Chemical Technology
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Module - 7
Petrochemical
Lecture - 2
Naphtha and gas cracking for the production of olefins

We are discussing organic course module 7 and I have given the introduction of petrochemical industry, how the evolution the petro chemicals industry that has taken place. And what are development that has taken place in the petro chemicals industry. What are the various feed is stock in petro chemicals industry? How the refine in the petro chemicals complex that can be integrated for more valuable product and to improve the economy of the refinery? Today, we will be discussing one very important part of the petro chemicals that is you can see the heart of the petro chemicals complex that is left hand cash tracking for the production of the olefins.

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Naphtha/NGL cracking furnaces for Reliance Industries Limited, Hazira.
Capacity : 750,000 TPA. Process know-how : SWEC, USA

This is the typical, you see the naphtha cracker plant, and which has heavy number of furnishes and I will be discussing in detail about this the naphtha cracking and the cash cracking.

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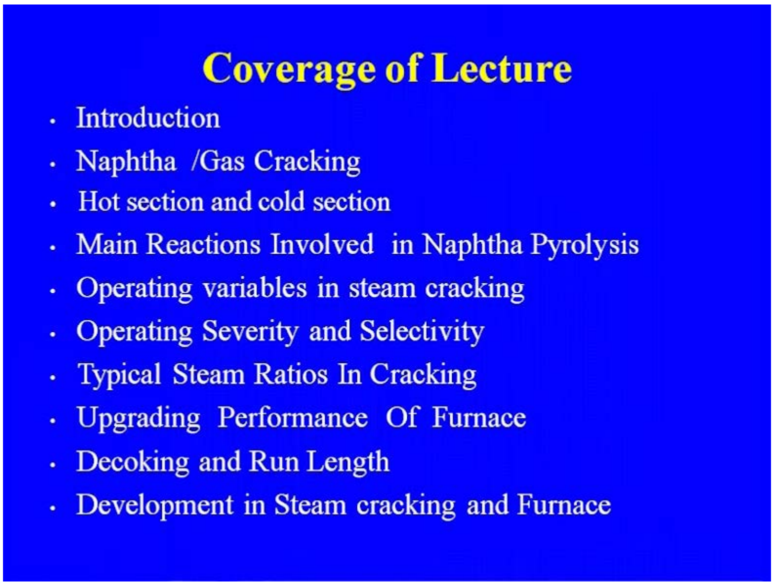

Coverage of Lecture

- Introduction
- Naphtha /Gas Cracking
- Hot section and cold section
- Main Reactions Involved in Naphtha Pyrolysis
- Operating variables in steam cracking
- Operating Severity and Selectivity
- Typical Steam Ratios In Cracking
- Upgrading Performance Of Furnace
- Decoking and Run Length
- Development in Steam cracking and Furnace

Because you see what does happen in case of the coverage of the lecture? That will be introduction naphtha gas cracking hot section and cold section of the cracker plant main reaction involved in the naphtha pyrolysis. Operating variable is the steam cracking operating severity and selectivity, typical steam ratio in cracking upgrading performance of the furnace, what the development, where has development has taken place? Because you see from the initial stage of the coming of the petro chemicals, there is lot of the changes in the furnace design from the horizontal to vertical, then the low capacity to high capacity with high residence time to low residence.

These are the some of the development to reduce the run coking in the furnace to increase the furnace. These are the, and then to better more and more flexibility of the feed stop for the, These are the some of the development that has taken place in case of the recovery. So, I will be discussing what are the various measures that has been taken for a waiting the performance of the furnace. Decoking and because that is very important, the run length of the furnace and, so the because that is unavoidable to because the carbon always the coke formation with layer only thing by properly operating and using of the some of the (( )) that you can reduce the coke formation. Then the as I told the development in the steam cracking and the furnace. Phi cracking, you see the I discuss while discussing the raw material for chemical process industry and that was the be started getting a ethylene through the moles is root (( )), but you see the importance of the ethylene that is a major raw material for the petro chemicals industry.

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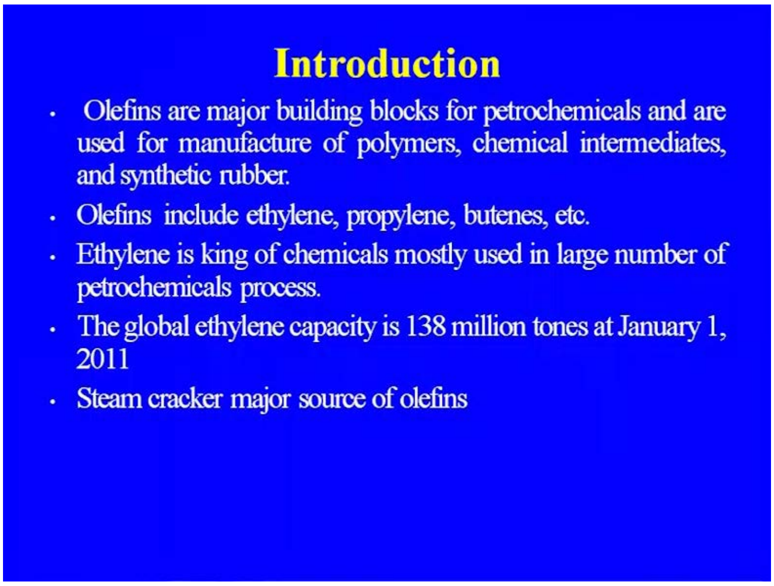

Introduction

- Olefins are major building blocks for petrochemicals and are used for manufacture of polymers, chemical intermediates, and synthetic rubber.
- Olefins include ethylene, propylene, butenes, etc.
- Ethylene is king of chemicals mostly used in large number of petrochemicals process.
- The global ethylene capacity is 138 million tones at January 1, 2011
- Steam cracker major source of olefins

So, the olefins ethylene and propylene are major building blocks for petro chemicals and are used for manufacture of polymers, chemical intermediates, synthetic rubber and large number for their products. Olefins includes ethylene, propylene and butanes again because in case of the cracking process or even in case of the BFCC, C 4 C 5 hydrocarbons are also produced. So, the recovery of strategies become very important. Ethylene, because that is the major product sometimes we called ethylene cracker also. So, ethylene is the king of the chemicals mostly using large number of the petro chemicals processes. The global ethylene capacity is 1.138 million tonnes as on January 2011. Steam cracker are major source of the olefins.

As, you see the, in case of the that we discussed earlier the FC there are two majors who sees of the olefins. Especially the propylene one is the naphtha cracker another is the F C C. Already we have discussed about the FCC and in detail and so I have no discussing that part, but recovery part again it will be discussing in while discussing propylene. So, the let us discuss about the some of the aspect of the naphtha cracking.

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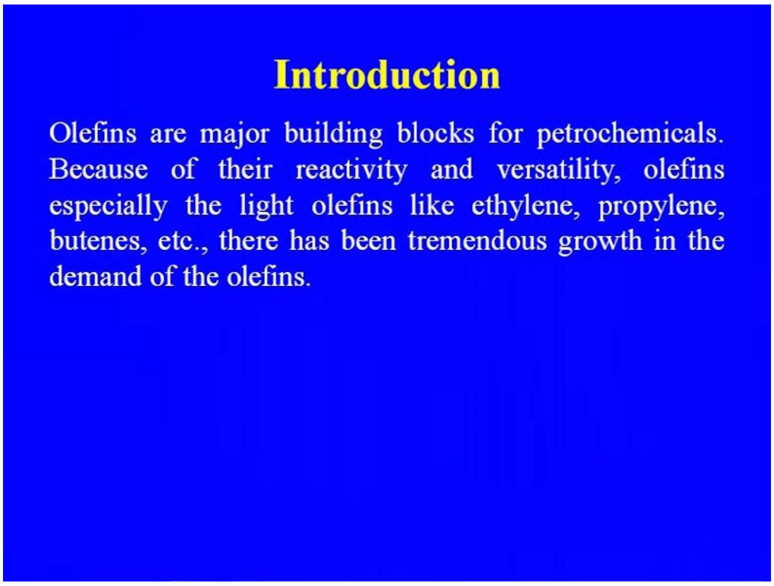

Introduction

Olefins are major building blocks for petrochemicals. Because of their reactivity and versatility, olefins especially the light olefins like ethylene, propylene, butenes, etc., there has been tremendous growth in the demand of the olefins.

So, olefins are major building blocks for petro chemicals because of their reactivity and versatility. Olefins is especially the light olefins like ethylene propylene butanes there has been tremendous growth in the demand of these olefins.

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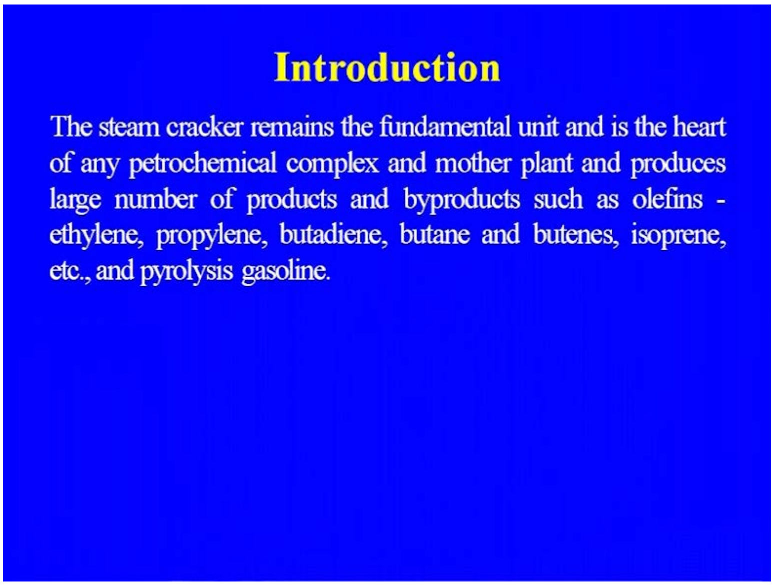

Introduction

The steam cracker remains the fundamental unit and is the heart of any petrochemical complex and mother plant and produces large number of products and byproducts such as olefins - ethylene, propylene, butadiene, butane and butenes, isoprene, etc., and pyrolysis gasoline.

The stream cracker remains the fundamental unit. And is the heart of any petro chemicals complex and mother plant and produces large number of products and byproducts such as olefins, ethylene, propylene, butadiene is a very valuable product are getting from the naphtha cracker plant. Butane, butanes, isoprene and pyrolysis gasoline that is one of the complementary steam that we are getting by product, which is rich in the automatic are after the, it can go for the production the after the retreatment remover of the compounds. It can be used for the separation of the aromatics form along with the reform.

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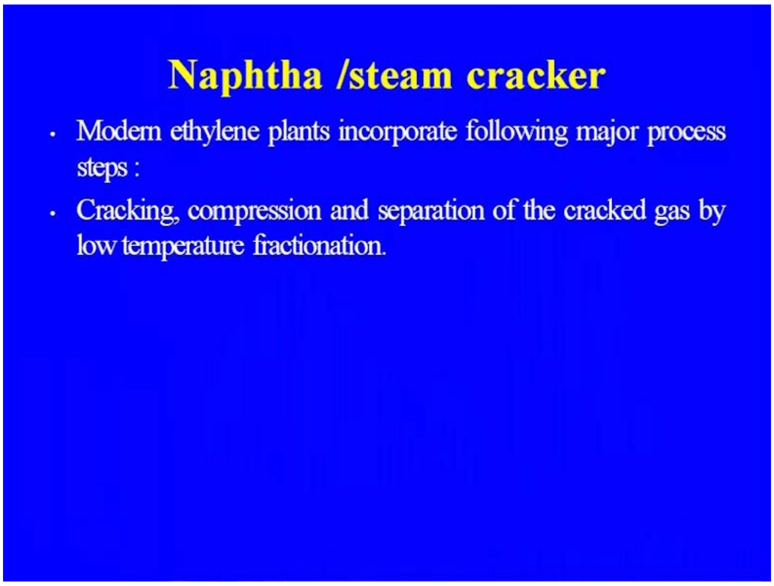

Naphtha /steam cracker

- Modern ethylene plants incorporate following major process steps :
- Cracking, compression and separation of the cracked gas by low temperature fractionation.

These are the some of the actually the complex of ethylene complex has been involved, which are making large amount of the ethylene and propylene. So, modern ethylene translator discuss in detail about the naphtha steam cracker actually the basic feed stock for the cracker plant is your naphtha and the natural gas which ethylene and portion. So, modern ethylene plants incorporate following major process steps cracking that is the hot section are the cracking of the naphtha the natural gas that is taking place in ethylene propylene. Compression of the gases and separation of the cracked gas by low temperature fractionation, because the temperature of boiling point us minus 165.

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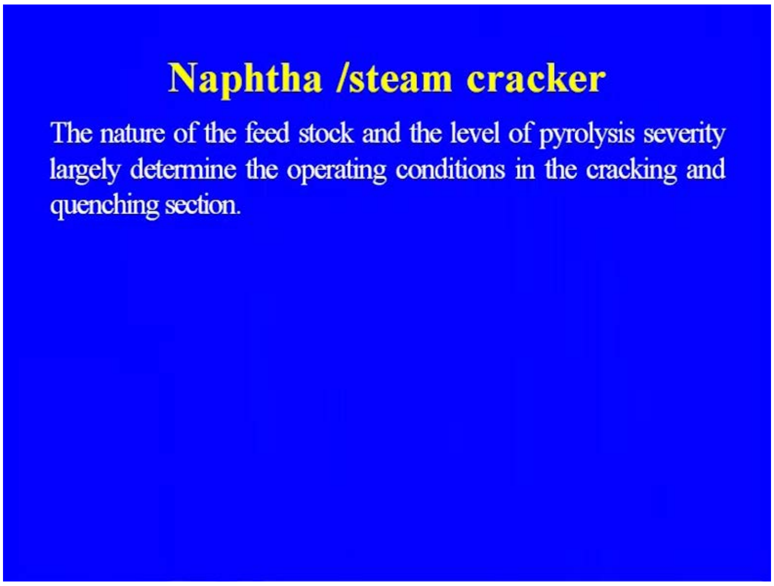

Naphtha /steam cracker

The nature of the feed stock and the level of pyrolysis severity largely determine the operating conditions in the cracking and quenching section.

So, the lotion we say that has to be maintain for the separation of various olefins and the other gasses components, which are being produced and from the cracking plant. The nature of the feed stock and the level of the pyrolysis severity largely determine the operating conditions cracking and quenching section. Because, you see the incase of the suppose if you are having the heavier even the gassier that can be cracked, but what will happen in case of the gas are the complexity of the separation. That incase because more heavier fraction we are getting rather than getting the olefins.

So, the level of the severity means the temperature, because that at what temperature we are. Because the, in case of the gas lower temperature that will be required if you are going per naphtha higher. And if you are going for gas I still have. And now we are also talking about the gas cracking or the in the cracking of the(( )), but only thing the complexity which I told you the separation of the process because incase of the more and more heavier feet it will be getting more heavier products like pyrolysis gasoline less olefins.

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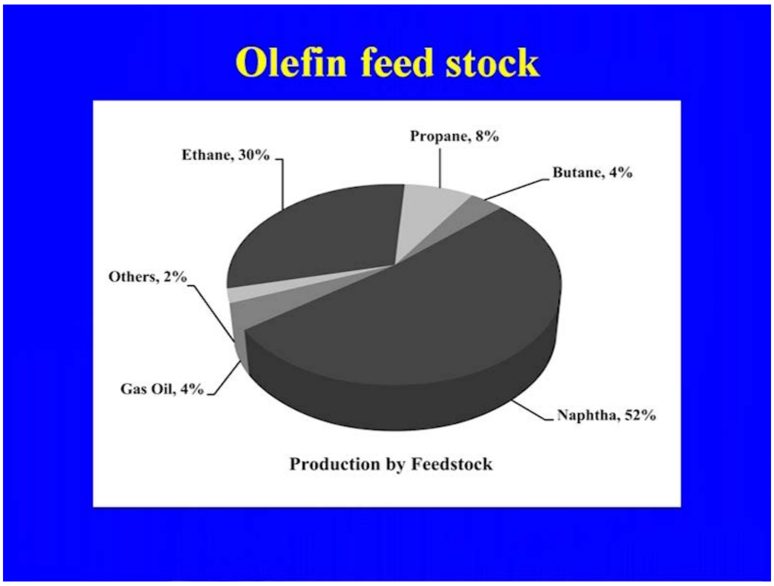

Olefin feed stock

This is the olefins feed stock. Which I told you that the of you see this figure this is around naphtha share of the feed stock is around 52 to 55 quench that is in major shares is of the and rest the ethylene and propylene that is also around 30 to 40 quench that is the because the availability of the natural. And at the same time now because the sell gases is coming in a big way; and it is US and the Canada. So, the ethylene propylene because the whole process that is going to be because earlier it was not possible to get this sell gas, it was the only after the development of the horizontal trading.

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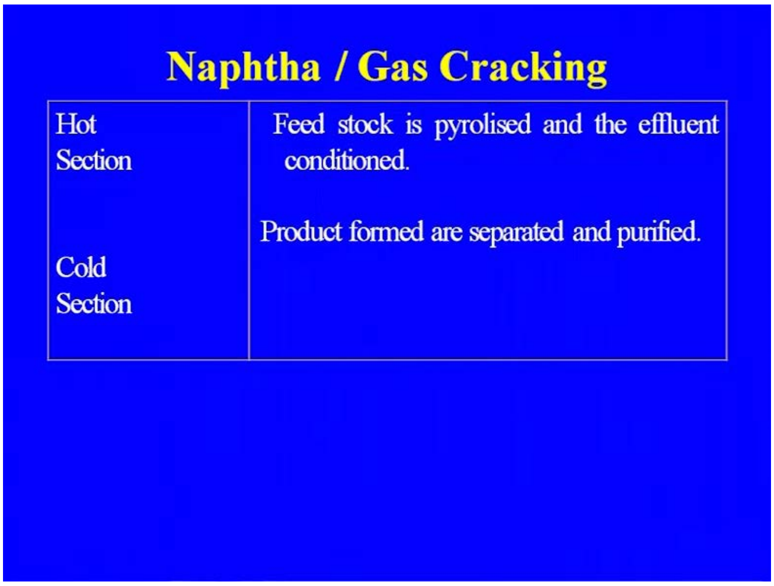

Naphtha / Gas Cracking

Hot Section	Feed stock is pyrolised and the effluent conditioned.
Cold Section	Product formed are separated and purified.

It has been possible the get the sell gas and so with the coming of the sell gas in the future ethylene and propylene that is going to be very valuable feed stock for the cracker plant. Others are the gas oil that may be there. So, this is the how the butane that may be also cracked, but the mostly the ethylene and propylene part is going to the. Because what we are doing in case of the natural gas we are separating the lighter fraction and the heavier fraction and after the fractionation only the ethylene and propylene that is going to the cracker plant. Ethylene and propylene that can be use separately or it can be combine ethylene and propylene that will go to the cracker plant.

This is the how the feed stock variation in the furnaces are there, but the still the naphtha cracker. So, while discussing the cracking plant we will be discussing process which we have been used both for the gas cracking or the naphtha cracking. Only difference is in case of the process. It is that the, in case of the gas cracker first major operation that is there a separation of ethylene and propylene and then the ethylene and propylene that is going to the after that cracking and the quenching the separation of the products all those thing that is the same process that you are using.

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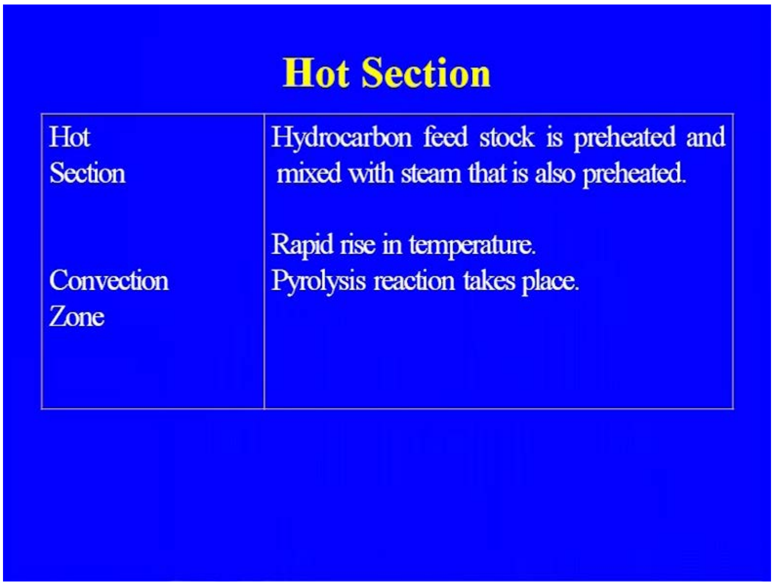

Hot Section

Hot Section	Hydrocarbon feed stock is preheated and mixed with steam that is also preheated.
Convection Zone	Rapid rise in temperature. Pyrolysis reaction takes place.

So, the naphtha the gas cracking that is why I am writing both the naphtha and gas cracking. There are two section, one is the hot section the feed stock is pyrolised and the effluent condition. This is because you are the height temperature that is required for the cracking of the feed stock. So, the next 6 after the, your reference that is which product that you are getting from the hot section that is that will be discussing while we are doing quench and all those thing.

But the the fluent is condition separation o of the heavier fraction that is there. And is going for the gasses that is going for the compression for removal of the impurities. Means the H 2 S another C O 2 that will be the in moisture that will be removed from that and after that that will go to the cold section of the cracking plant where the separation of the various steam that will take place. Hot section hydrocarbon feed stock is preheated and mixed with steam that is also preheated.

That is what we doing in case of the it may be the hydrocarbon feed stock means it may be naphtha and the ethylene propylene both that will be there. So, the even ethylene new furnace which was started very that is the multi feed because normally in many of the incase of the fertilizer what we are doing we are going for the multi feed because incase the gas is not available that place the plant can be run with a help of the naphtha are in case of the naphtha is not available then the natural gas.

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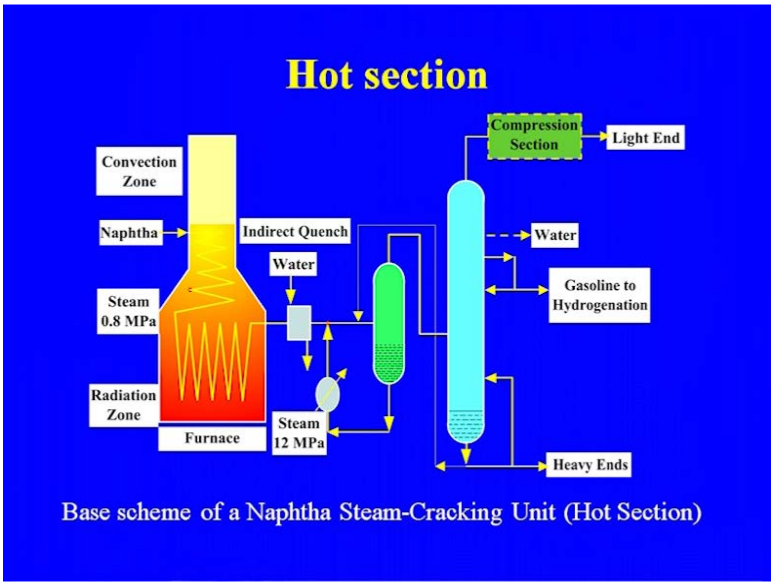
Hot section

Base scheme of a Naphtha Steam-Cracking Unit (Hot Section)

So, the reliance naphtha cracker is the multi feed, so hot section means hydrocarbon feed stock is preheated and mixed with the steam that is also preheated then the rapid rise in the temperature is taking place in the convection zone, because 2 sections are there in the upper part and lower part. So, convection zone rapid rise the temperature pyrolysis action takes place and the refinery action the both the convection addition that is taking place.

So, rapid rise the temperature is there in the convection zone this is the actually the typical you can say that was telling about the furnace where you were having the convection zone, naphtha along with this team that is going there and the radiation zone. This is the furnace because different type of the arrangement of the tubes that may be there after that it is going to the quenching indirect quenching then direct quenching and finally, it is going for the separation of the heavy ends.

Gasoline, which will for the hydrogenation means that will go for the that can be combine with the reformate for production they are aromatics or it may go the high octane. Pyrolysis gasoline that will go to the rest of the even that can be use as a fuel also and the light end after the compression the top product of this that will go to the further separation that is the cold end of the fund.

Here the steam and the other parameters are playing very important the temperature residence quenching. All those thing that will discussing in detail in the next few slides. So this is the hot section of the cracker plant. As I told you the amount of the steam require that will depend upon the I have been the temperature that will depend upon the type of the feed stock you even the product which type of product you are going to get from the that will depend upon the feed stock you are procession.

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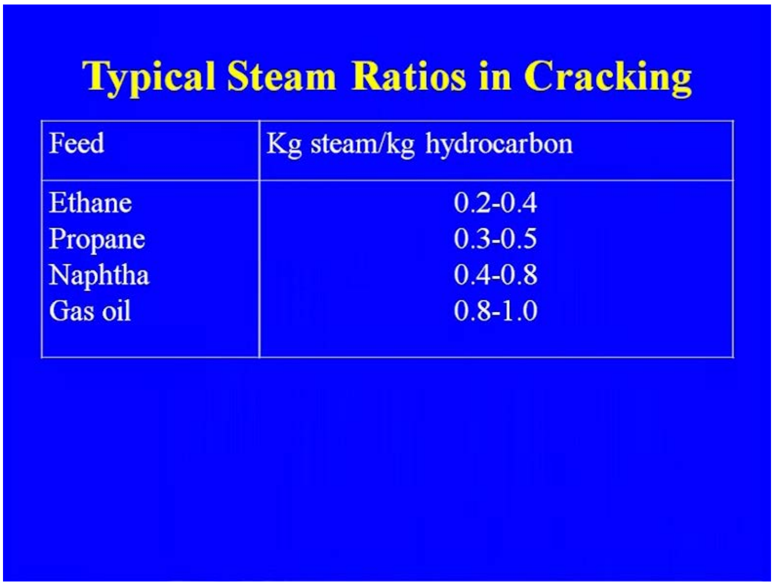

Typical Steam Ratios in Cracking

Feed	Kg steam/kg hydrocarbon
Ethane	0.2-0.4
Propane	0.3-0.5
Naphtha	0.4-0.8
Gas oil	0.8-1.0

So, if you see the figure in case of the thing if you see the figure ethylene propylene naphtha gas oil the requirement of these steam is higher in case of gas oil lowest is the in case of the ethylene propylene then propylene and then the naphtha. So, actually what is happening even the cracking during the cracking if you are cracking only ethylene it will be higher percentage of ethylene will be there. Both if you are ethylene and propylene then the propylene will be also there in point will naphtha both the ethylene propylene and C 4 C 5.

And if you calculating the gas at then the more pyrolysis gas will be produce and less lighter component that will produce. So, this is about the steam requirement similarly, the cost of the plant total energy cost and the total cause of the plant that is also in the same that is varying that is the for the ethylene energy requirement is minimum. In case of the naphtha is higher than the ethylene propylene and the gas and the gas oil is still higher. So, the same pattern that is also we are getting we are manufacturing the synthesis gas for the production the ammonia.

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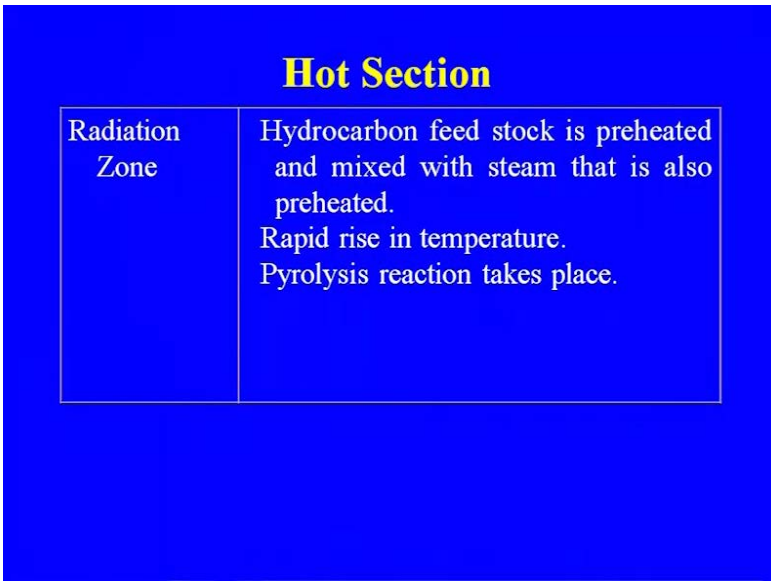

Hot Section

Radiation Zone	Hydrocarbon feed stock is preheated and mixed with steam that is also preheated. Rapid rise in temperature. Pyrolysis reaction takes place.

So, the radiation zone which I was telling about the hot section there are 2 section one is the convection zone and other the radiation zone. So, radiation zone the hydrocarbon feed stock preheated and mixed with steam. That is also preheated and rapid rise in the temperature that takes place pyrolysis reaction takes place. Quench, quenching that is very important as I told you that the if temperature if it is going high. The chance are the actually the formation of the coke that will be more. To avoid such reaction because these team is reaction of the… It has to be stopped immediately and for, this is the reason why we are going now for the shorter resistance time in the…

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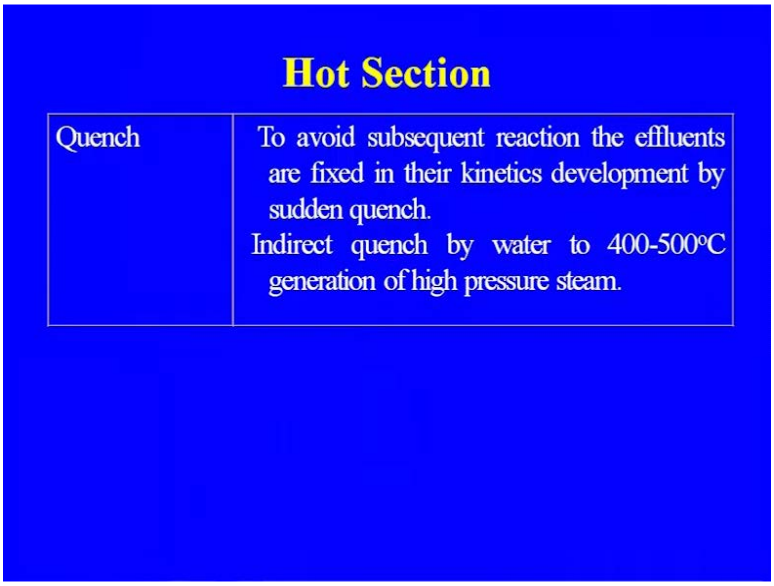

Hot Section

Quench	To avoid subsequent reaction the effluents are fixed in their kinetics development by sudden quench. Indirect quench by water to 400-500°C generation of high pressure steam.

So, to avoid this subsequent reaction the effluents are fixed in their kinetics development. By sudden quench indirect quench by water to 400-500 centigrade and which we are using for the steam. We are generating that is using the system so this is the indirect quench that we are doing in case of the cracking plant. Because that is important quenching because the transfer line what will happen if the more and more coke formation is there than the run length.

That will be reduce so this is the why the quenching immediately to have hard the polymerization reaction which may takes place if the longer residence time is give are the if it is not quenching immediately. That will be the (( )) we avoided, we are doing the quenching direct and the indirect and the direct quenching.

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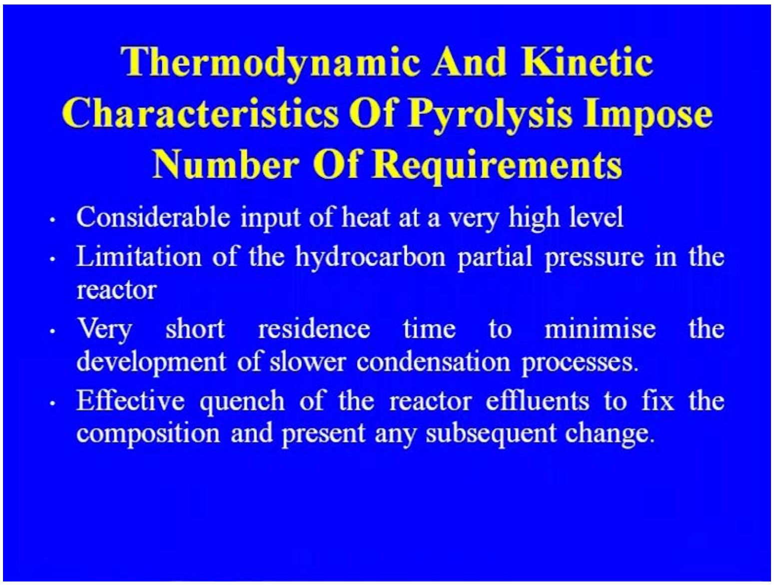

Thermodynamic And Kinetic Characteristics Of Pyrolysis Impose Number Of Requirements

- Considerable input of heat at a very high level
- Limitation of the hydrocarbon partial pressure in the reactor
- Very short residence time to minimise the development of slower condensation processes.
- Effective quench of the reactor effluents to fix the composition and present any subsequent change.

Thermodynamics and kinetic characteristics of pyrolysis impose number of the requirement considerable input of the heat at a very high level, because you know the cracking, so cracking that will be and so the we need the heat limitation of the hydrocarbon partial pressure in the reactor very short residence time. That is also require to minimize the development of slower condensation processes because the coke formation is because of the condensation process that is taking place and the are the aromatic from points. Because during the process and the cracking in large amount the products we are getting.

So, effective quench of the reactor effluents to fix the composition and present any subsequent change in process. So, in the hot section the or the quenching because the quenching as I told you it may be direct indirect and the direct quenching direct indirect quenching. Direct quenching we are using the gas pyrolysis gasoline, which we are getting or the gasoline what getting from the faractionist. That is being use for the as I discuss in the while discuss in the your this part the quenching from the after the separation of the heavier fraction of this column. That will be use for the direct quenching of the your product which we are getting from the (( )) as here it immediately the reaction that has to be stopped.

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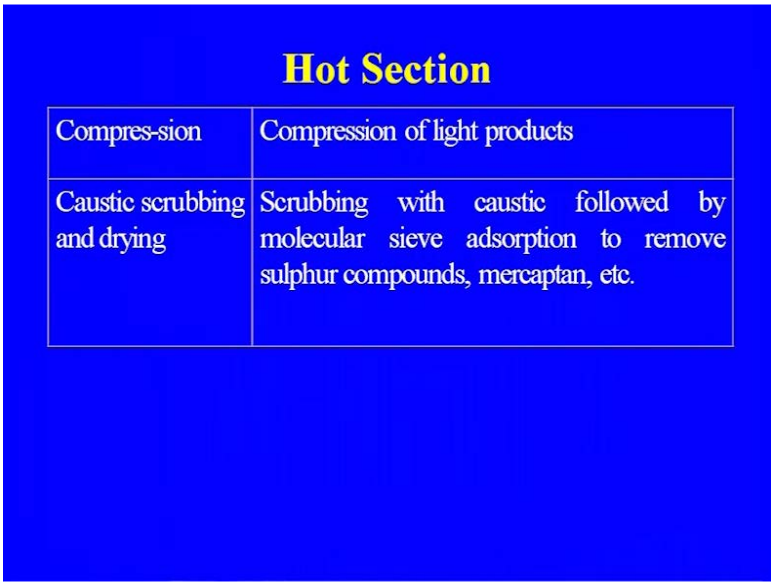

Hot Section

Compres-sion	Compression of light products
Caustic scrubbing and drying	Scrubbing with caustic followed by molecular sieve adsorption to remove sulphur compounds, mercaptan, etc.

So, this is the importance of the quenching that we are having. Now after the quenching the next important section is the compression of the light product. So, here we are also doing the caustic scrubbing and drying as I told you the both are very important drying and scrubbing of the sour gases. It has been sure to that may be present because in calculation that may be form. Scrubbing with the caustic followed by molecular sieve adsorption and also H 2 S that may the end the feed and, so the H 2 S has to be removed the sulfur compound are the mercaptanity present in the…

That is very important and, so the huge amount of the caustic that is being generated in the your petro chemicals complexes and so we are going per the we are there continuation for to the how to utilize this first? Some of the process that in develop just like oxidation that was the developed by collaboration of with the department of chemical engineering I I T Roorkie and so that process has been commercialize also in 1 of the refinery.

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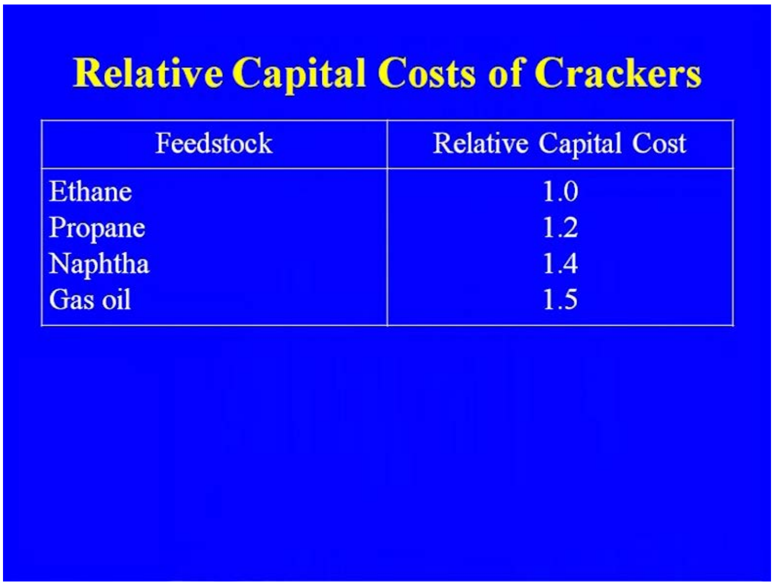

Relative Capital Costs of Crackers

Feedstock	Relative Capital Cost
Ethane	1.0
Propane	1.2
Naphtha	1.4
Gas oil	1.5

This is the as I told you the relative cost cost is also increasing if you are going from the lighter feed stock to the heavier feed stock ethylene propylene naphtha. So, if you take the ethylene 1, so the cost that will be increase 1.2, 1.4, 1.5. So sometimes you are also having the of ethylene propylene. If the naphtha gas oil normally, the percentage at the gas at which are using that is less because of the production the lighter gas are the olefins are less than the naphtha propylene ethylene. Now, let us come to the cold section of the cracker term, because that is 1 of the important section where the separation of the various product which you are getting from the heart from the halt section of the furnace that has to be separated. Especially the ethylene and the propylene and the other C 4 compounds also that you are separating.

So, after the compression and caustic scrubbing and drying the light effluent from the, your halt section that enters the cold section of the unit, which performs the separation of various product. Here are the temperature refrigeration is there and ethylene and the propylene that is being used for maintaining the low temperature.

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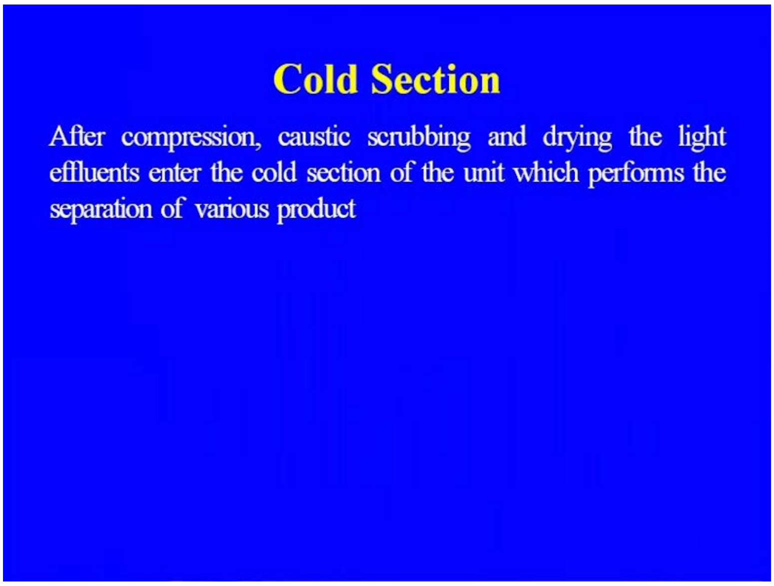

Cold Section

After compression, caustic scrubbing and drying the light effluents enter the cold section of the unit which performs the separation of various product

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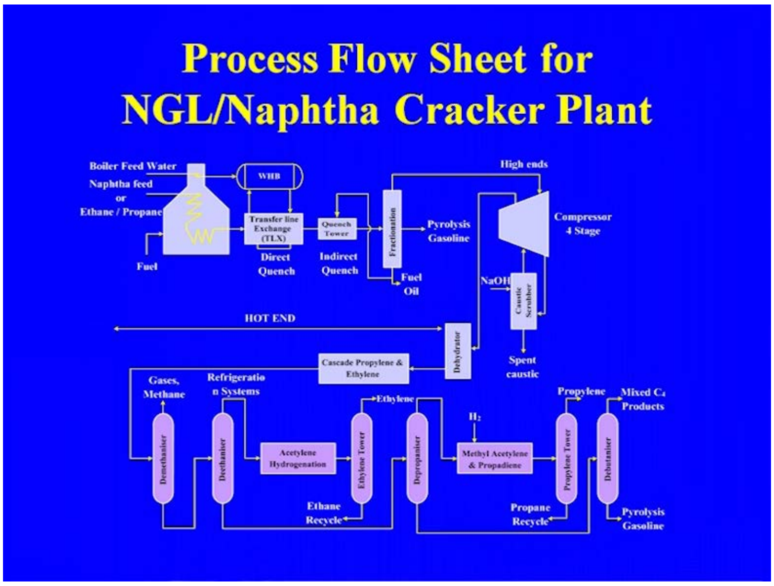

Process Flow Sheet for NGL/Naphtha Cracker Plant

This is the actual the complete a cracker plant, where after the cracking that is the naphtha then the here also this is the your ethylene propylene or this this part that will only after the separation of the ethylene propylene from the natural gas fuel. After the cracking that is the what you call the transfer land exchanger where it is this part that is the your steam generation is there than direct quenching then direct quenching is there. And then the after the completion and the removal of the impurities. Which I told you the which is scrubbing so spent caustic that will be there and then the after that removal of the impurities. And the your C O 2 are the H 2 S then it will go to the separation where the demethanizer is there.

And demethanizer gases methane that we are separating these are the series of the fractionating column and they are operating at different temperature depending upon the boiling point of the component. So the incase of the methane that is the round minus 165 degree centigrade, so from the demethanizer the product which you are getting here after the drying and the scrubbing that is going to the demethanizer, where the separation is taking place. And the gas is lighter in use the gases gases that may be hydrogen also methane that is separated here.

And then the bottom product of the demethanizer that is way to demethanizer from the demethanizer bottom, again it will go to depropanizer for the separation of the propylene. From the demethanizer the top order, which is ethylene that is going to do a asteline hydrogenation with a (( )) catalyst that we are using and, so after the hydrogenation that is going to the for the separation of the ethylene. And the ethane fraction that will be again recycle to the system. And the steam which you are getting here from the and deethanizer that will go to the depropanizer.

Again as we did in case of the asteline compound which are present because that is the requirement of the ethylene or the propylene, which is going to be the for the paramization. So, still compound that is way very very less. And, so the and it is going to the after the separation here it is going this team to the depropanizer and the from the depronizer. Again this is team that is going to the removal of this team and with the same hydrogen in the presence of the hydrogen and then the, it is going to the final separation of the propylene and this propylene again.

It is going for the various and the product of this propylene is again this cycle and as I told you the propylene that you are using for the in the refrigerator cycle. Similarly here the bottom of the your this column that will go to the another column for this what we call it debutanizer for the mix products C 4 and almost because that is getting and then the pyrolysis again. This C 4 which will be discussing separately the recovery of the C 4 C 5 gases from the cracker and F C C. That is 1 of the very important feed stock for getting the some of the very important your feed stock for synthetic rubber industry. And some of the C 5 they are also being used in the pesticide industry. Another various chemicals edetive that we are making specially the crop production and cyclopentadine isoclyn here we are getting the butadiene or the.

So, these C 4 gases they are very important from the point of the petro chemicals and the pyrolysis. Gasoline that is the complementary we are getting steam that will go for the further processing that can be that can be combine with the your reformate for and it it will go for the separation of the aromatics. Depending upon the process, which you are having sometimes it may be also use as a fuel. In case of the if you having the gas cracker and the reason, but if you are having the integrated part of the refinery, but the reforming section is also they also that can be combine with the deformate and further production.

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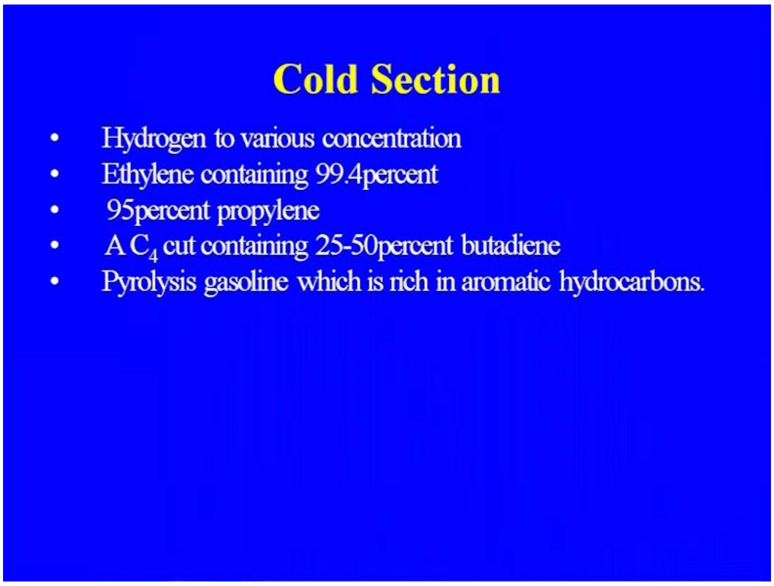

Cold Section

- Hydrogen to various concentration
- Ethylene containing 99.4percent
- 95percent propylene
- A C_4 cut containing 25-50percent butadiene
- Pyrolysis gasoline which is rich in aromatic hydrocarbons.

So, they cold section the hydrogen to the various concentration that may be there ethylene containing 99.4 percent 95 percent propylene is that is the purity of the product. Which you are getting a C 4 cut containing 25 to 50 percent of the butadiene, because this is 1 of the very important product, which we are producing in case of the cracker plant. That is the butadiene and this has been recover by all the cracker plant, which is based on the naphtha because the butadiene that can be used for the making of the polybutedeine or it can used for making the (( )) butadiene. As Indian Oil Corporation Panipat refinery they are going to have the S V R they are going to manufacture. And the plant is already under construction and the circulated the commission.

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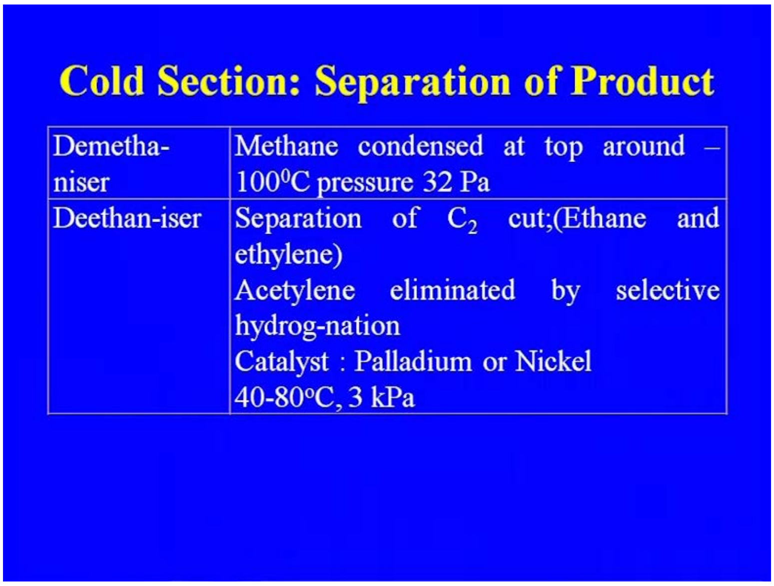

Cold Section: Separation of Product

Demetha-niser	Methane condensed at top around –100^0C pressure 32 Pa
Deethan-iser	Separation of C_2 cut;(Ethane and ethylene) Acetylene eliminated by selective hydrog-nation Catalyst : Palladium or Nickel 40-80°C, 3 kPa

So, another product which you are getting from the cracker plant at the pyrolysis gasoline which is reach in the aromatic hydrocarbons. So, that aromatic that can be separated all it can some of the part of the pyrolysis gasoline which is having oxygen number that can be used along with the gasoline. Now come to the each section, which is discussed in the flow diagram demethanizer methane condensed at the top around minus 100 degree centigrade.

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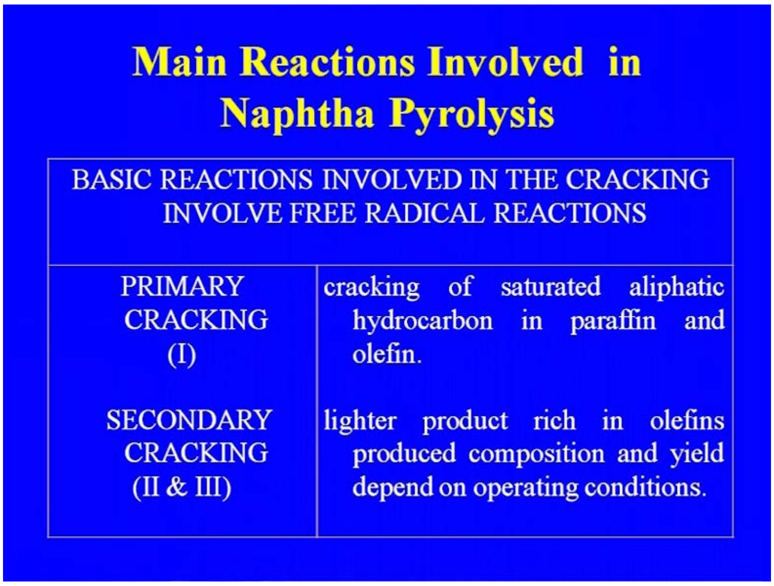

Main Reactions Involved in Naphtha Pyrolysis

BASIC REACTIONS INVOLVED IN THE CRACKING INVOLVE FREE RADICAL REACTIONS	
PRIMARY CRACKING (I)	cracking of saturated aliphatic hydrocarbon in paraffin and olefin.
SECONDARY CRACKING (II & III)	lighter product rich in olefins produced composition and yield depend on operating conditions.

This is the pressure acetylene eliminated by selective hydrogenation catalyst palladium or the nickel catalyst that we are using basic reaction which are taking place that the primary cracking and secondary cracking cracking of the saturated aliphatic hydrocarbon in paraffin and olefins. Lighter product rich in the olefins produced composition and yield depend on the operating conditions and the type of the feed stock you are having Then they come to the separation of the demethanizer as I told you this team of the separation of the methane and the hydrogen.

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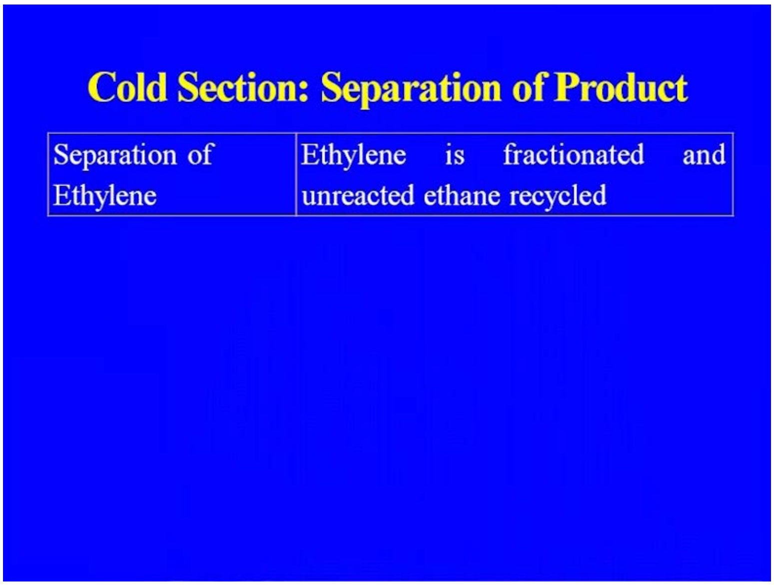

Cold Section: Separation of Product

Separation of Ethylene	Ethylene is fractionated and unreacted ethane recycled

The bottom product that is going for this separation of ethylene. So, ethylene fractionated un reacted part of the ethane that is recycle. Then come to the, and in between that is the that is steam that is going for the removal of the ethylene compound and after that finally it is separated. So, before going for the ethylene directly that will go first to the hydrogenation section for mole of the esteel compound and then it will go finally, for the separation.

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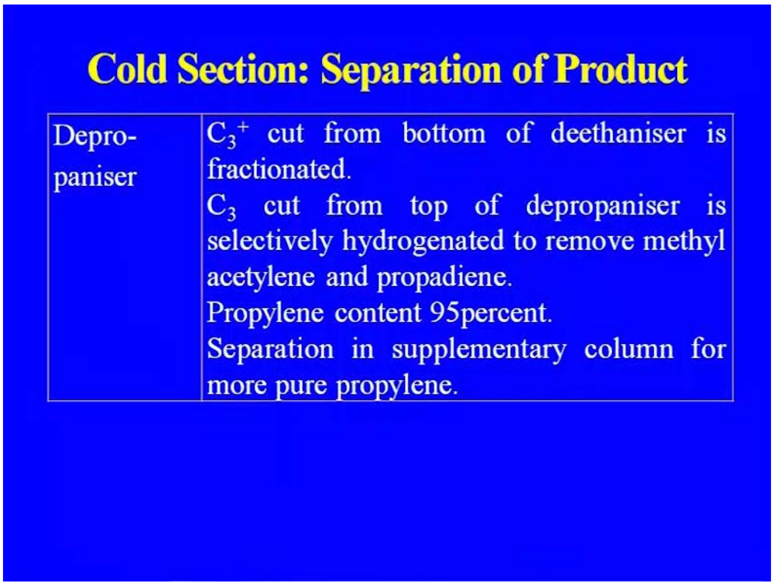

Cold Section: Separation of Product

Depro-paniser	C_3^+ cut from bottom of deethaniser is fractionated. C_3 cut from top of depropaniser is selectively hydrogenated to remove methyl acetylene and propadiene. Propylene content 95percent. Separation in supplementary column for more pure propylene.

So, depropanizer C 3 cut from the bottom of the deethanizer is fractionated C 3 cut from the top of the depropanizer is selectivity hydrogenated to remove the methyl acetylene and the propadiene. This is the what we are doing in case of the deethanizer, also the ethylene steam that is going to the for the selective hydrogenation of the steel compound. Pro contain 95 percent separation in supplementary column for more pure propylene after the treatment after the hydrogenation that steam again it will go to the another column are the separation of the pure propylene. That will take place. And the bottom unreacted propylene that will be recycle this.

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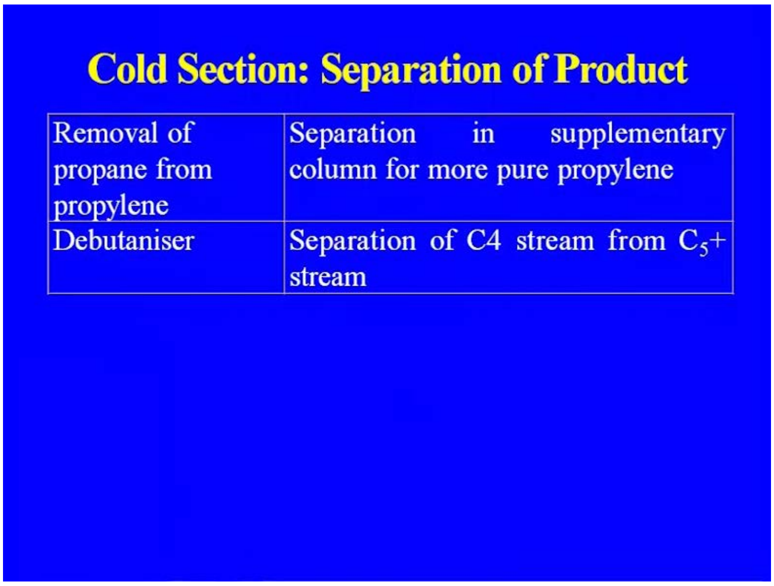

Cold Section: Separation of Product

Removal of propane from propylene	Separation in supplementary column for more pure propylene
Debutaniser	Separation of C4 stream from C_5+ stream

That is from the propaniser count from the bottom of the propylene that will be recycle and the depropanizer bottom and the first column that will go for the separation of the C 4 gasoline. So, removal of propane from the propylene separation of the supplementary column for more pure propylene, which I showed you in the diagram where we are separating and the depropanizer separation of the C 4 steam from the C 5 steam. Because the C 5 plus steam that will be separated as the bottom product and C 4 5 C 4 and C 5 some steam that will go to the top product and rest will be C fi5ve plus will be in the bottom product which call the pyrolysis gasoline.

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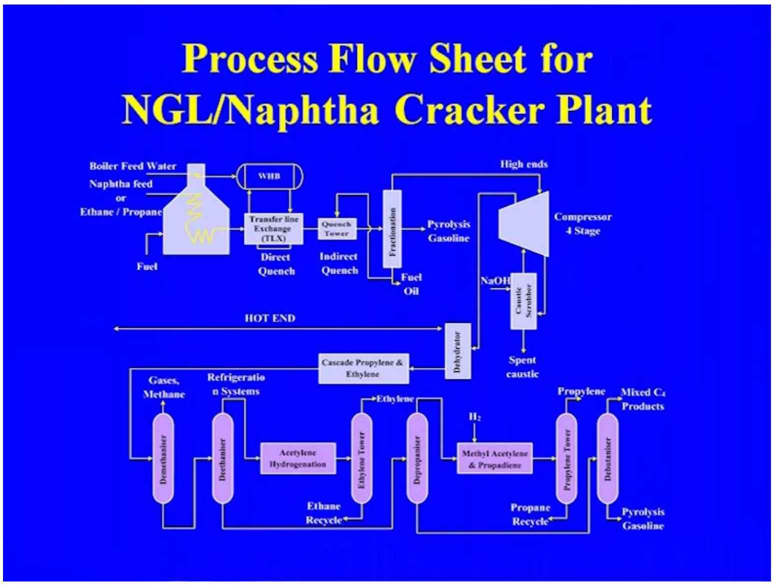

Process Flow Sheet for NGL/Naphtha Cracker Plant

So, let us again revive this is the actually I was telling about the hot section after the hot section that is going to demethanizer. From demethanizer it is going to the deethanizer and the remove the top product that is going for the ethylene hydrogenation in the both the cases. In case of the propylene steam and the ethylene steam then it is going the for final separation here. This another column which I was telling. And here from with deethanizer this is going to the depropanizer and from the depropanizer the steam again for removal of the esteel compound.

Then it is finding a another column where the propylene separation that will take place and the propylene is recycle here. Similarly, the ethylene ethane that is recycle from the this column and the finally, from the depropanizer it is going to debutanizer the mix C 4 products and here the pyrolysis gasoline that will be getting.

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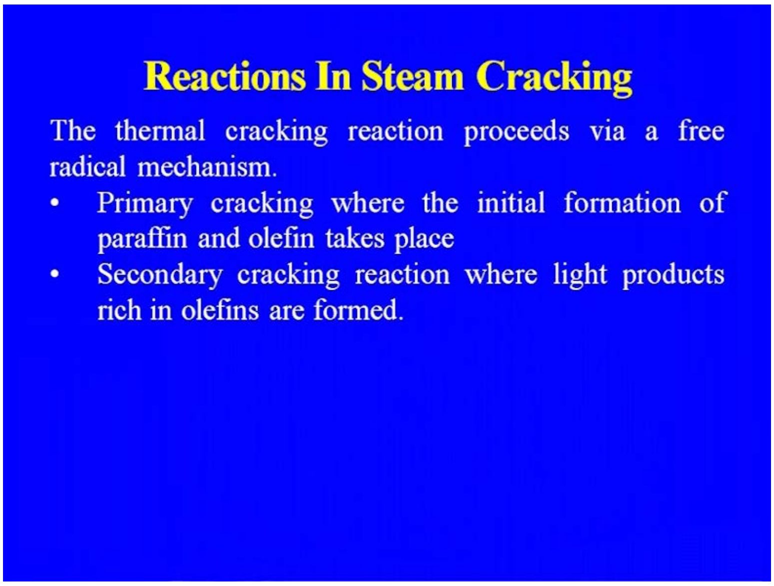

Reactions In Steam Cracking

The thermal cracking reaction proceeds via a free radical mechanism.

- Primary cracking where the initial formation of paraffin and olefin takes place
- Secondary cracking reaction where light products rich in olefins are formed.

So, these are the some of the major reaction we have free radical mechanical that is taking place and the for the primary cracking where the initial formation of the paraffin olefins takes place. Secondary cracking reaction where light olefins rich in olefins are formed. And during the process as I told you the other reactions are also taking place and the aromatic are also produced and these aromatics are the for the of the coke formation. So, series of reaction condensation reaction that is taking place and because of the we are getting the finally, the coke formation in there.

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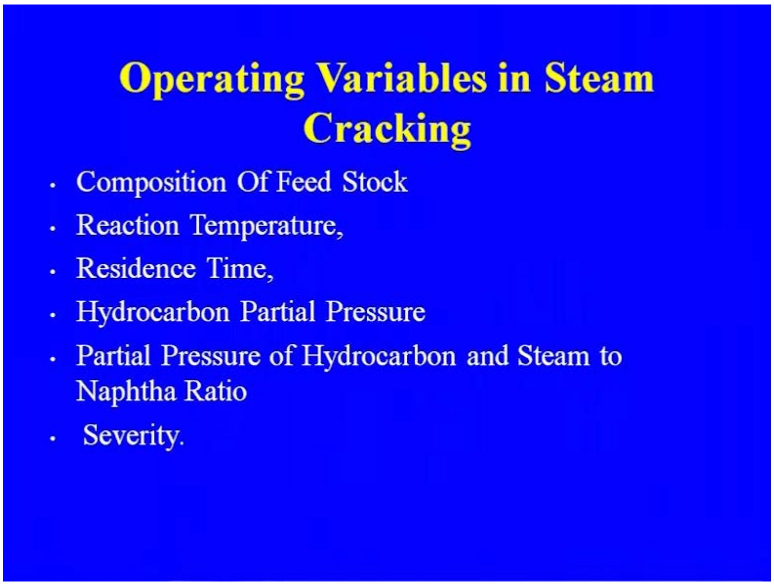

Operating Variables in Steam Cracking

- Composition Of Feed Stock
- Reaction Temperature,
- Residence Time,
- Hydrocarbon Partial Pressure
- Partial Pressure of Hydrocarbon and Steam to Naphtha Ratio
- Severity.

And that cannot be avoided because always there is some coke formation only thing how to minimize this coke formation, because that will affect the run length of the furnace. So, now let us discuss the operation valuables of the distinct packing because depending upon the operating variables the type of the product that you are getting that will vary. First important is the composition of the feed stock. As, I told you the we are using the white raw material from ethane propane to gas oil, so the type of the product shall getting that will total depend upon the feed stock. Because the ethane more ethylene will be there ethane propane the olefins production we had other is just like the heavier fraction that will be less in case of the ethane propane. In that end so far naphtha is concern that is in between the ethane propane and the gas oil.

Then the other important parameter that is the reaction temperature the temperature may be the severity it should not be to low or not too high. Because the chances of the more coke formation live there at high temperature and lower temperature the yield of the lighter component olefins that will be less. Residence sign as I told you that is very important furnace so again we will be discussing always hydrocarbons partial pressure and the partial pressure of the hydrocarbon and steam to naphtha ratio. Because the steam that is playing important role that is in that is in the partial pressure. Then the severity and severity and the reaction temperature they are interrelated parameters.

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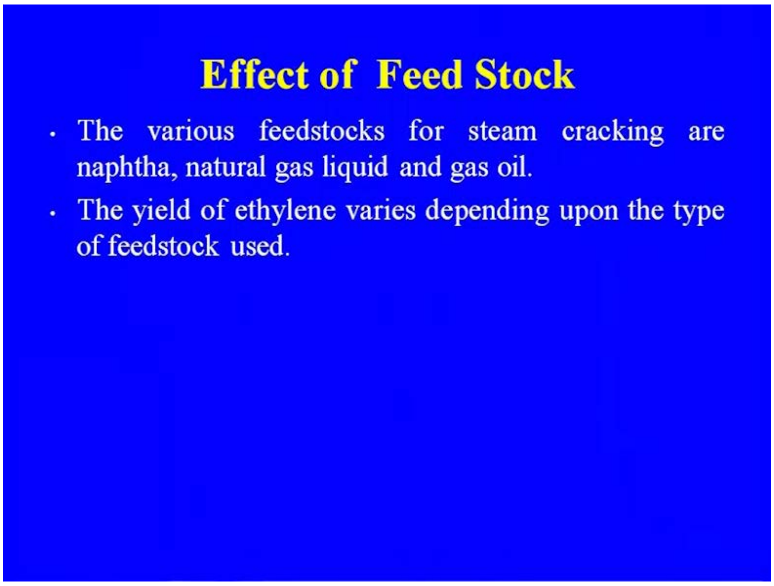

Effect of Feed Stock

- The various feedstocks for steam cracking are naphtha, natural gas liquid and gas oil.
- The yield of ethylene varies depending upon the type of feedstock used.

The various feed stock that discussed that the steam cracking or naphtha natural gas are the may be natural gas condense sheet also and gas oil. The yield of the ethylene varies depending upon the type of the feedstock used.

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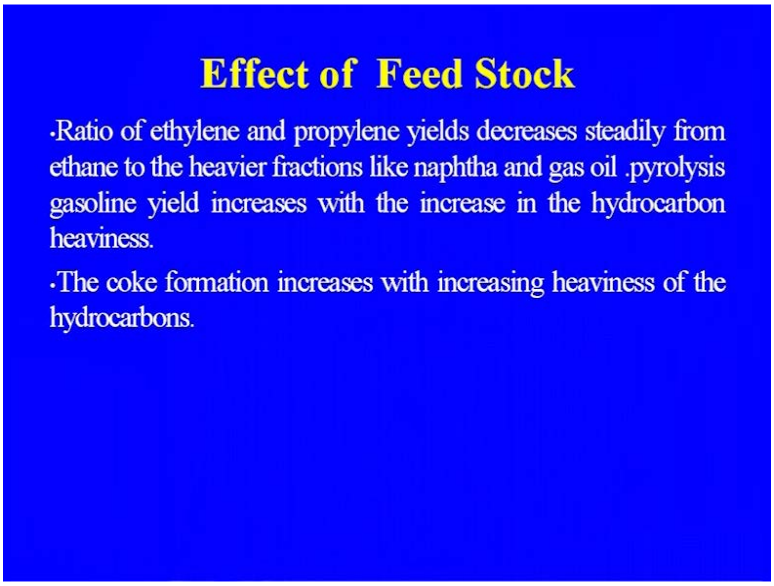

Effect of Feed Stock

- Ratio of ethylene and propylene yields decreases steadily from ethane to the heavier fractions like naphtha and gas oil .pyrolysis gasoline yield increases with the increase in the hydrocarbon heaviness.
- The coke formation increases with increasing heaviness of the hydrocarbons.

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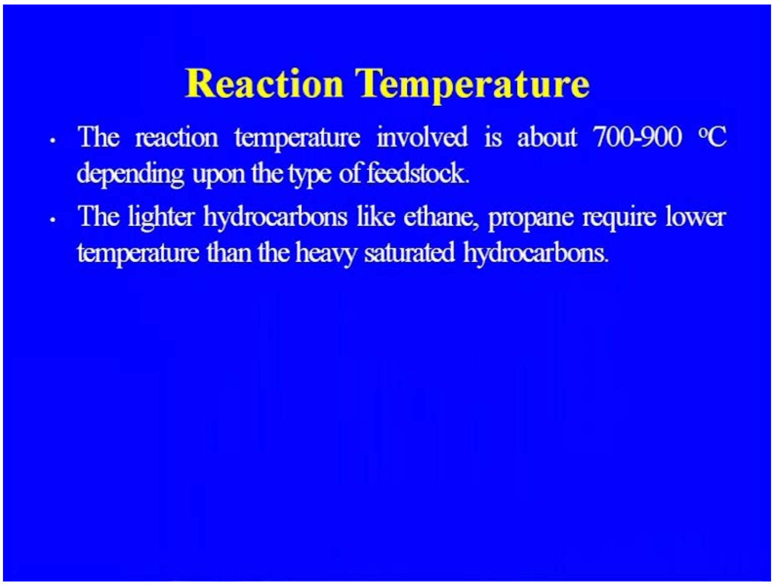

Reaction Temperature

- The reaction temperature involved is about 700-900 °C depending upon the type of feedstock.
- The lighter hydrocarbons like ethane, propane require lower temperature than the heavy saturated hydrocarbons.

Ratio of ethylene and propylene yields decreases steadily from ethane to heavier fraction like naphtha and gas oil. Pyrolysis gasoline yield increases with the increase in the hydrocarbon heaviness. As I told you the incase of if you are going for the gas oil you can crack the gas oil you can get olefins, but the formation of the heavier fraction and the pyrolysis gasoline that will be more, then the lighter feedstock ethane propane. The coke formation increases with increasing heaviness of the hydrocarbons the chances of coke formation will be more, if you are using the heavier fraction reaction temperature.

The reaction temperature involved is about 700 to 900 degree centigrade depending upon the type of the feedstock because in case of the ethane propane lower temperature that will require, if you are going for gas oil the higher temperature that will require. In case of the naphtha it is in between the ethane propane and again. The lighter the lighter hydrocarbons like ethane, propane require lower temperature that the heavy saturated hydrocarbons, which I told you. The reaction temperature involved which is around 7 to 900, already we have discussed this part.

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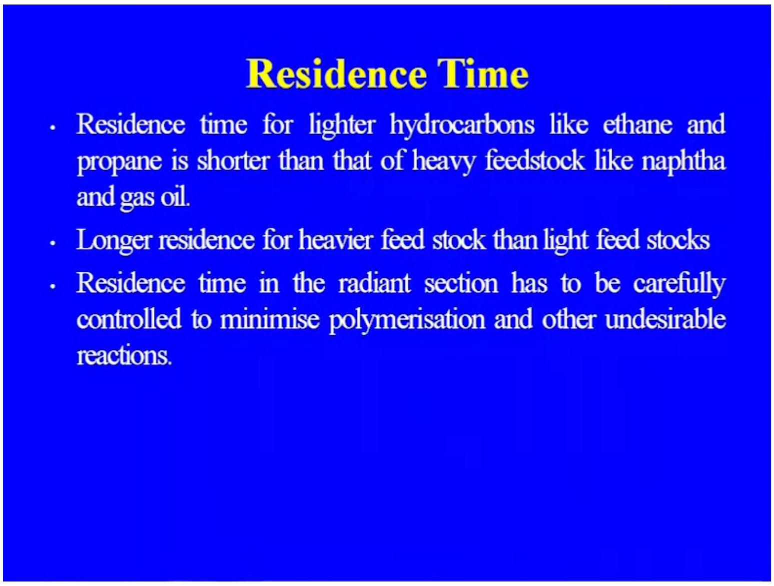

Residence Time

- Residence time for lighter hydrocarbons like ethane and propane is shorter than that of heavy feedstock like naphtha and gas oil.
- Longer residence for heavier feed stock than light feed stocks
- Residence time in the radiant section has to be carefully controlled to minimise polymerisation and other undesirable reactions.

Now, let us come to the residence time. Residence time again that will residence time for lighter hydro carbons like ethane and propane is shorter than that of the heavy feedstock like naphtha and the gas oil. So, this is the very important parameter incase of putting variable incase of the furnace longer residence for heavier feed stock is require, then the lighter feed stock. Residence time in the radiant section has to be carefully controlled to minimize the polymerization and other undesirable reactions which is taking place in the furnace. So, that is very important the residence and that is the very short residence time we are maintaining in the furnace.

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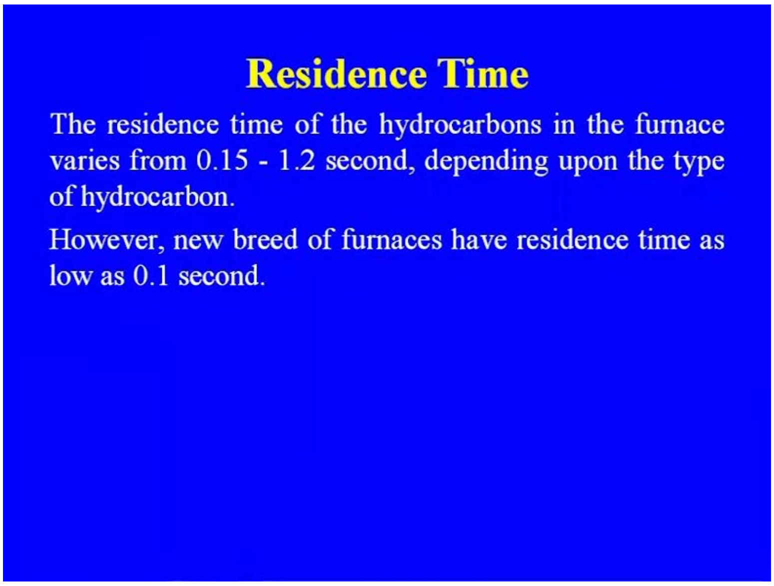

Residence Time

The residence time of the hydrocarbons in the furnace varies from 0.15 - 1.2 second, depending upon the type of hydrocarbon.

However, new breed of furnaces have residence time as low as 0.1 second.

The residence time of the hydro carbons in the furnace varies 0.15 to 1.2 second depending upon the type of the feed stock you are having. However, new breed of the furnaces have residence time as low as 0.1 second.

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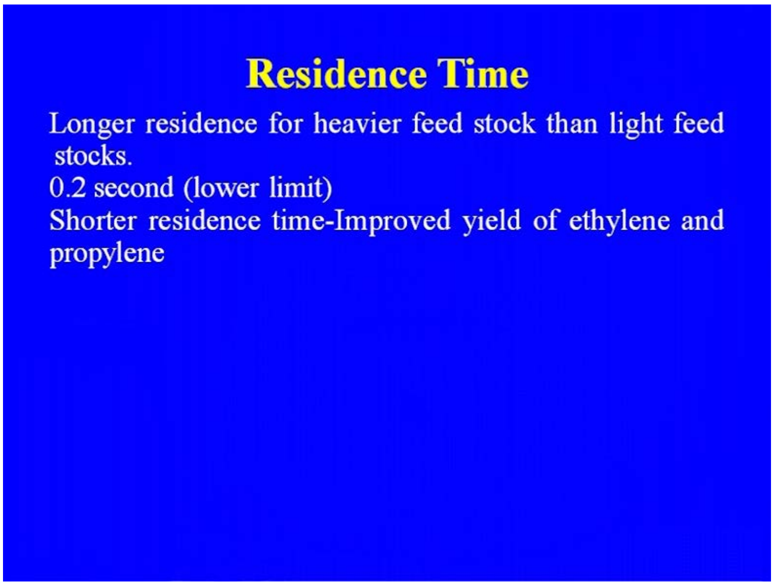

Residence Time

Longer residence for heavier feed stock than light feed stocks.
0.2 second (lower limit)
Shorter residence time-Improved yield of ethylene and propylene

This already I told you the longer residence for heavier feed stock than the light feed stock shorter residence time improved yield of the ethylene and propylene. Because if you are having the shorter residence time yield of the ethylene and propylene that will be more if you are going for the longer residence time the formation of the heavier, even ethylene and propylene if the shorter residence time lower ethylene will be there.

If you are slightly increasing the formation of propylene that many more hydro carbons, partial pressure and role of the steam whichever is telling because steam that is playing very important role pyrolysis reaction, more advanced at lower temperature lower pressure ethylene yield decreases as the partial pressure of the hydro carbons increases. So, here you see the there are why we are using this steam because that will lower the partial pressure of the hydro carbons. Otherwise yield of ethylene that will be affected.

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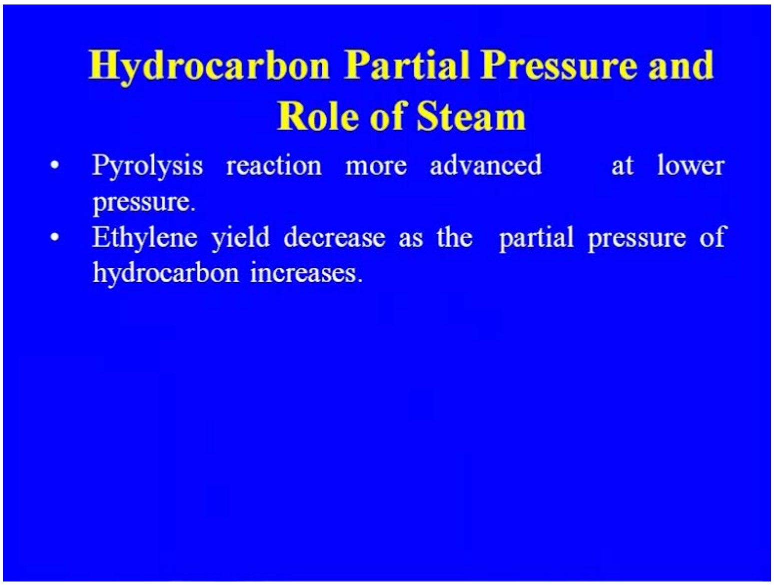

Hydrocarbon Partial Pressure and Role of Steam

- Pyrolysis reaction more advanced at lower pressure.
- Ethylene yield decrease as the partial pressure of hydrocarbon increases.

Role of the steam which I was telling that why we are using steam due to say that overall reaction rate enhance the selectivity of pyrolysis on favor of the light olefins, which I desired and increases the temperature of the feed stock. So, that they also helping in the increasing the temperature before it is going to the cracker.

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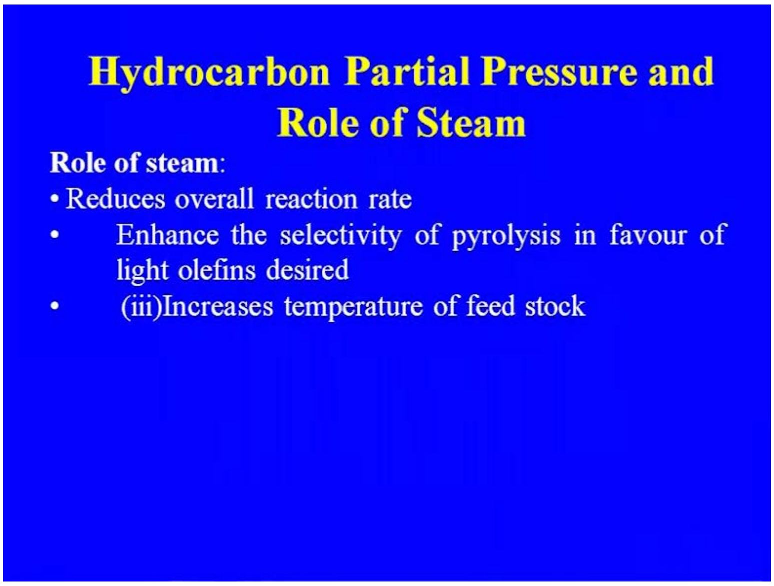

Hydrocarbon Partial Pressure and Role of Steam

Role of steam:

- Reduces overall reaction rate
- Enhance the selectivity of pyrolysis in favour of light olefins desired
- (iii)Increases temperature of feed stock

As I told you the 1 term very important term that we are using incase of the furnaces that the operating severity and selectivity, because this, what we need incase of the cracking that the more and more lighter product then the heavier product.

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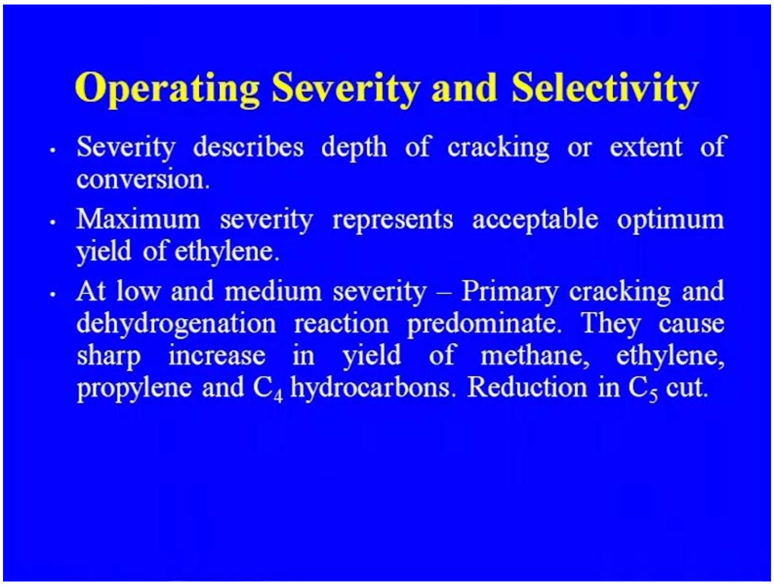

Operating Severity and Selectivity

- Severity describes depth of cracking or extent of conversion.
- Maximum severity represents acceptable optimum yield of ethylene.
- At low and medium severity – Primary cracking and dehydrogenation reaction predominate. They cause sharp increase in yield of methane, ethylene, propylene and C_4 hydrocarbons. Reduction in C_5 cut.

So, severity that is term we are using that is define as the depth of cracking or the extend of conversion that is taking place. And the severity may the high temperature we are applying the more severe condition, so they want antique severity function that term that I have given and based on that just I will discuss in the next slide about the how much the kinetic severity function that is the, we should mention. So, maximum severity represent the acceptable optimum yield of the ethylene. At low and medium severity primary cracking and dehydrogenation reaction predominate they cause sharp decrease in the yield of methane ethylene propylene and C 4 hydro carbons reduction in the C 5.

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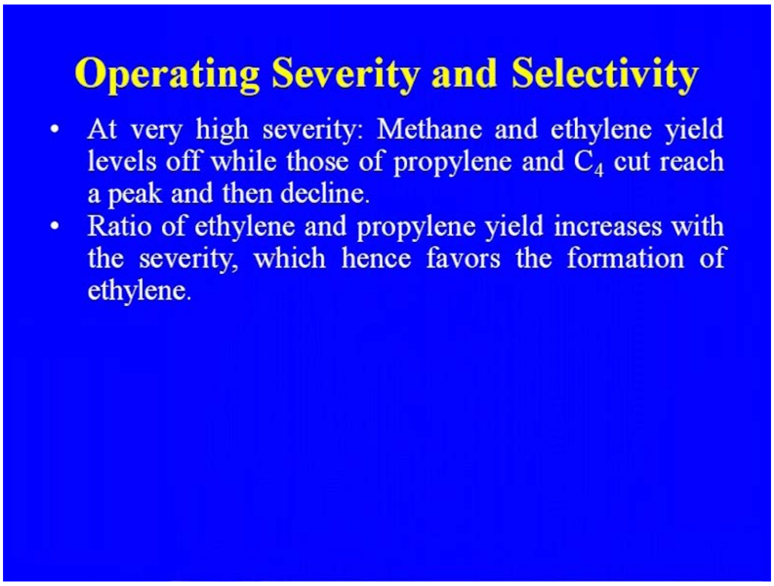

Operating Severity and Selectivity

- At very high severity: Methane and ethylene yield levels off while those of propylene and C_4 cut reach a peak and then decline.
- Ratio of ethylene and propylene yield increases with the severity, which hence favors the formation of ethylene.

At very high severity methane and ethylene yield levels off while those of propylene and C 4 cut reach a peak. Then decline ratio of the ethylene and propylene yield increases with the severity, which hence favors the formation of the ethylene.

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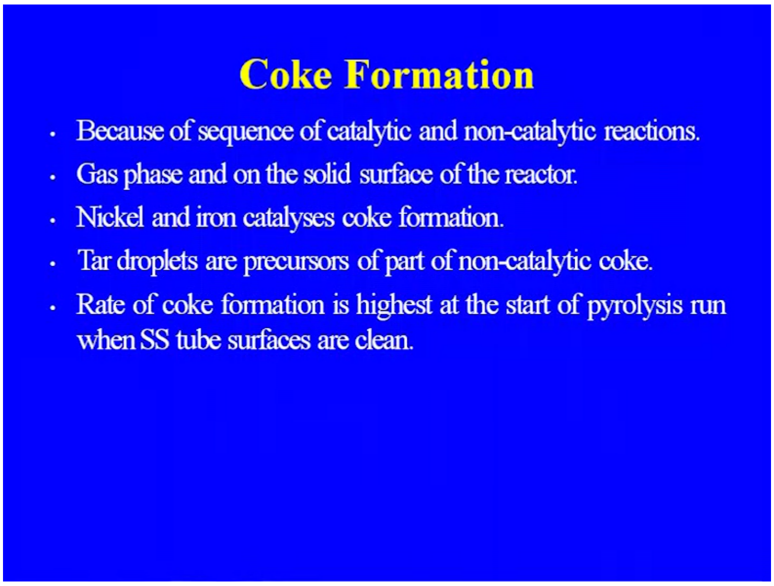

Coke Formation

- Because of sequence of catalytic and non-catalytic reactions.
- Gas phase and on the solid surface of the reactor.
- Nickel and iron catalyses coke formation.
- Tar droplets are precursors of part of non-catalytic coke.
- Rate of coke formation is highest at the start of pyrolysis run when SS tube surfaces are clean.

Now, let us discuss the coke run length of the furnace because as I told you during the operation of the furnace always the coke formation. So, what are these reasons for this formation of. So, that may be the because of the sequence of catalytic and non catalytic reactions that is taking place, gas phase and on the solid surface of the reactor. Nickel and iron because the they are presenting the they are the material of the construction. The nickel allow that may be they are because high temperature in the furnace high nickel alloy to where we are using so nickel and iron capitalizes the coke formation.

Tar droplets are precursors of the part of the non catalytic coke. Again we are having the two type of the coke as I have defined 1 is the non catalytic coke another is catalytic coke. Catalytic coke means, which has been formed due to the because of the presence of the some of the metals like nickel and iron which catalyses there. Rate of coke formation is highest at the start of the pyrolysis run when the S S tube or surfaces are clean because they are coming indirect and after that some you can say the cotene is there. And, so the always the rate of coke formation is higher at the initial stage of running of your furnace.

So, what is the effect of the coke why we are bothering about these movable of the coke and the formation of the coke because the total run length of the furnace that will depend upon the coke or the less coke mean the you can increase the run length if the higher coke formation is there, so definitely run length or the furnace that will go down. So, the coke reduces the cross section of the tube necessitate higher pressure.

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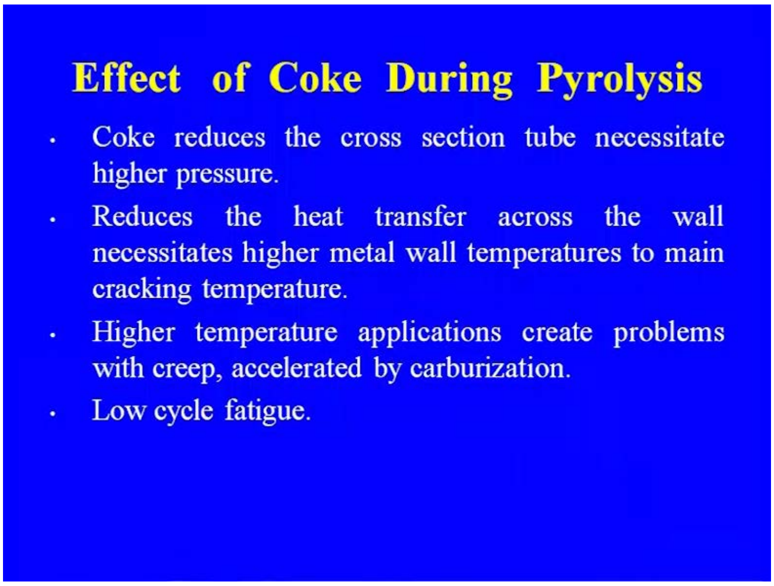

Effect of Coke During Pyrolysis

- Coke reduces the cross section tube necessitate higher pressure.
- Reduces the heat transfer across the wall necessitates higher metal wall temperatures to main cracking temperature.
- Higher temperature applications create problems with creep, accelerated by carburization.
- Low cycle fatigue.

What will happen if the coke is deposited inside the tube? That will increase in the outside temperature of the tube. At the same time the high pressure top higher pressure that will be require that reduces the heat transfer across the wall, necessitate the higher metal wall temperature to maintain the cracking temperature. So, because of that reason because you need the higher temperature, the skin, tube skin temperatures are the outer temperature that will increase.

Higher temperature application create problems with a creep accelerated by carburization low cycle fatigue. These are the some of the problem, which may be there because of the formation of the coke in the tube. Ah this is we define the furnace run length because you see the normal the furnace run length that is very widely depending upon the type of the feed stock. And the operating condition you are maintaining that may be form the you can say the 25 to 50, 60 days that may be the run length of the furnace depending upon the. Because that time survey that is round 40 to 50 that is the optimal run length that is consider.

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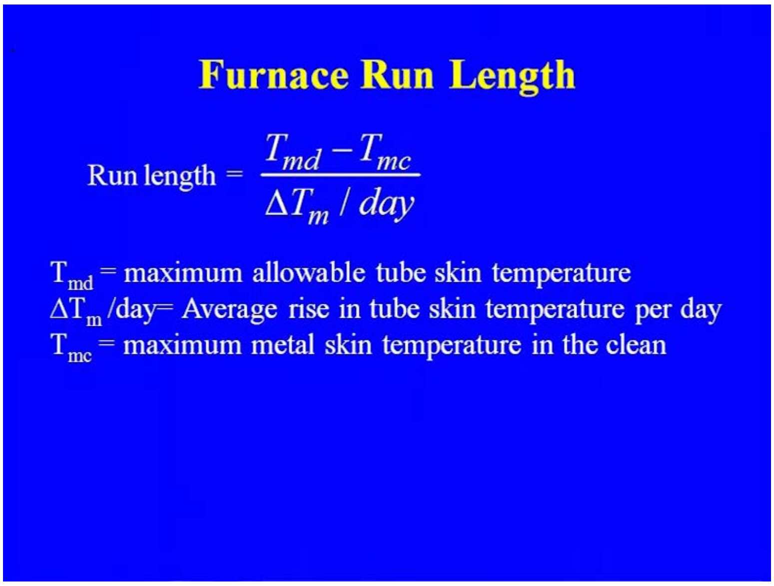

Furnace Run Length

$$\text{Run length} = \frac{T_{md} - T_{mc}}{\Delta T_m / day}$$

T_{md} = maximum allowable tube skin temperature
ΔT_m/day= Average rise in tube skin temperature per day
T_{mc} = maximum metal skin temperature in the clean

So, run length this is define as the T M is the maximum allowable tube skin temperature and delta T M is the average rise in the tube skin temperature T M C is the maximum metal skin temperature when it is clean. So, this is the how you can determine the run length of the furnace. Now, let us discuss because the coke formation as I told you you cannot avoid only you can minimize, but even after that you will have to 1 furnace that you will have to bypass if the excessive coke formation is there. Because the high coke formation is there the pressure drop and the skin temperature of the tube and then at the same time more fuel that will be required. So, the whole operation of the furnace that will be upset.

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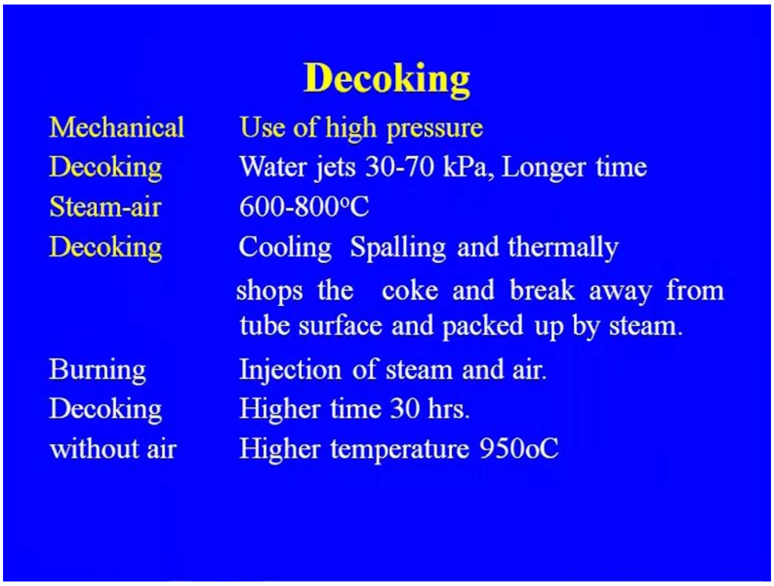

Decoking

Mechanical	Use of high pressure
Decoking	Water jets 30-70 kPa, Longer time
Steam-air	600-800°C
Decoking	Cooling Spalling and thermally
	shops the coke and break away from tube surface and packed up by steam.
Burning	Injection of steam and air.
Decoking	Higher time 30 hrs.
without air	Higher temperature 950oC

So, the decoking that is the we are having the 2 type of the decoking 1 is the mechanical decoking where you are using the high pressure water jets and the longer time that will be require. So, steam we are decoking that is the at high temperature we are doing the decoking where it is the cooling spaling and the thermally thermal shops the coke and break away from the tube surface and packed by the steam. Burning decoking without air injection of steam and air higher time is require and higher temperature is required.

Now, let us discuss about the development which has taken place in the steam. U see the there has been continuous development in the steam cracking process specially in the furnace design from very low V in you say the. In India we started only with the 20,000 ton capacity ethylene cracker first cracker plant, which was started by Indian carbohydrate in Bombay.

So, that was the lower capacity then we started 60,000, 1000 then it was 1,00,000 ton capacity IPCL and then the new breed of the for furnace, which you are having justly we take a reliance are the pan put refinery 8,00,000 ton capacity. So, the what are the parameter that has consider in the development of the cracking because 1 of the basic because you see the whether you are going in the petro chemicals complex any operation of incase of the refinery very appreciable amount of the cost operating cost is in the form of the energy.

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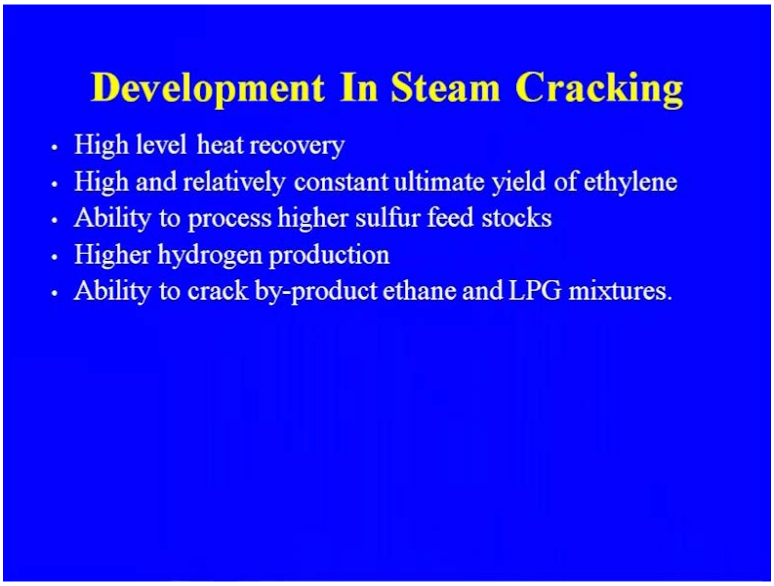

Development In Steam Cracking

- High level heat recovery
- High and relatively constant ultimate yield of ethylene
- Ability to process higher sulfur feed stocks
- Higher hydrogen production
- Ability to crack by-product ethane and LPG mixtures.

So, the high heat level it heat recovery that will very important factor while going for the better design high and relatively constant ultimate ultimate yield of the ethylene ability to process higher sulfur feed stocks, higher hydrogen production ability to crack by product ethane and LPG mixtures. Because, now the even in case of the ability to higher sulfur feed and at the same time variation the higher hydro carbons means the gas oil cracking now we are talking about the gas oil.

Even in case of the steam cracking now the development that has be the catalytic cracking to reduce the temperature and to improve the selectivity of the the reaction towards a particular more ethylene and the propylene. So, in the future you may have the just like FCC air also the catalytic cracking process, which will lower the temperature and at the same time that will also the purity of the product that will be better.

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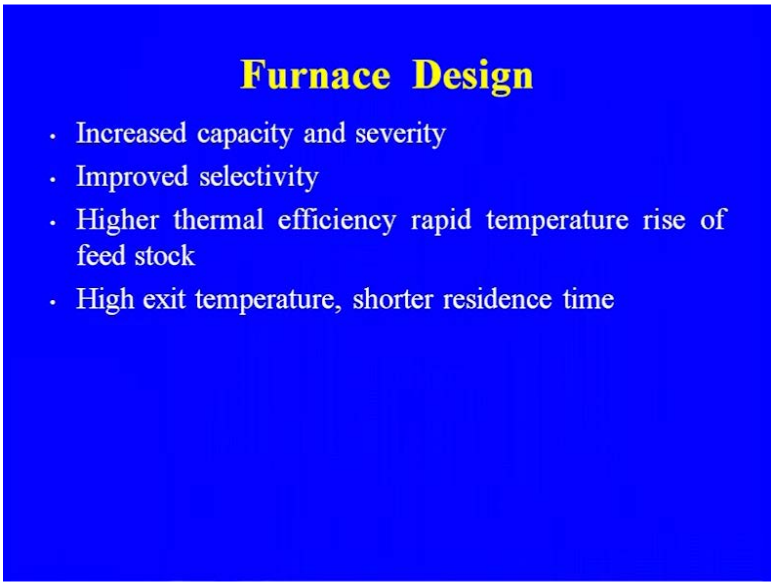

Furnace Design

- Increased capacity and severity
- Improved selectivity
- Higher thermal efficiency rapid temperature rise of feed stock
- High exit temperature, shorter residence time

So, these are the some of the actually the major development that has taken place, which I told you the increase capacity and the severity improved selectivity severity means the optimal severity in the that is your own if 3 to 3.5. That is the severity antique severity function that the cave that we are maintaining around 3 to 3.5. Improved selectivity higher thermal efficiency rapid temperature rise of the feed higher exit temperature shorter residence time, you see the why higher exits temperature means the less coke formation is there?

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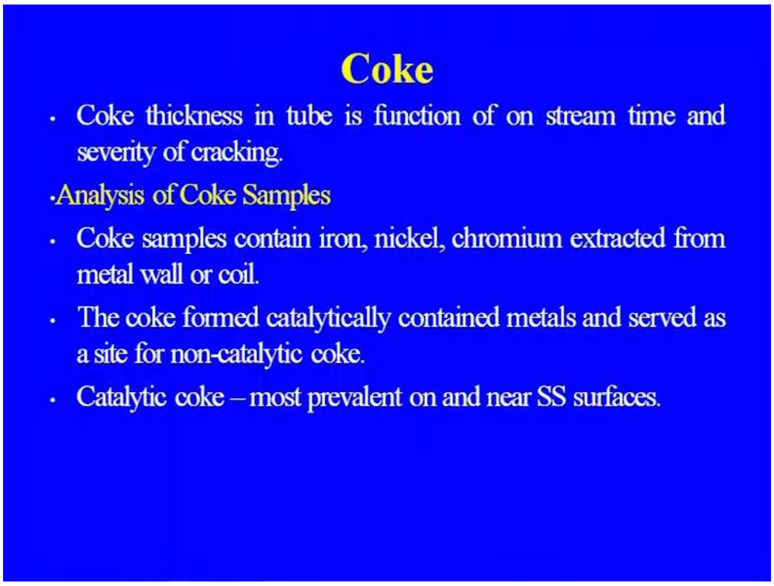

Coke

- Coke thickness in tube is function of on stream time and severity of cracking.

·Analysis of Coke Samples

- Coke samples contain iron, nickel, chromium extracted from metal wall or coil.
- The coke formed catalytically contained metals and served as a site for non-catalytic coke.
- Catalytic coke – most prevalent on and near SS surfaces.

So, the temperature differentitive, we have if the more coke formation is there temperature that will be go down. So, we can control the temperature also from the outer skin temperature of the tube and then the exit temperature of the gas. The coke thinness in the tube is function of on steam time and the severity of the cracking, analysis of the coke samples, because you see the way this function of this steam time, because the residence time and the temperature that you are maintaining depending upon the formation of the coke that will vary. So, analysis of coke sample that has been then, so the coke samples contain iron nickel chromium extracted from the metal wall or the oil.

If you problem is also there and the furnace because the temperature is required as we discussed earlier, because some of the problem are the high temperature collision is there. The coke formed catalytically contained metals and served as a site for the non catalytic coke. Catalytic coke most prevalent on and near surface, so that is the catalytic and non catalytic.

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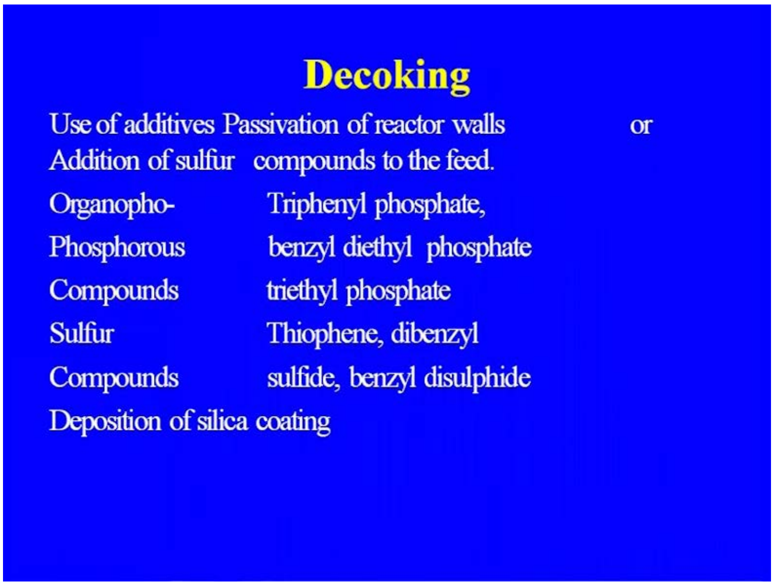

Decoking

Use of additives Passivation of reactor walls or Addition of sulfur compounds to the feed.

Organopho-	Triphenyl phosphate,
Phosphorous	benzyl diethyl phosphate
Compounds	triethyl phosphate
Sulfur	Thiophene, dibenzyl
Compounds	sulfide, benzyl disulphide

Deposition of silica coating

Decoking, how to remove that? Because one was the mechanical decoking, but the use of the additives which passivate the reactor walks addition of the sulfur compound to the feed. So, we are having the 2 types of the organic compound, which has been actually all the various after the study they have found at the organophosphorous compounds and the some of the sulfur compound, the triphenyl phosphate, benzyl, diethyl, phosphate, di triethyl phosphate, thiophene dibenzyl, sulfide benzyl sulfide. These are the some of the sulfur compounds and the organophosphorous compounds, which can be added to reduce the coke formation. Deposition of the silica coating on the tube side. So, that is because I was telling the iron and nickel they capitalizes the coking reaction.

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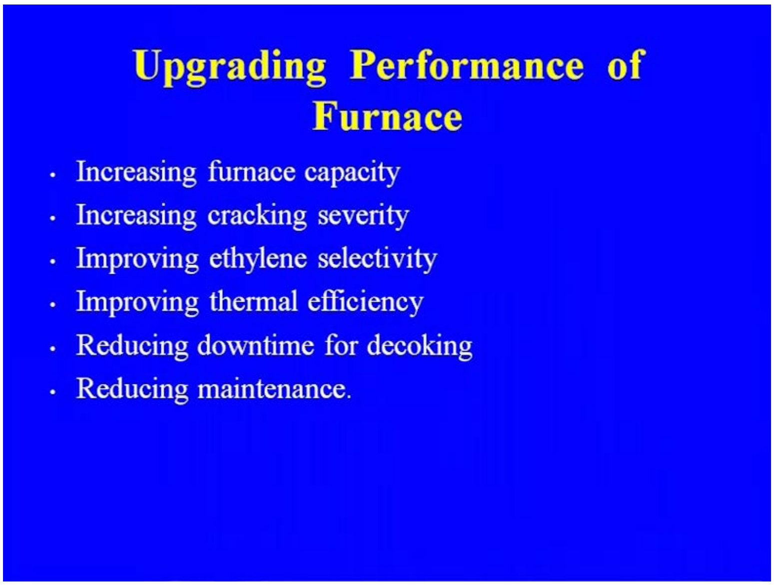

Upgrading Performance of Furnace

- Increasing furnace capacity
- Increasing cracking severity
- Improving ethylene selectivity
- Improving thermal efficiency
- Reducing downtime for decoking
- Reducing maintenance.

So, this already I discussed about the one of the point which I told you the increasing the furnace capacity increasing the cracking ethylene selectivity because that is our (( )). But now in the future it may be the requirement of the propylene as increasing so it may be the now the two sorts are there which are populating at the ethylene and the propylene more beaches the ethylene.

Earlier ethylene was called the king of the chemicals propylene that was the crown prince, but now the in some times the usage of the propylene more than the ethylene reducing the down time of the decoking, because that is also very important. Because normally, what is happening after certain run length, when the excessive coke formation is there, the furnace is bypass for the removal of the coke. Then the, so that down time that has to be a avoided reducing the maintenance because this also one of the important factor, which effect the overall running of the furnace.

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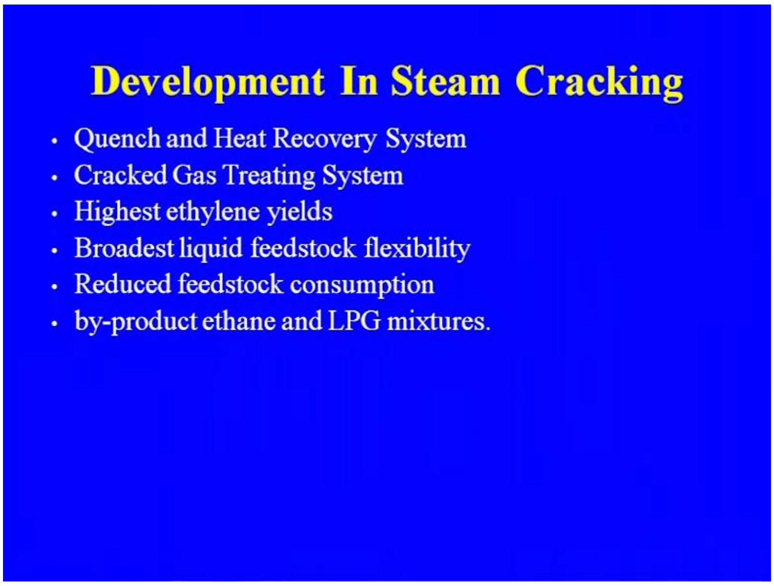

Development In Steam Cracking

- Quench and Heat Recovery System
- Cracked Gas Treating System
- Highest ethylene yields
- Broadest liquid feedstock flexibility
- Reduced feedstock consumption
- by-product ethane and LPG mixtures.

These are the some of the development, which has taken place just to improve the efficiency quench and heat recovery system cracked gas treating system then the highest ethylene yields broadest liquid feed stock flexibility. Now, they should operate with the test like that I told you the cracker plant of the reliance that is the both multi feed. We can use the naphtha or we can use the gas also reduce feed stock consumption by product ethane and LPG mixture that can be if you can use the LPG also the beaches. What is happening now with the LPG is this mini of the LPG surplus to that LPG also can because this the mixture of the propane and butane so that can be also crack.

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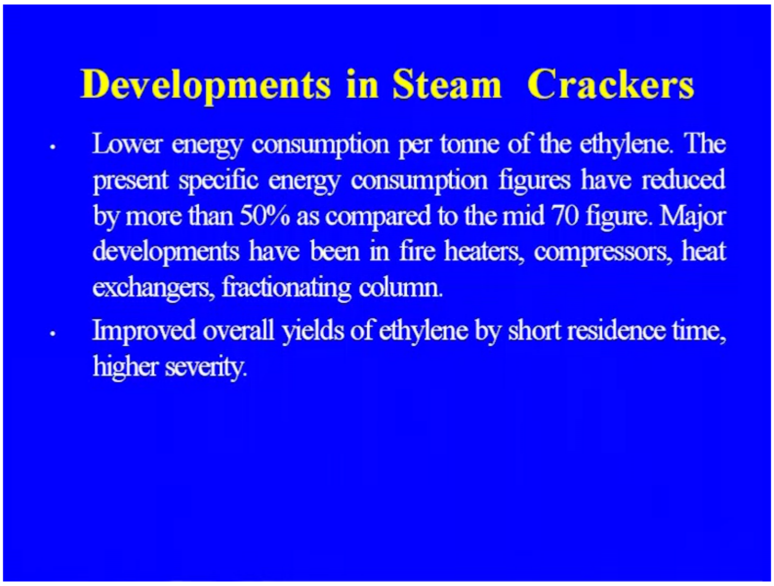

Developments in Steam Crackers

- Lower energy consumption per tonne of the ethylene. The present specific energy consumption figures have reduced by more than 50% as compared to the mid 70 figure. Major developments have been in fire heaters, compressors, heat exchangers, fractionating column.
- Improved overall yields of ethylene by short residence time, higher severity.

So, just to summarize this is the development lower energy consumption pot of the ethylene. This space the present space fig energy consumption figures have reduced where more than 50 percent as compare to the mid 70 figure. Because you see the capacity, which I told you that is the 20,000 to 6,000 to 8,00,000 ton capacity. So, this has been the major development has been in.

So, what are the value major development at the fire heaters compressor heat exchanger fractionating column improved overall yields of ethylene by short residence time higher severity because, there is there with two diameter. Then if you are increasing the tube diameter decreasing the if the less tube diameter means it is yours velocity removal less residence time removal more ethylene will be there. If, then you are having the high diameter the more propylene, it will be there and the hats severity means severity 3.5 there will be optimal. If you are going beyond that or less than that, then both are going to effect the product yield. So, in case of the furnace some of the other development specially from the coke formation point of view and the corison point of view, adding the development in the decoking process to have higher run length with use of additive.

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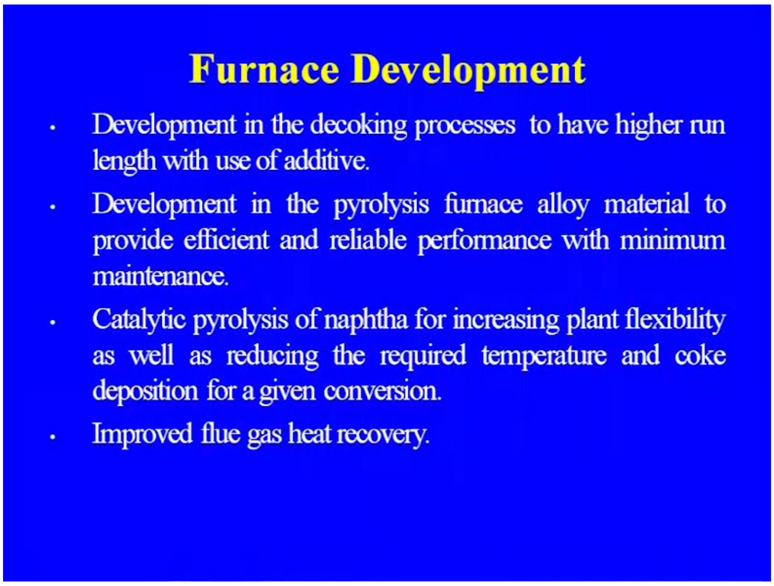

Furnace Development

- Development in the decoking processes to have higher run length with use of additive.
- Development in the pyrolysis furnace alloy material to provide efficient and reliable performance with minimum maintenance.
- Catalytic pyrolysis of naphtha for increasing plant flexibility as well as reducing the required temperature and coke deposition for a given conversion.
- Improved flue gas heat recovery.

Development in the pyrolysis furnace allows material to provide efficient and reliable performance with minimum maintenance, because you see the that is one of the problem in case of the refinery and the petro chemicals complex also because you are using the large number the furnaces. So, the corison problem severe every feed is not properly detect are the removal of these sole gases is not there properly.

So, catalytic pyrolysis of naphtha this I was telling now, what we are talking about the catalytic pyrolysis of the naphtha for increasing the plant flexibility as we as reducing the required temperature and coke deposition for a given conversion. Because this is one of the very important, now you may have the catalytic pyrolysis of the naphtha, so that you can choose the catalytic and with a particular selectivity towards a desired product.

So, this is what did fisher development that is going to take place and fuel gas heat recovery, because we are what we doing we are the gases they are coming at a high temperature. And we are doing the quenching or the direct or indirect, so temperature that has to be from high temperature to low temperature you are going for this operation. So, the improve in the gas it recovery system that is very important.

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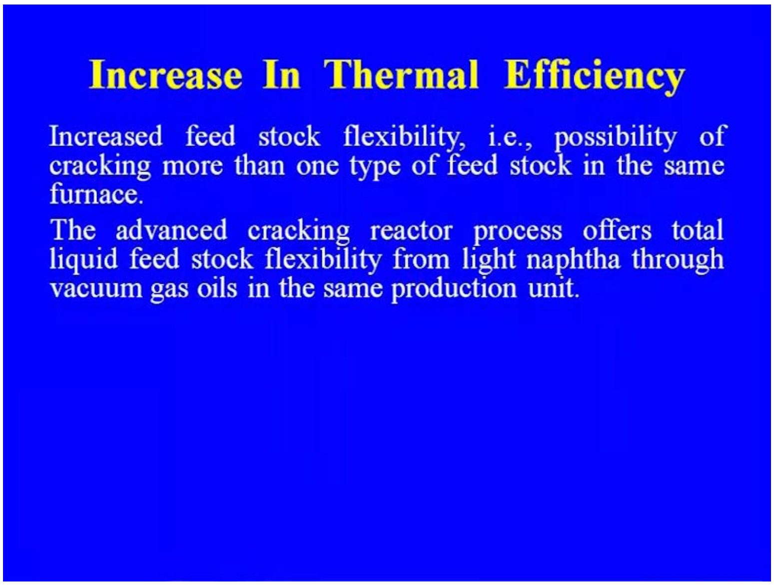

Increase In Thermal Efficiency

Increased feed stock flexibility, i.e., possibility of cracking more than one type of feed stock in the same furnace.

The advanced cracking reactor process offers total liquid feed stock flexibility from light naphtha through vacuum gas oils in the same production unit.

Increased feed stock flexibility, which I told you that has been one of the acculitive again development in the furnaces if possibility of cracking more than one type of the feed stock in the same furnace. The advanced cracking reactor a CR, which you call the process offer total liquid feed stock flexibility from light naphtha through the vacuum gas oil in the same production unit. So, this is the as I told the gas and naphtha, now we are talking about the naphtha and the gas oil both can be cracked in the same furnace with a better efficiency.

So, this was the about the naphtha the gas cracking which is the heart of the petro chemicals complex and the large number of the important product you are getting specially the olefins and the pyrolysis gasoline as a complementary. So, in the process as I told the separation of the C 4 C 5 gases because so far the ethylene and propylene is that is there main product. So, many of the refinery are there they are not separating the various bi product; one is the but adiene, another is the your isobutylene or it may be the butane 1 butane 2 isobutene, all the product that you are getting there in case of the because now the requirement of the MTV, they are oxygenate are the team are the requirement isoprene for a manufacture are the butadiene for the rubber manufacture is there. So, we can go for the separation of the C 4 C 5 gases which will be discussing in the next lecture that is on the upgradation of the C 4 C 5 gases of the naphtha cracker or the steam cracker and the F C C.