gasoline pool. Because the cracked gasoline which we are getting from the FCC; that is going to the gasoline pool that is in the form of the reformative gasoline. FCC is the multi component catalyst system with circulating fluid bed reactor system with the Reactor Regenerator system configuration. Because here in case of the FCC we are having the reactor and regenerator both the are there.

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### **Major Land Marks in the History of FCC**

- Introduction of large number of additives for boosting of gasoline octane/yield of light naphtha
- SO<sub>x</sub> control
- Nickel and vanadium passivation
- Gasoline to Propylene mode operation

Introduction of large number of the additives for boosting of the gasoline octane yield of the light naphtha, SO<sub>x</sub> control, nickel and vanadium passivation, gasoline to propylene mode operation. Because now, the many of the about that around 30 percent of the Propylene that is coming from the FCC. So, many of the refinery they are operating FCC in the propylene mode, not the gasoline mode.

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### **FCC as Source of Propylene**

- Although FCC units are major conversion process in Refinery, however desired product slate is shifting increasingly towards light olefins production.
- Conventional FCC units typically produce about 3-6% propylene
- FCC propylene accounts for almost 30% of the global propylene

Although, FCC units are major conversion process in Refinery, however desired product slate is shifting in increasing towards light olefin production, especially the Propylene.

Conventional FCC units typically produce about three to six percent Propylene. But FCC propylene accounts for almost 30 percent of the global propylene now, so the shift in the technology or the shift in the catalyst which is resulted in the increase Propylene.

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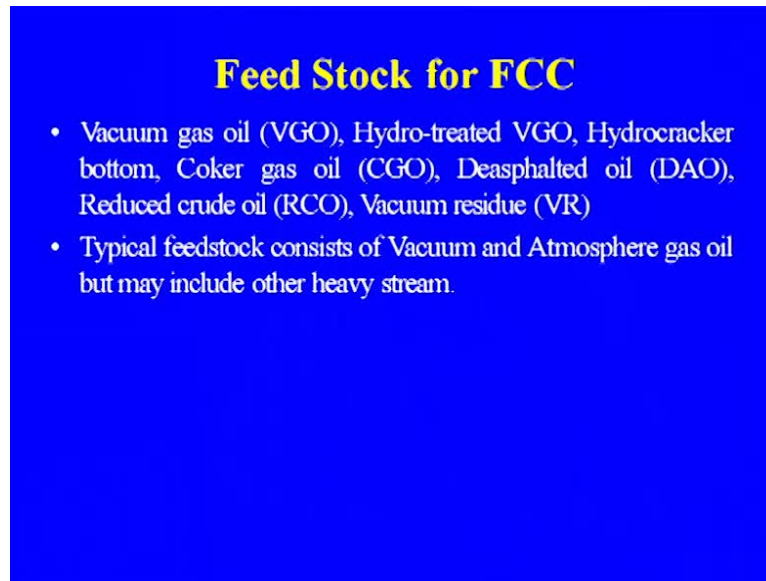
### **Major Land marks in the History of FCC**

- Introduction of zeolite catalyst during 1960 which has resulted in lower residence time
- Introduction of ultra stable Y-zeolite in mid 60's
- Switch over from bed cracking to riser cracking

Similarly C 4, C 5 gases that can be recover from the FCC gases. And that is now providing a very valuable product. And one of the major product from the FCC that is m t b and tame that is the oxygenated we are producing. Introduction of zeolite catalyst during 1960 which has resulted in lower residence time. Introduction of ultra stable Y-zeolite in mid 60s switch over from fixed bed cracking to the riser cracking technology. Feed stock for the FCC. Because what is happening, as we discuss during the crude oil distillation, we are getting the residue from atmospheric column. Then the that residue that is going to the vacuum column and where we are separating the light vacuum in the form of the light vacuum gas oil and the heavy vacuum gas oil.

So, these are the some of the actually from feed stock for the FCC. Apart from that just like the Vacuum gas oil, Hydro-treated VGO that you are getting there from the vacuum gas column. Hydrocracker bottom because now the many of the refineries, they are having the Hydrocracker that is also producing heavy residue. Coker gas oil that is also from we are getting from the thermal cracking process.

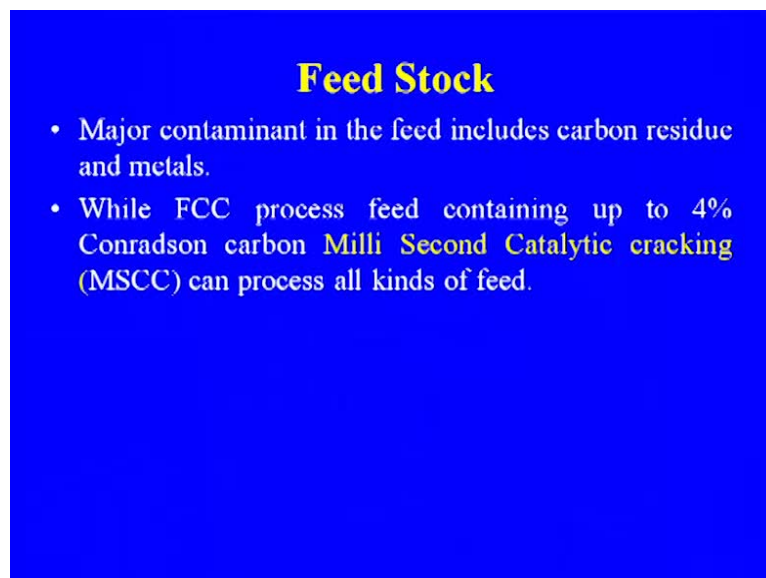
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**Feed Stock for FCC**

- Vacuum gas oil (VGO), Hydro-treated VGO, Hydrocracker bottom, Coker gas oil (CGO), Deasphalted oil (DAO), Reduced crude oil (RCO), Vacuum residue (VR)
- Typical feedstock consists of Vacuum and Atmosphere gas oil but may include other heavy stream.

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**Feed Stock**

- Major contaminant in the feed includes carbon residue and metals.
- While FCC process feed containing up to 4% Conradson carbon Milli Second Catalytic cracking (MSCC) can process all kinds of feed.

Deasphalted oil, Reduced crude oil and Vacuum that is the why that is the residue FCC. Now, some of the units they are having the they call it the residue FCC. So, typical feed stock consists of Vacuum and Atmosphere gas oil but may include other heavy stream also. As I told you that many from the Hydrocracker that may be from the Coker and other units also they have been residue that will go to the either the Catalytic cracking, may the FCC or it may be the Hydrocracking. Major contaminant in the feed includes carbon residue and the metals while FCC process feed containing up to 4 percent Conradson carbon.



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## Catalytic Cracking

- Catalytic cracking cracks low value high molecular weight hydrocarbons to more value added products (low molecular weight)
- Gasoline, LPG Diesel along with very important petrochemical feedstock like propylene, C<sub>4</sub> gases like isobutylene, Isobutane, butane and butane

So, Milli second Catalytic cracking process can process all kinds of the feed. That is the development in case of the FCC where the residence time that has been decreased. Catalytic cracking cracks low value high molecular weight hydrocarbons to more value added product low molecular weight hydrocarbon. So, product or Gasoline, LPG, Diesel along with the very important petrochemical feedstock like petrochemical C 4 gases like isobutylene, Isobutene, butane and butane.

Because these are the some of the very important hydrocarbons we are getting from the C 4 stream of the FCC and some of the refinery apart from the propylene, they are recovery isobutylene that is converted to m t b in the process in some of the refinery. Although, there is ban on the m t b in many of the countries but m t b and isobutene that can be used for the conversion to isobutene or some other, similarly butane and butane. Also, there a large number of the C 4 gases that we are getting and that processing of the C 4 gasoline will be discussing while discussing the petrochemical part.

Main reaction involved in the Cracking. Cracking of the paraffins, naphthenes and side chain of the aromatic, isomeristion, dehydrogenation of naphthenes and olefins. Hydrogen production with the cyclization and condensation of the olefins alkylation and dealkylation.

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### **Main Reactions Involved In Cracking**

- Cracking of paraffins, naphthenes and side chain of aromatics
- Isomerisation
- Dehydrogenation of Naphthenes and olefins + Hydrogen
- Cyclization and condensation of olefins
- Alkylation and dealkylation

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### **Major Primary Reactions Taking Place In Catalytic Cracking**

Alkyl naphthene  $\longrightarrow$  naphthene + olefin

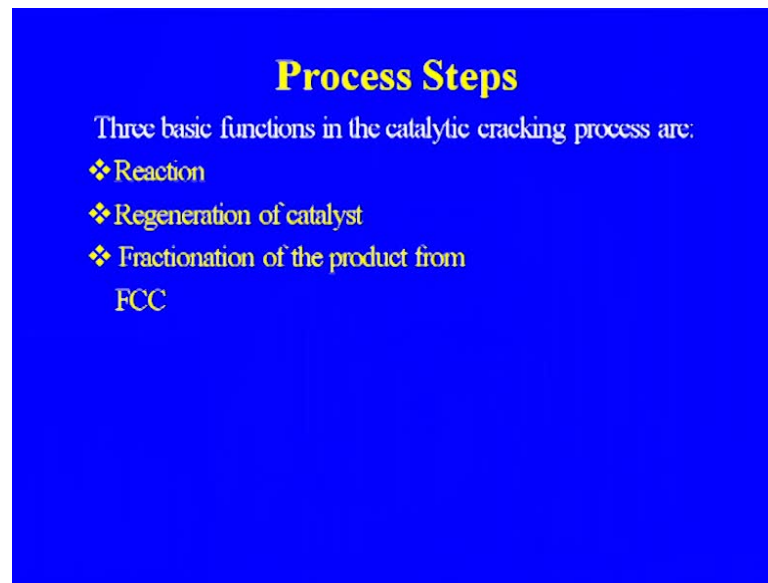
Paraffins  $\longrightarrow$  Smaller paraffins + olefins

Alkyl aromatic  $\longrightarrow$  aromatic + olefin

Multiring naphthene  $\longrightarrow$  Alkylated naphthene  
with fewer rings

A series of reaction that is taking place these are the some of the reaction that is taking place major primary reaction in the catalytic cracking. The alkyl naphthene, paraffins, alkyl aromatic, the naphthene. So, these are the some of the products which we are getting from them.

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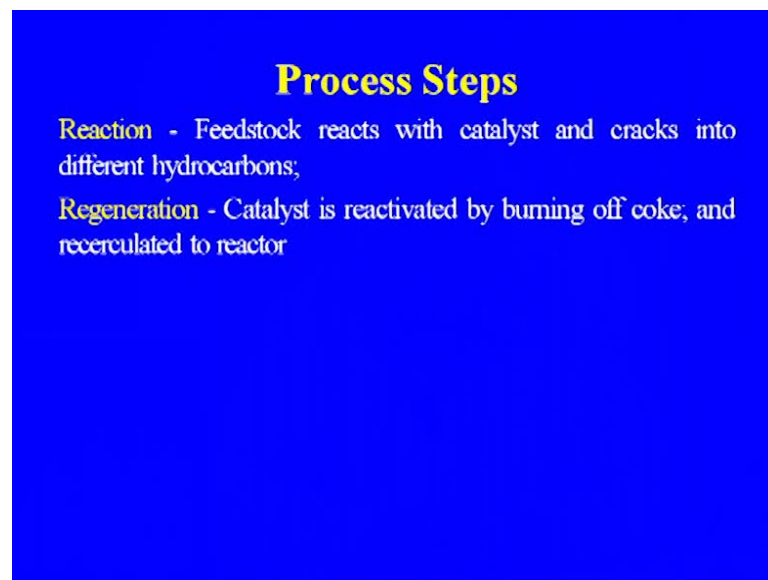
**Process Steps**

Three basic functions in the catalytic cracking process are:

- ❖ Reaction
- ❖ Regeneration of catalyst
- ❖ Fractionation of the product from FCC

So, the processes steps. What are the process steps in case of the catalytic cracking? When I am talking about catalytic means the FCC, that is the reaction regeneration of the catalyst and the fractionation of the product which we are getting from the FCC.

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**Process Steps**

Reaction - Feedstock reacts with catalyst and cracks into different hydrocarbons;

Regeneration - Catalyst is reactivated by burning off coke, and recirculated to reactor

So, these are the three major steps involved and degeneration of catalytic that has, that is very important part of the catalytic cracking process. Reaction, the reaction what is happening? Feed stock reacts with the catalyst and cracks into different hydro carbon. Regeneration catalyst is reactivated by burning off coke. Because normally in the all the

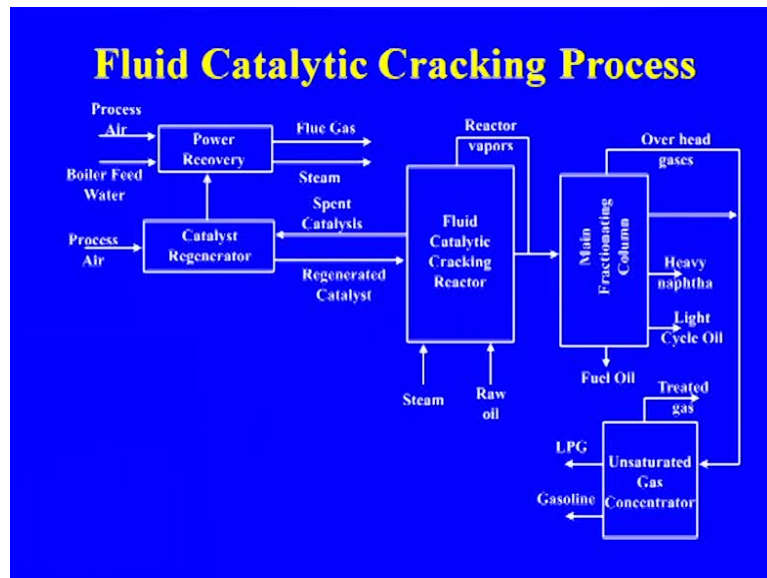
cracking process some formation of the coke, because of the various reaction that is taking place that takes place. And that coke has to be removed for long longer life of the catalytic to improve the performance of the catalyst. And so, the continuous regeneration of the catalytic is there and then it is recirculated as well reactor.

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### Process Steps

- Fractionation:**  
 Cracked hydrocarbon stream is separated into various products like LPG and gasoline, like light cycle oil and heavy cycle oil are withdrawn as side stream

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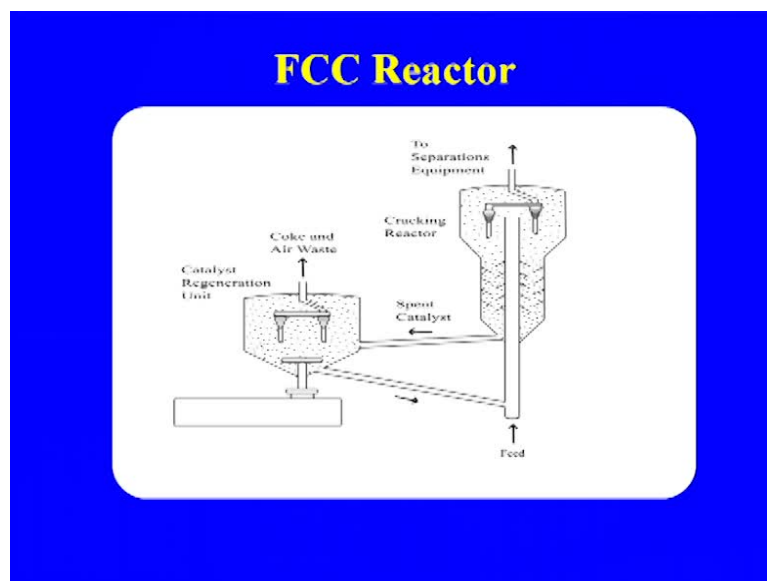
Then the third part after the reaction degeneration is complete, the product, which we are getting from the catalytic cracking that is going to the distillation column for separation

of the various products like LPG and Gasoline, light cycle oil that is also actually another that is low value added product that we are getting.

Light cycle oil and heavy cycle oil are withdrawn that from the side stream of the (( )). I will discuss about the flow diagram, there it is clear. Here you see the, this is the typical fluid catalytic process where you are getting. This is the fluid catalytic cracking reactor and then the process here boiler feed water, because here the catalyst is regenerated catalyst that is going to the fluid catalytic cracking. And then this is the main fractionating column where the catalyst continuous from the fluid catalytic cracking catalyst that will go to regenerator and the because fuel is also there, so that is going to the Gasoline.

That is going to CO boiler that is called the. Here in the power generation and then the after the fractionation what is happening? We are getting the FCC that is a major source of LPG in the refinery. So, the over head from the over head will be getting the, that will go to the stabilization column, where the LPG is separated and then you will be getting the Gasoline. Heavy naphtha also here also we are getting light light cycle oil fuel oil. The bottom product that be the heavy residue that will getting the from the catalytic cracking. So, this is process we are using in case of the catalytic fluid catalytic cracking process. This is the typical actually the feed that is going to the reactor riser.

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What about calling the riser here? The reaction is taking place and then, these are the cyclones they are they and the cyclones. The catalyst is separated in continuous the cyclone, this catalytic that is going to for the catalytic regeneration. And after the regeneration the catalytic that is continuously that is again that is joining the feed stream and then it is going to the fluid FCC reactor. So, this is the actually the typical FCC reactor which we are using in the refinery.

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### **Reactor and Regenerator**

- The feed to unit along with recycle streams is preheated to temperature of 365°C-370°C and enters the riser where it comes in contact with hot regenerated catalyst at a temperature of about 640-660°C.

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### **Reactor and Regenerator**

- Finely divided catalyst is maintained in an aerated or fluidized state by the oil vapors.
- The catalyst section contains the reactor and regenerator & catalyst recirculates between the two.

The reactor, let us now discuss in detail about the reactor, regenerator and the fractionator. The feed to the unit along with the recycle stream is preheated to temperature of about 365 degrees centigrade to 379 centigrade and enters the riser. As I told you in the flow diagram it is going to the riser, where it comes in contact with the hot regenerated catalyst, which we are getting from the regenerator from catalyst regeneration section at that they which are at a temperature of 640 to 660 degree centigrade.

Finely divided catalyst is maintained in aerated or fluidized state by the oil vapors. And the fluid they behave like just it is the fluid with very fine particles are there. And so, they it is called not they actually fluid catalytic cracking.

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### **Reactor and Regenerator**

- ❖ Spent catalyst flows through the catalyst stripper to the regenerator, where most of the coke deposits burn off at the bottom where preheated air and spent catalyst are mixed.
- ❖ Fresh catalyst is added and worn-out catalyst removed to optimize the cracking process

The catalyst section contains the reactor and regenerator. And catalyst recirculate between this two continuously. The continuous regeneration of the catalyst is there and then it go to the reactor. Spent catalyst that is regenerated to get rid of the coke that collects on the catalyst during the process, which I told you that during the cracker is normal some carbon rejection is there, that carbon which is there and that carbon that is that has to be removed from the catalyst before it is being recycle to the system. Spent catalyst flow through the catalyst stripper to the regenerator, where most of the coke deposit burn off at the bottom, where preheated air and spent catalyst are mixed.

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## **Fractionation**

Cracked hydrocarbon stream is separated into various products. LPG and gasole are removed overhead as vapour. Unconverted product like light cycle oil and heavy cycle oil are withdrawn as side stream.

Fresh catalyst is added and worn out catalyst removed to optimize the cracking process. Cracked hydrocarbon stream is separated into various product which I told you. LPG one of the very important product of the FCC. Gasoline are removed at the overhead as vapor unconverted product like light cycle oil and heavy cycle oil are withdrawn as side stream.

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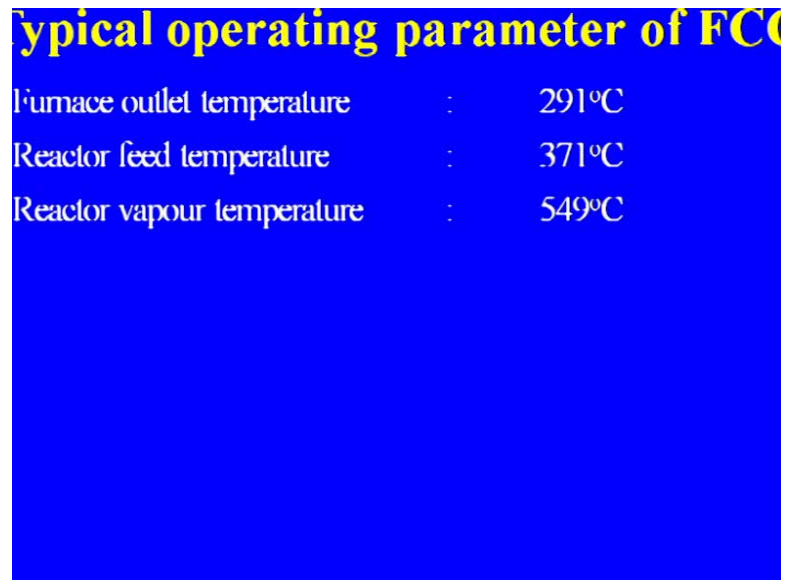
## **Fractionation**

Overhead product is sent to stabilisation section where stabilised gasoline is separated from light products from which LPG is recovered.



Overhead product is sent to the stabilization section, because which containing the Gasoline and the LPG where is stabilized Gasoline is separated from light products from which LPG is recovered.

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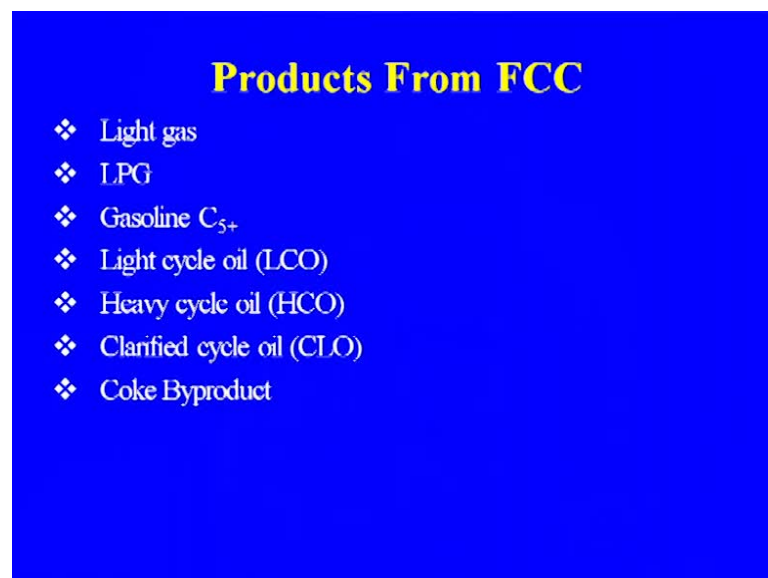


**Typical operating parameter of FCC**

Furnace outlet temperature	:	291°C
Reactor feed temperature	:	371°C
Reactor vapour temperature	:	549°C

So, typical this is a typical operating parameter in case of the FCC. These are the products already we have discuss in the.

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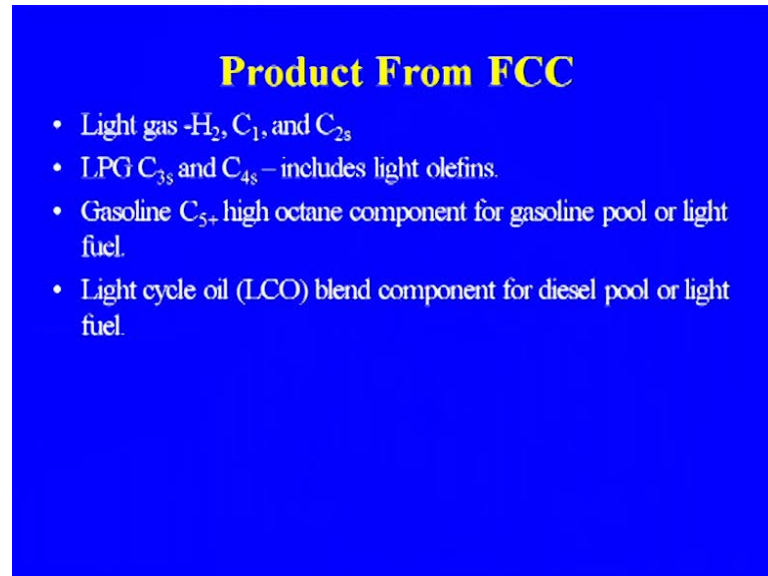
**Products From FCC**

- ❖ Light gas
- ❖ LPG
- ❖ Gasoline C<sub>5+</sub>
- ❖ Light cycle oil (LCO)
- ❖ Heavy cycle oil (HCO)
- ❖ Clarified cycle oil (CLO)
- ❖ Coke Byproduct

What are the product that you are getting? Light gases after the separation of the LPG, Gasoline, high octane gasoline that you are getting that will go to the Gasoline pool, light

cycle oil, heavy cycle oil, clarified cycle oil and coke as a Byproduct. Then the product from the other product that already I discuss about the.

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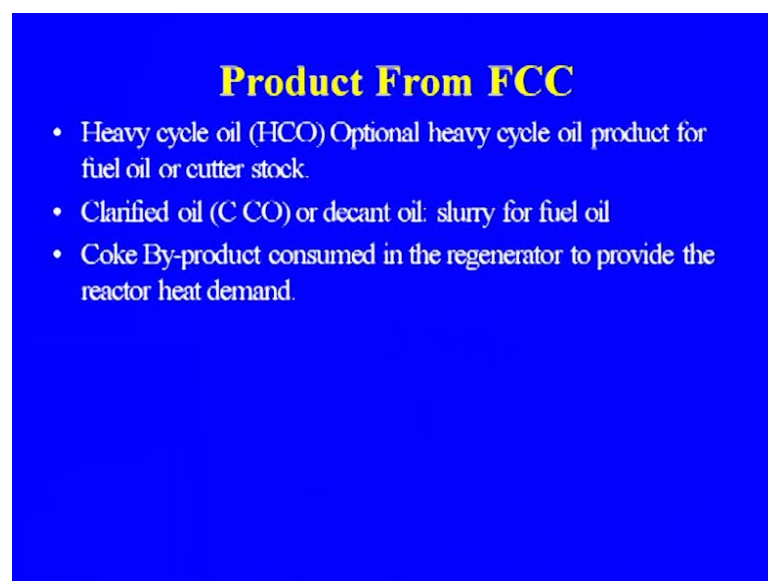


**Product From FCC**

- Light gas -H<sub>2</sub>, C<sub>1</sub>, and C<sub>2s</sub>
- LPG C<sub>3s</sub> and C<sub>4s</sub> – includes light olefins.
- Gasoline C<sub>5+</sub> high octane component for gasoline pool or light fuel.
- Light cycle oil (LCO) blend component for diesel pool or light fuel.

Some of the problem in the utilization of the lot of the work that is going on. How to get the convert this light cycle oil to the more value added product? Light cycle oil blend component for diesel pool or the light fuel. Because all the part of the light cycle or the heavy cycle that cannot go to the diesel pool.

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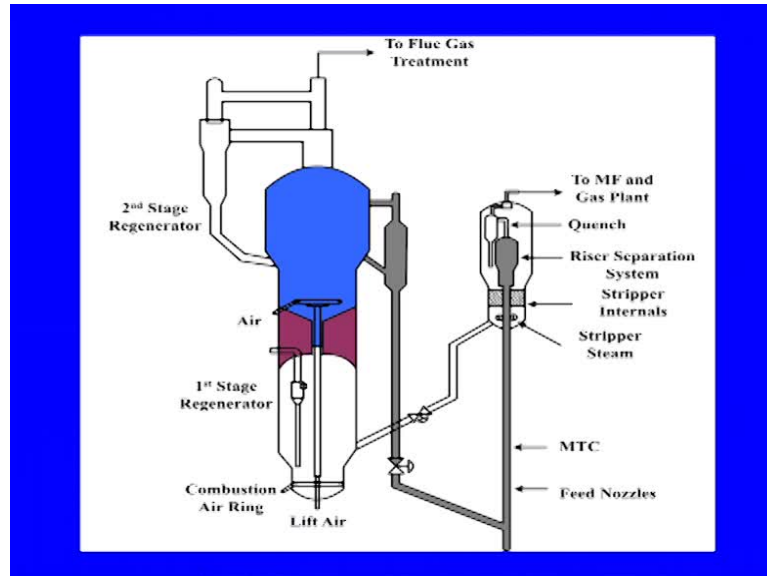


**Product From FCC**

- Heavy cycle oil (HCO) Optional heavy cycle oil product for fuel oil or cutter stock.
- Clarified oil (C CO) or decant oil: slurry for fuel oil
- Coke By-product consumed in the regenerator to provide the reactor heat demand.

Heavy cycle oil, Optional heavy cycle oil product for fuel or the cutter stock, clarified oil or decant oil. Slurry for fuel oil, coke byproduct consumed in the regenerator to provide the reactor heat demand.

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This is a typical again the reactor part in case of the where the continuous regeneration of the catalyst and then it is going to the. Combustion is taking place, first stage is the regenerator is there and then here this is the your feed nozzles are there and then the second stage regeneration is there.

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## FCC Catalysis

Major breakthrough in the catalytic cracking process was development zeolite catalysts which demonstrated superior activity, gasoline selectivity, and stability characteristics compared to original amorphous silica alumina catalyst

Year	1950	1970	1990
Zeolite content, wt%	0	10	Upto 40
Particle density, g/cc	0.9	1	1.4
Relative Attrition Index	20	5	1

So, the two stage reactor that is there in case of the FCC catalyst. Now, let us come to the FCC catalytic. Major breakthrough in the catalytic cracking process was development of zeolite catalyst is demonstrated superior activity Gasoline selectivity and the stability characteristic compared to the original amorphous silica alumina catalyst. This is the how the development from the, from 1950 to 1990, the zeolite content that has increase. Similarly, the relative vertex index that has count down because the attrition index that is very important in case of the catalyst.

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### **FCC Catalyst**

- Today's FCC catalysts Porous spray dried microspherical powder
- Particle size distribution of 20 -120 micron & particle density ~ 1400 kg/m<sup>3</sup>
- Supplied under various grades of particle sizes & attrition resistance

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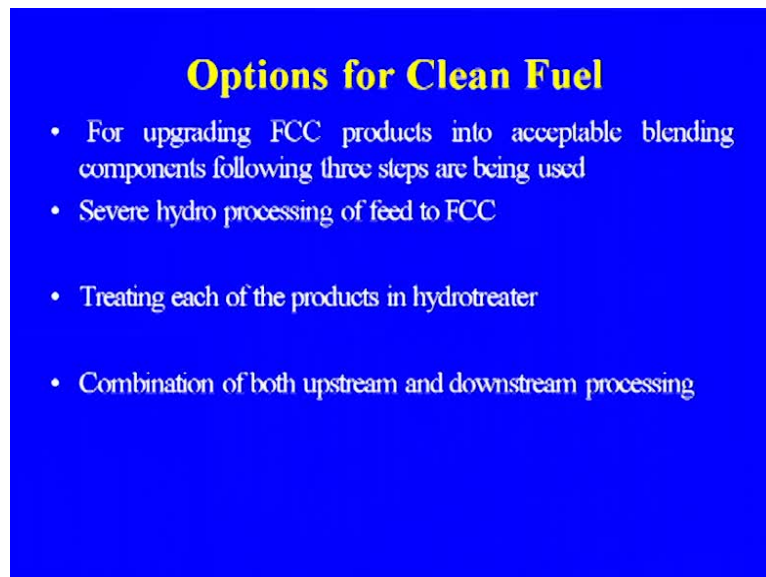
### **FCC Catalyst**

- Continuing improvement metal tolerance, coke selectivity
- New breed of catalyst are high metal tolerance with high matrix catalyst having better accessibility, regenerability and strippability

Today FC catalyst porous spray dried micro spherical powder, particle size distribution of 20 to 120 micron and particle density 1400 supplied under various grades of the particle size attrition resistance, because this is one of the very important property in case of the catalyst.

Continuing improvement in the metal tolerance, coke selectivity. Because what we are interested less coal formation and the it should be have the more and more resistance towards the better. So, new breed of the catalyst are high metal tolerance with high matrix catalyst having better accessibility regenerability and strippability.

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**Options for Clean Fuel**

- For upgrading FCC products into acceptable blending components following three steps are being used
- Severe hydro processing of feed to FCC
- Treating each of the products in hydrotreater
- Combination of both upstream and downstream processing

Option for clean fuel. For upgrading FCC products into acceptable blending component following three steps are being used. Severe hydro processing of a feed to the FCC, because they as a removal of the your impurities is representing the what is in feed that is going to the FCC, treating each of the product in hydrotreater combination of the both stream, upstream and the downstream processing.

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## **Modified Catalytic Cracking Processes**

### **Resid FCC (RFCC) Process:**

The RFCC process uses similar reactor technology as the FCC process and is targeted for residual feeds greater than 4 wt-% Conradson carbon.

A two stage regenerator with catalyst cooling is typically used to control the higher coke production and resulting heat.

As I told you the in some of the refinery the heavy residue from the hydrocracker that is also being process, so we called it the rigid FCC. But the residue is also along it is not the vacuum gas or direct which you are getting some of the residue which we are produced during the various cracking process that is also going to the rigid FCC. The RFC process uses similar reactor technology as the FCC used to be. So, for the technology reactor regenerator system, this is the same.

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## **Milli Second Catalytic cracking (MSCC) Process**

- The benefits of shorter catalyst-and oil contact time have been lower dry gas yields, lower delta coke on catalyst and more selective cracking to gasoline and light olefins.
- Due to improvement in reactor design there is lower regenerator temperature and higher catalyst recovery.

And the but only here is the it is targeted for residual feeds greater than 4 weight percent of the Conradson carbon. More heavy residue that is being process. A two stage regenerator with catalyst cooling which I told you the two stage regenerator was there is typically used to control the higher coke production and resulting. Because here we were more heavier residue.

So, the coke formation is more in comparison to conventional FCC where we are using the vacuum gas oil like vacuum gas oil. Improvement in the riser termination devices have led to significant decreases in the post riser residence time and post riser cracking. The benefits of the shorter catalyst and oil contact time have been lower by dry gas yields lower delta coke on catalyst and more selective cracking to Gasoline and light olefin. This is the benefit of the shorter residence time that we are having. Due to improvement in the reactor design there is lower regenerator temperature and higher catalyst recovery.

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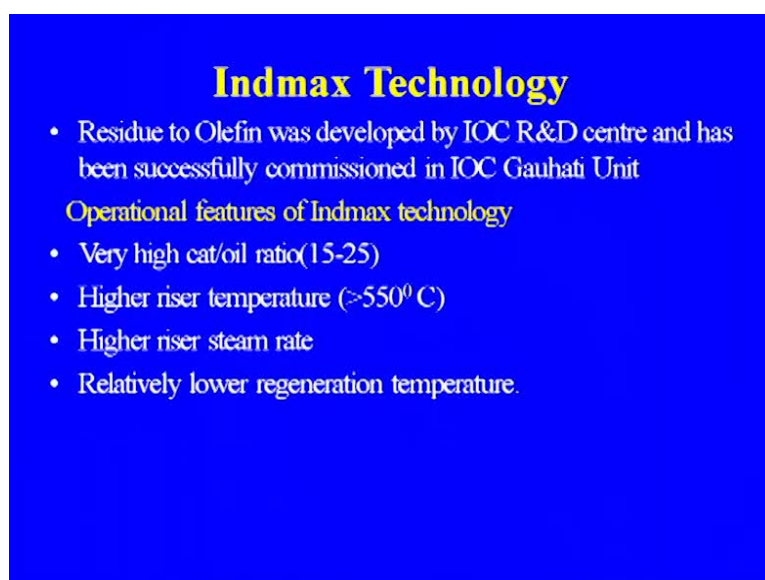
### **Petro FCC Process**

- The Petro FCC process targets the production of petrochemical feedstock rather than fuel products.
- This new process, which utilizes a uniquely designed FCC unit, can produce very high yields of light olefins and aromatics when coupled with an aromatics complex.

Some of the various version of the FCC are there the this is one of the process, the petro FCC process. The petro FCC process targets the production of the petrochemical feedstock rather than the fuel. As I told you that in future refinery that may be the petro refinery or the Gasoline feed refinery. Means the gasoline no gasoline from the it will be completely it may be on the propylene mode and very less amount of the Gasoline. So, that was the Gasoline free refinery that is also now the word that has come.

So, the here what is our main objective is to produce more petrochemical feed stock like propylene and the C 4 gases that may be there. This new process, which utilizes uniquely designed FCC unit can produce very high yields of the light olefins and aromatics then coupled with an aromatic complex; so integration of the FCC with the petrochemical complex that may be there. The catalyst section of the petro FCC's processes use a high conversion short contact time reaction zone that operates at elevated reactor riser outlet temperature. This is the technology in max technology that is has been developed by Indian Oil Corporation or in the division and this unit already in the Gauhati refinery of the IC. They have successfully that has been commission.

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**Indmax Technology**

- Residue to Olefin was developed by IOC R&D centre and has been successfully commissioned in IOC Gauhati Unit

**Operational features of Indmax technology**

- Very high cat/oil ratio(15-25)
- Higher riser temperature (>550<sup>o</sup> C)
- Higher riser steam rate
- Relatively lower regeneration temperature.

The operational feature of the indmax technology: very high catalyst to oil ratio, higher riser temperature, higher riser steam rate, relatively lower regeneration temperature. These are the some of the benefits in case of the indmax technology. Propylene is higher, higher octane number you are getting and the multi functional proprietary catalyst that we are using, higher propylene selectivity, superior metal tolerance and lower coke formation is there.

Maximizing the propylene out in the FCC, because as I told you the future refinery that may be more through the Propylene mode. Because the it is more valuated product than the Gasoline. So, the now many of the refinery because if you see the our requirement of the total propylene 32 around 35 percent is from the FCC we are getting.



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### **Maximizing Propylene Output in FCC**

- New FCC processes are being operated to maximize the yield of propylene due to growing demand of propylene.
- Significant scope exists in the refinery in Asia region to enhance the production of propylene in Asia region.

So, new FCC processes are being operated to maximize the yield of the propylene due to growing demand of the propylene. Because the propylene huge amount of the propylene now we are using in the auto mobile industry. Apart from the other usage poly propylene fiber or the, in the replacement of the glasses glass wares which where use glass bottles that was being used in hospital.

(Refer Slide Time: 25:38)

### **Maximizing Propylene Output in FCC**

- Maximizing propylene yield from FCC is typically accomplished by combining a low rare earth catalyst system with severe reaction condition.

Significant scope exists in the refinery in Asia region to enhance the production of the propylene in this region. Maximizing propylene yield from FCC is typically

accomplished by combining a low rare earth catalyst system with severe reaction condition.

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**Maximizing Propylene Output in FCC**

- Some of the olefin maximizing technology are deep catalytic cracking (DCC) based on riser bed catalytic cracking, Propylene -Max technology by ABBS Lummus global, Maxofin Process by Mobil-M.W. Kellog, Superflex , Advanced Catalytic cracking by KBR

Because normally when you are having the more severity means the more lighter product that will be getting. Some of the technology which are available are deep catalytic cracking based on the riser bed catalytic cracking, propylene Max technology by ABBS slimmer, Maxofin process by Mobil, kellog, Superflex, advanced catalytic cracking by KBR.

(Refer Slide Time: 26:52)

**Emerging FCC based Propylene Technologies**

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

So, these are the some of the technology that is available for maximizing the propylene from FCC. This is the actually the some of the technology and the propylene yield. Here you can say the conventional normally 5 to 6 percent propylene was there and now with the coming of these technology or the operating the FCC in the propylene mode the propylene percent that is increase.

So, from the deep catalytic cracking 14 to 23, catalytic pyrolysis process 18 to 24, high severity FCC 17 to 25, indmax technology that is the indigenous technology we are having developed by ICRND division 17 to 25 percent, maxofin 15 to 25, petro FCC 20 to 25 and select component cracking that is 24 percent. This was about the FCC and the why the importance of FCC is there.

(Refer Slide Time: 27:45)

## Hydrocracking

- Hydrocracking can process wide variety of feed stocks producing wide range of products.
- **Feed:** Straight run gas oil, Vacuum gas oils, Cycle oils, Coker Gas oils, thermally cracked stocks, Solvent deasphalted residual oils, straight run naphtha, cracked naphtha.

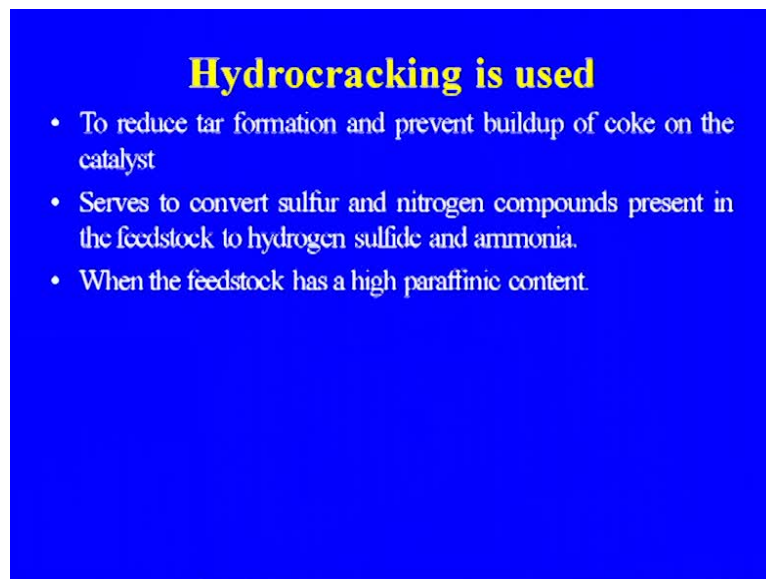
Next development that has taken place in case of the catalytic cracking is the hydrocracking. Because now the as I told you earlier also in most of the refinery now they have they are having both the FCC and the hydrocracking. So, hydrocracking is one of the most versatile process for the conversion of the low quality feed stock into high quality products like gasoline, naphtha, kerosene and diesel and hydrowax which can be used as a petrochemical feed stock. Because here what we are doing the cracking is being done in presence of the hydrogen.

So, the both the pretreatment and the cracking both the process that is taking place and the quality of the... Here the advantage because we are able to process more heavier

residue. Its importance is growing more as a refiner surge for the low investment option for producing clean fuel because they are going more and heavier feedstock. New environmental legislation requires increasing and expensive efforts to meet the stringent product quality demands because here we are doing the hydro treatment.

The quality of the Gasoline that is better, sulfur compounds are less. Hydrocracking can process wide variety of the feed stock producing wide range of the products. Feed it may be straight run gas oil, which we are getting from the atmospheric residue, vacuum gas oils, cycles oils, coke gas oils, thermally cracked stocks, Solvent deasphalted residual oils, straight run naphtha, cracked naphtha. These may be the feedstock to the hydro cracker, means the naphtha which is having the higher octane number. Sorry not a higher octane number but low octane number.

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**Hydrocracking is used**

- To reduce tar formation and prevent buildup of coke on the catalyst
- Serves to convert sulfur and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia.
- When the feedstock has a high paraffinic content.

Hydrocracking is used to reduce the tar formation and prevent the buildup of coke on the catalyst. Serves to convert serves to convert the sulfur and nitrogen compounds present in the feed stock to hydrogen sulfide and ammonia when the feed stock has a high paraffinic content. So, these are the some of the why the we are going for the hydrocracking. These are the product as you see the product are similar to the FCC, but only thing here we are not operating in the propylene mode.

(Refer Slide Time: 30:14)

## Hydrocracking

- **Products:** Liquefied petroleum gas (LPG), Motor gasoline, Reformer feeds, Aviation turbine fuel, Diesel fuels, heating oils, Solvent and thinners, Lube oil, FCC feed.

So, the in case of but only advantage other advantage is there here we are processing in case of the hydrocracker more heavier feed stock. So, the product which we are getting from hydrocracker, Liquefied Petroleum Gas, Motor gasoline, Reformer feeds that may be in naphtha that may go to that catalytic reforming, Aviation turbine fuel, Diesel fuel, heating oil, solvent and thinners lube oil and FCC feed.

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## Hydrocracking

- Hydro cracking is a two-stage process combining catalytic cracking and hydrogenation
- Feedstock are characterized usually by a high polycyclic aromatic content
- High concentrations of the two principal catalyst poisons, sulfur and nitrogen compounds.

As I told you the rigid FCC, where the hydrocracker bottom product that is going to the FCC. Hydrocracking is a two stage process combining catalytic cracking and the

hydrogenation. And that is also solving the purpose of pretreatment you can say the hydro treatment. Feed stocks are characterized usually by a high polycyclic aromatic content, high concentration of the two principal catalyst poisonous sulfur and nitrogen compound.

(Refer Slide Time: 31:21)

<b>Comparison of Catalytic Cracking and Hydrocracking</b>	
Catalytic Cracking	Hydro-cracking
Carbon rejection	Hydrogen addition
Riser-regenerator-configuration	Down flow packed bed
LPG/gasoline	Kerosene/diesel
Product rich in unsaturated components	Few aromatics, low S- and N-content in product

These are the two major catalyst poison that may be represent in the feed stock. Let us compare now the catalytic cracking process with the hydrocracking. Catalytic cracking, the carbon rejection hydrogen addition is there, riser regenerator configuration, down flow packed bed because here it is the flow bed. And in case of the hydrocracking it is the fixed bed reactor.

The LPG gasoline here it is more kerosene diesel that we are getting. Few aromatics, low sulfur and nitrogen content, products are rich in the unsaturated compound. Components in case of the catalytic cracking means FCC, the hydrocracking process. Let us now discuss about the hydrocracking process. We are having the single stage hydrocracking process. So, there what we are doing? Treating and cracking in a single reactor.

(Refer Slide Time: 32:21)

## **Type of Hydrocracking Process**

### **Single stage Hydrocracking Process**

- a) Treating and cracking in a single reactor
- b) Work under high  $H_2S$  and  $NH_3$  partial pressure

### **Two stage Hydrocracking Process**

- a) First hydrotreated followed by hydrocracking
- b) Low  $H_2S$  and  $NH_3$  partial pressure

In case of the two stage we are having the two reactor. Here all the reaction that is taking place in a single reactor. Work under high  $H_2S$  and  $NH_3$  ammonia, partial pressure. Two stage hydrocracking process: first hydro treated followed by hydro cracking. Because in the first stage mostly is the hydro treating.

(Refer Slide Time: 32:46)

## **Recent Development in Hydrocracking**

- There has been continuous development in the hydro-cracking technology both in process and catalyst.
- Some of the important development in hydro-cracking has been mild hydro-cracking and resid hydro-cracking.

Some hydrocracking may take place and then the here actually the low  $H_2S$  and  $NH_3$  ammonia partial pressure. Recent development in the hydrocracking: There has been continuous development in the hydrocracking technology both in the process and the

catalyst. Some of the important development in the hydrocracking has been mild hydro cracking and rigid hydrocracking like FCC.

(Refer Slide Time: 33:06)

### **Recent Development Hydrocracking**

- Mild hydro-cracking is characterized by relatively low conversion (20-40%) as compared to conventional hydro-cracking which give 70-100% conversion of heavy distillate at high pressure.

Mild hydrocracking is characterized by relatively low conversion as compared to the conventional hydrocracking, which gives 70 to 100 percent conversion of heavy distillate at high pressure. Here in case of the mild it is around 20 to 40 percent.

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### **Recent Development Hydrocracking**

- Mild hydro-cracking (MHC) route produces low sulphur (10 ppm sulphur as desired by future diesel specification) diesel.
- New mild hydrocracking route produces 10 ppm sulphur diesel which is produced by hydro-cracking under mild pressure.
- MHC allows increasing diesel production through VGO hydro-conversion.

Mild hydrocracking route produces low sulfur desired by the future diesel specification. Now, mild hydrocracking route produces 10 ppm and which is produced by



hydrocracking under mild condition. MHC allows increasing diesel production through the VGO hydro conversion. Hydro treatment and the hydrocracking catalyst.

(Refer Slide Time: 33:57)

## **Hydro-treatment & Hydrocracking Catalyst**

Hydrocracking processes involved two types of catalyst:

- Hydro pretreatment catalyst
- Hydrocracking catalyst.

Hydrocracking process involved two steps of the catalyst. Hydro pretreatment catalyst and hydrocracking catalyst. This is the how we are achieving both the pretreatment and the hydrocracking.

(Refer Slide Time: 34:14)

## **Hydrotreating (Pretreat) Catalyst**

- The main objective of pretreat catalyst is to remove organic nitrogen from the hydro cracker feed allowing
- Better performance of second stage hydrocracking catalyst.

The main objective of the pretreat catalyst is to remove the organic nitrogen and other impurities like sulfur from the hydro cracker feed allowing better performance of the

second stage hydrocracking catalyst. That is what happening in case of the two stage hydro cracker.

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### **Hydrotreating (Pretreat) Catalyst**

- The initiation of the sequence of hydrocracking reactions by saturation of aromatic compounds.
- Pretreat catalyst must have adequate activity to achieve above objectives within the operating limits of the hydrogen partial pressure, temperature and LHSV.

The initiation of the sequence of the hydro cracking reaction by saturation of the aromatic compound. Pretreat catalyst must have adequate activity to achieve above objective within the operating limits of the hydrogen partial pressure, temperature and the LHSV.

(Refer Slide Time: 34:56)

### **Hydrocracking Catalyst**

- Hydrocracking catalyst is a bifunctional catalyst and has a cracking function and hydrogenation-dehydrogenation function.
- The former is provided by an acidic support whereas the latter is imparted by metals.

Hydrocracking catalyst: Hydrocracking catalyst is a bifunctional catalyst and has a cracking function and hydrogenation dehydrogenation function. The former is provided by an acidic support whereas, the latter is imparted by the metals.

(Refer Slide Time: 35:15)

### **Hydrocracking Catalyst**

- Acid sites (Crystalline zeolite, amorphous silica alumina, mixture of crystalline zeolite and amorphous oxides) provide cracking activity.
- Metals [noble metal (Pd, Pt) or non noble metal sulphides (Mo, W or Co, Ni)] provide hydrogenation dehydrogenation activity.

Acid sites the crystalline zeolite, amorphous silica alumina, mixture of crystalline zeolite and amorphous oxide provide cracking activity. Metals, noble metals, palladium, platinum are the non noble metal molybdenum and other metals cobalt nickel provide the hydrogenation and dehydrogenation activity.

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### **Hydrocracking Catalyst**

- These metals catalyze the hydrogenation of feed stocks making them more reactive for cracking and hetero-atom removal as well reducing the coke rate.

These metal catalyze the hydrogenation of feed stocks making them more reactive for cracking and hetero atom removal as well as reducing the coke rate formation.

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## Hydrocracking Catalyst

- Zeolite based hydrocracking catalysts have following advantages of greater acidity resulting in greater cracking activity, better thermal/hydrothermal stability, better naphtha selectivity, better resistance to nitrogen and sulphur compounds, low coke forming tendency, and easy regenerability.

Zeolite based hydro cracking catalysts have following advantage: greater acidity resulting in greater cracking activity, better thermal hydrothermal stability, better naphtha selectivity, better resistance to nitrogen and sulfur compounds, low forming coke forming tendency and easy regenerability.

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## Single Stage Hydrocracking Process

- Furnace
- First stage Reactor section.
- Second stage Reactor section
- High pressure separator
- Fractionation Section
- Light Ends Recovery section

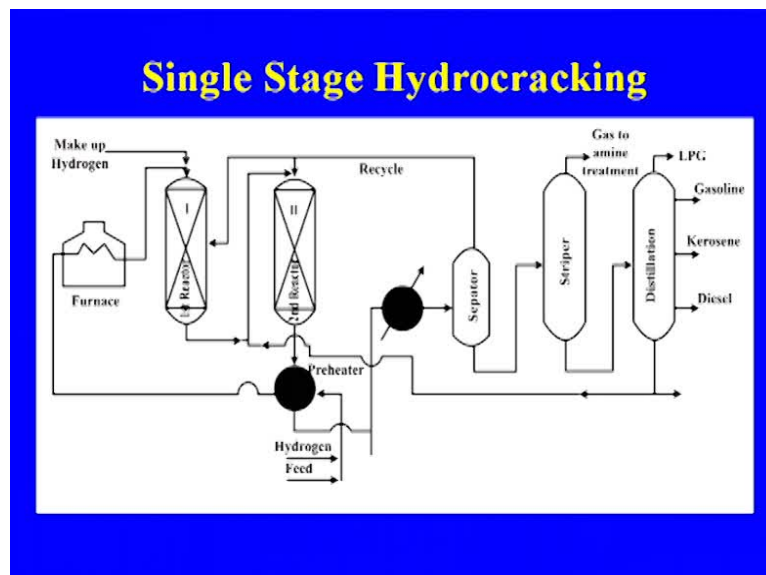
These are the some of the advantage of the zeolite based hydrocracking. Single stage hydro. These are the process step furnace: First stage Reactor section, second stage Reactor section, high pressure separator, fractionation section, Light Ends Recovery section.

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### Single Stage Hydrocracking Process

- In single stage process both treating and cracking steps are combined in a single reactor.
- In this process the feed along with recycle unconverted residue from the fractionator is first hydro-treated in a reactor and then the combined stream gases are fed to second reactor where cracking takes place in the presence of hydro-cracking catalyst.
- In the single stage process the catalysts work under high  $H_2S$  and  $NH_3$  partial pressure.

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Single stage hydro cracking process: In single stage hydro cracking both treating and cracking steps are combined in a single reactor which I told you. In this process, the feed along with the recycle unconverted residue from the fractionator is first hydro treated in

a reactor and then the combined stream are fed to the second reactor, where the cracking takes place in the presence of the hydrocracking catalyst. In the single stage process, the catalyst work under high H<sub>2</sub>S and the ammonia partial pressure.

This is the single stage, actually the reactor that we are having. Sorry, this is the second two stage reactor that we are having. In case of the here is the two, two stage reactors are there. In case of the two stage hydrocracking process again the furnace process is reactor, second stage reactor section, third stage reactor section and fractionation section, light and recovery section that is there.

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### **Two Stage Hydrocracking Process**

- Preheated feed is first hydro treated in a reactor for desulphurization and denitrogenation in presence of pretreat catalyst followed by hydrocracking in second reactor in presence of strongly acidic catalyst with a relatively low hydrogenation activity.

Two stage hydrocracking process: Preheated feed is first hydro treated in a reactor for desulphurization and denitrogenation in presence of pretreat catalyst followed by a hydrocracking in second reactor in presence of the strongly acidic catalyst with a relatively low hydrogenation activity. So, this is what happening in case of the two stage hydro cracking process.

As I told you in case of the two stage process, in the first stage reactor the sulfur and nitrogen compounds are converted to hydrogen sulfide ammonia with limited hydrocracking. And the two stage process employs inter stage product separation that removes H<sub>2</sub>S and ammonia. In case of the two stage process hydro cracking catalyst works under low hydrogen sulphide and ammonia.

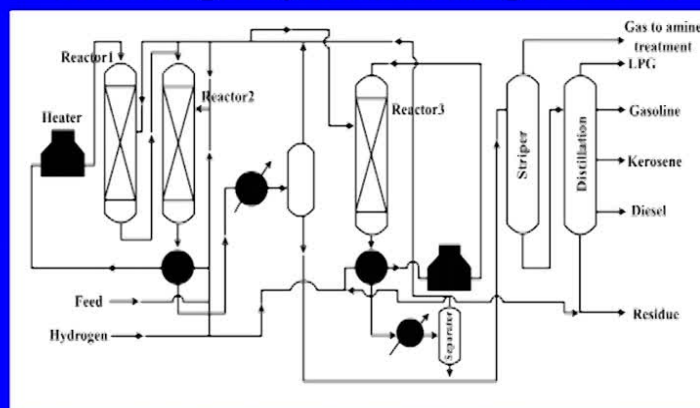
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## Two Stage Hydrocracking Process

- In the first stage reactor the sulphur and nitrogen compounds are converted to hydrogen sulphide and ammonia with limited hydrocracking.
- The two stages process employs inter stage product separation that removes  $H_2S$  and  $NH_3$ . In case of two stage process, hydrocracking catalyst works under low  $H_2S$  and  $NH_3$ .

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## Two Stage Hydrocracking Process



This is the two stage hydro cracking process where we are having the reactor 1, reactor 2, reactor 3 and this is the stripper section. This is the distillation section where we are separating the various product, LPG, Gasoline, Kerosene and Diesel. So, this is the two stage and if you see the earlier diagram which I show you that is the single stage. We do not have the third reactor. Here only two reactors are there. Here also we are separating the LPG, Gasoline, Kerosene, Diesel and the residue from the hydro cracker that may go to the rigid FCC.

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<b>Hydrocracking Technology Provider</b>	
Distillate Hydrocracking	: Fixed bed reactor
Chevron	: Isocracking
UOP	: Uni-cracking
IFP	: Hydrocracking
B.P.U.K	: Hydrocracking
Shell	: Hydrocracking
Standard Oil	: Ultracracking
Linde	: Hydrocracking

These are the various hydrocracking technology provider. Distillate cracking, fixed bed, Chevron, UOP, IFP, B.P.U.K, shell, standard oil and Linde. So, the chevron they are isocracking they called. In case of the UOP it is uni cracking. In case of the IFP they called the hydrocracking. So, these are the some of the commercial hydrocracking processes that is available.

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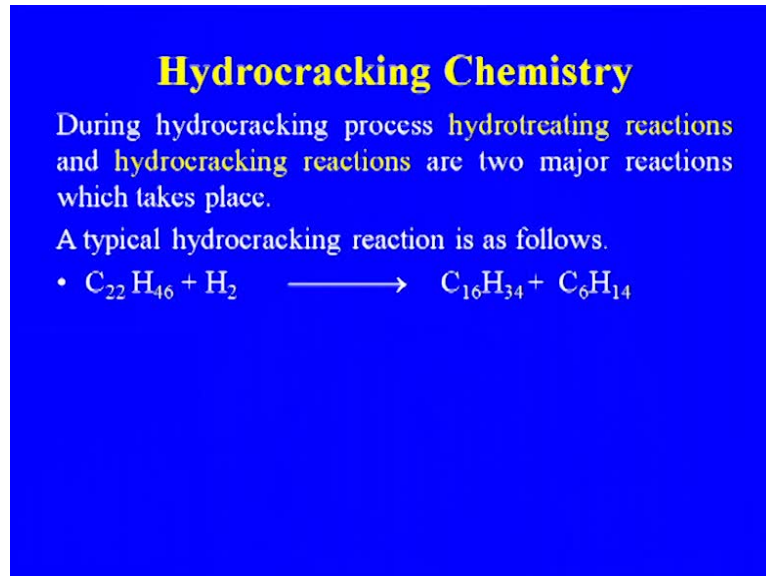
<b>Hydrocracking Chemistry</b>
<ul style="list-style-type: none"><li>• Hydrocracking process is a catalytic cracking process which takes place in the presence of an elevated partial pressure of hydrogen and is facilitated by bifunctional catalyst having acidic sites and metallic sites.</li></ul>

So, the chemistry of the hydrocracking; Hydro cracking process is a catalytic cracking process which takes place in the presence of an elevated partial pressure of hydrogen and



is facilitated by bio functional catalyst having acidic site and metallic site, which I discussed earlier also.

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**Hydrocracking Chemistry**

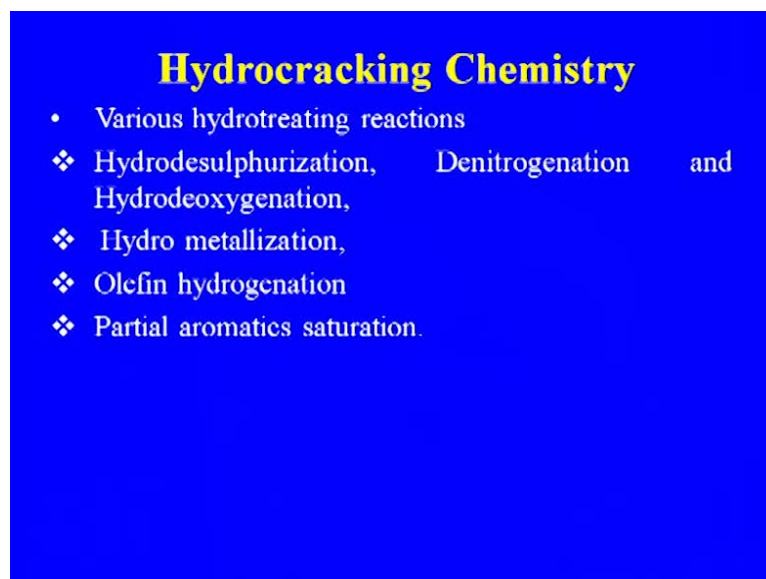
During hydrocracking process hydrotreating reactions and hydrocracking reactions are two major reactions which takes place.

A typical hydrocracking reaction is as follows.

- $C_{22}H_{46} + H_2 \longrightarrow C_{16}H_{34} + C_6H_{14}$

These are the some of the hydrocracking reaction that is taking place during the hydro treating reaction and the hydrocracking reaction. As I told you the both the things are because we are using the hydrogen along with your heavy residue. So, the hydro treating operation is also taking place. They are in the hydro cracking process.

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**Hydrocracking Chemistry**

- Various hydrotreating reactions
  - ❖ Hydrodesulphurization, Denitrogenation and Hydrodeoxygenation,
  - ❖ Hydro metallization,
  - ❖ Olefin hydrogenation
  - ❖ Partial aromatics saturation.

So, various hydrocracking reactions which are taking place in case of the hydrocracking is the hydrodesulphurization, denitrogenation, hydrodeoxygenation, hydro metallization, olefin hydrogenation, partial aromatic saturation. So, these are the series of reaction that is taking place in case of the hydro cracker.

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### **Hydrocracking Chemistry**

- Various hydrocracking reactions are splitting of C-C bond and or C-C rearrangement reaction (hydroisomerisation process). Hydrogenation and dehydrogenation catalyst.

So, again in more various hydrocracking reactions are splitting of carbon carbon bond and or carbon carbon bond arrangement reaction. And that is the hydroisomerisation, hydrogenation and dehydrogenation reaction that is taking place.

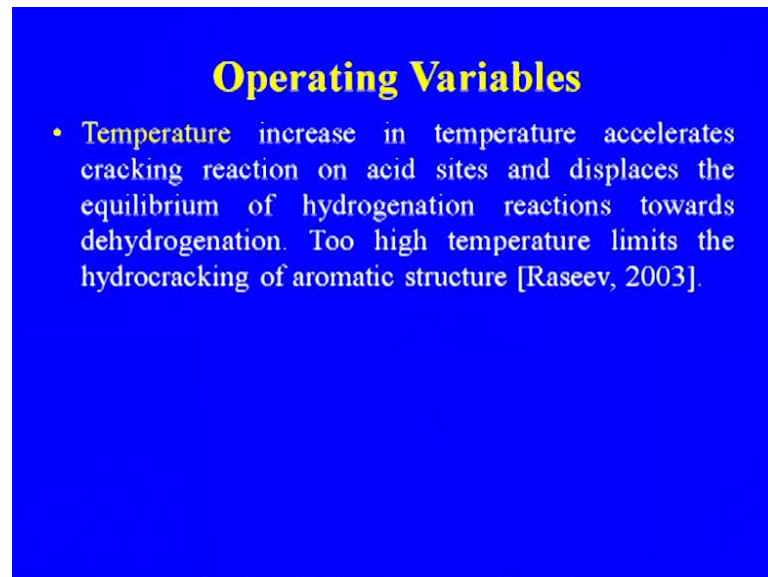
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### **Operating Variables**

- ❖ Hydrogen partial pressure
- ❖ Reaction temperature
- ❖ Hourly feed velocity of the feed
- ❖ Hydrogen recycle ratio
- ❖ Temperature
- ❖ Feed Stock and feed Impurities

These are the some of the operating variables in case of the hydro cracker. Hydrogen partial pressure, reaction temperature, hourly feed velocity, liquid hourly feed velocity that is the LHSP of the feed, hydrogen recycle ratio, temperature, feed stock and the feed impurities.

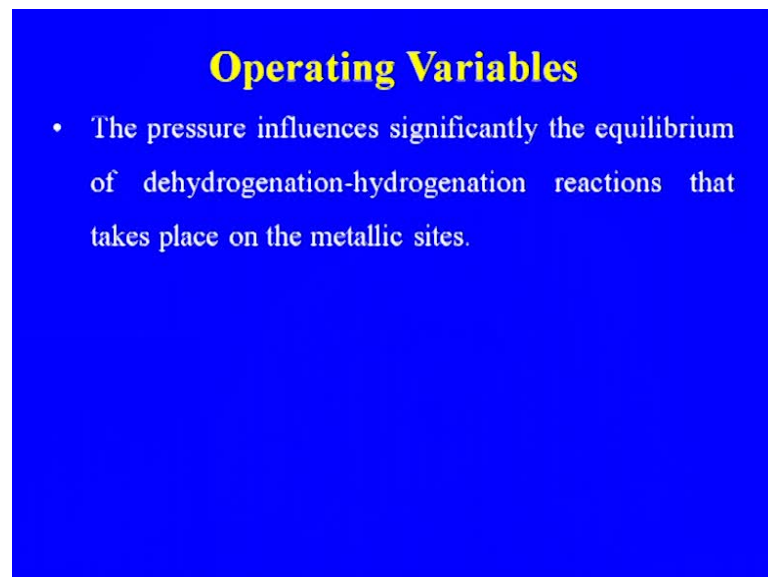
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**Operating Variables**

- Temperature increase in temperature accelerates cracking reaction on acid sites and displaces the equilibrium of hydrogenation reactions towards dehydrogenation. Too high temperature limits the hydrocracking of aromatic structure [Raseev, 2003].

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**Operating Variables**

- The pressure influences significantly the equilibrium of dehydrogenation-hydrogenation reactions that takes place on the metallic sites.

Let us go in more detail about the some of the important parameters. Operating variables: Temperature and increase in the temperature accelerates cracking reaction on acid sites and displaces the equilibrium of the hydrogenation reaction towards dehydrogenation.

Too high temperature limits the hydrocracking of the aromatic structure. The pressure influences significantly the equilibrium dehydrogenation and hydrogenation reaction that takes place on the metallic site.

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### **Operating Variables in Hydrocracking**

The increase in pressure for a given molar ratio  $H_2$ /feed corresponds to increase in the partial pressure of hydrogen, will produce an increase the conversion of the aromatic structures to saturated products which will improve the quality of jet fuel, diesel fuel and oil with very high viscosity index.

The increase in the pressure for a given molar ratio of hydrogen feed correspond to increase in the partial pressure of the hydrogen, will produce a increase in the conversion of the aromatic structures to saturated products which will improve the quality of the jet fuel, diesel fuel and oil with very high viscosity index.

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### **Operating Variables**

- Effect of feed stock: a higher content of aromatic hydrocarbons requires higher pressure and higher hydrogen/feed ratio, the lowest possible temperature and a higher hydrogen consumption of hydrogen and the severity of the process

Effect of the feed stock; A higher content of the aromatic hydrocarbons require higher pressure and higher hydrogen feed ratio, the lowest possible temperature and higher hydrogen consumption of the hydrogen and the severity of the process.

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### **Operating Variables in Hydrocracking**

- **Effects of Feed Impurities:** Hydrogen sulphide, nitrogen compounds and aromatic molecules present in the feed affect the hydrocracking reactions. Increase in nitrogen result in lower conversion.

Effects of the feed impurities: Hydrogen sulphide, nitrogen compounds and aromatic molecules present in the feeds affect the hydro cracking reaction. Increase in the nitrogen results in the lower conversion.

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### **Operating Variables in Hydrocracking**

- **Effects of Feed Impurities**
- Ammonia inhibits the hydrocracking catalyst activity, requiring higher operating temperatures. Polymeric compounds have substantial inhibiting and poisoning effects.
- Polynuclear aromatics present in small amount in the residue deactivate the catalyst.

Ammonia inhibits the hydrocracking catalyst activity requiring higher operating temperature, Polymeric compounds have substantial inhabiting and poisoning effects. Polynuclear aromatics present in the small amount in the residue deactivate the catalyst. This is the effect of various variable feed rate, increase, decrease, change effect on the catalyst side. Conversion increase, decrease, hydrogen partial pressure, reactor pressure, recycle gas rate, recycle (( )). So, some are increase or decrease, some of the increase that will be there.

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### **Operational Features of Indmax Technology**

- Very high cat/oil ratio(15-25)
- Higher riser temperature ( $>550^{\circ}\text{C}$ )
- Higher riser steam rate
- Relatively lower regeneration temperature.

#### **Benefits**

- LPG 35-65 wt%
- Propylene 17-25 wt% feed
- High octane gasoline (95+)

Let us discuss in brief about the indmax technology, which is the indigenous technology available from the Indian alcohol position. They are already as I told you they successfully it has been commissioned in the IOC. What is refinery? The operational feature of the indmax technology is the very high catalyst to oil ratio, higher riser temperature, higher riser steam rate, relatively lower regeneration temperature. Benefits; LPG 35 to 65 percent propylene. It is also high, high octane gasoline we are getting from the process.

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### **Multifunctional proprietary catalyst**

- Higher propylene selectivity.
- Superior metal tolerance.
- Lower coke matc.

Multifunctional proprietary catalyst: Higher propylene selectivity, superior metal tolerance and lower cate formation. As I told you that the catalyst regeneration that is important; so in case of the hydro cracker also the catalyst regeneration done by burning of the carbon and the sulphur. Circulate the nitrogen and the recycle compressor, injecting a small quantity of air, catalyst temperature above the coke ignition temperature. So, these are the some of the references.

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So, this was about the FCC and the hydro cracker. I have gone very quickly about the FCC and the hydrocracking and the, as I told you the future refinery, what we are expecting? That is being more and more propylene mode because of the more and more evaluated product we are getting; so the continuous development that has been taking place in the refinery to improve the quality of the product, to increase the propylene or to have the longer life of the catalyst.



So, these are the some of the development that taking place and that was how the FCC to hydrocracking why we have gone to the hydro crack cracking or it may be rigid FCC, where the more hydro heavier products we are. By heavier products means the heavier residue we are cracking there. So, this is the about the catalytic cracking part. In the next lecture we will be discussing about the catalytic reforming process, which is also one of the very important conversion process in the refinery from the petroleum refinery point of view and at the same time from the catalytic reforming for the from the petro chemical point of view.

Because both the refineries where they are improving the octane number of the low octane naphtha, they are having the catalytic. Now, it is the integral part of the (( )). So, similarly in case of the, because the, because the reforming which we are getting this is rich in your aromatics. We are also using this catalytic reforming for the production of aromatic.