Technologies for Clean and Renewable Energy Production
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Lecture-18
Residue Upgradation 2

Hi friends now we will start discussion on the topic Residue Upgradation. This is the part 2 of residue of gradation. In the part 1 we have discussed how the vacuum residue can be upgraded to liquid fuels, which is and how to make the products more cleaner.

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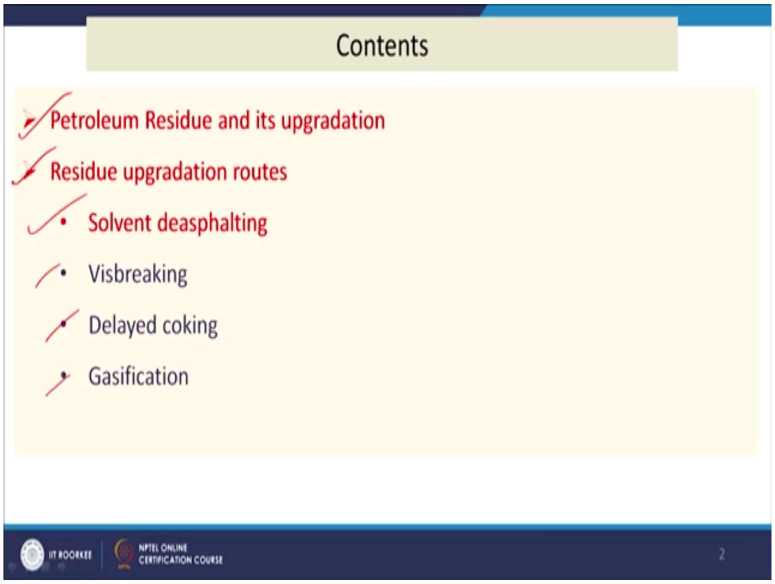

Contents

- Petroleum Residue and its upgradation
- Residue upgradation routes
  - Solvent deasphalting
  - Visbreaking
  - Delayed coking
  - Gasification

And basically we have discussed on solvent deasphalting process and in this class we will discuss on visbreaking, delayed coking and gasification. If we think the term visbreaking it itself indicates the viscosity breaking. So in this process will apply heat and the vacuum residue will be converted to lighter fractions with lower viscosity than the here.

And it will also have another part that is more viscous part that the residue and that can be processed further through the delayed coking. And in this viscosity breaking process we will be applying moderate condition so that the asphaltenes and resins which are available in this will not convert into coke. So, moderate conditions is needed in this method as our target product is the liquid product or lighter products with lower viscosity.

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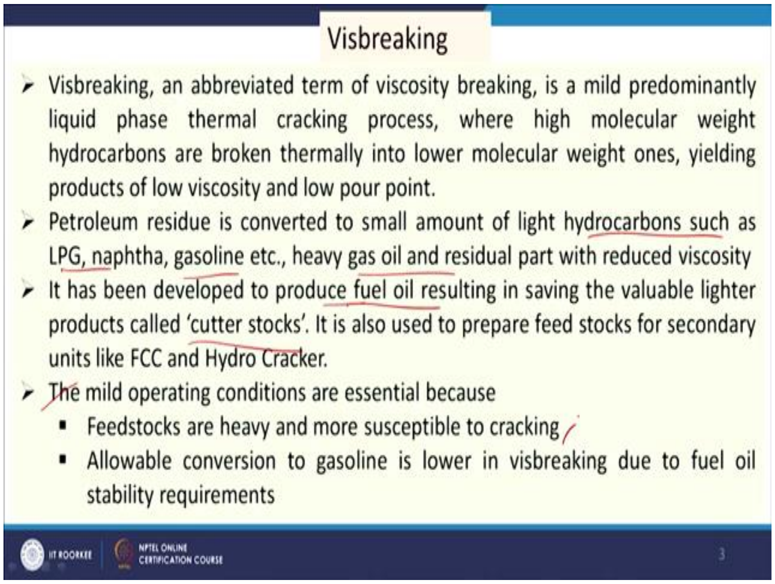

Visbreaking

- Visbreaking, an abbreviated term of viscosity breaking, is a mild predominantly liquid phase thermal cracking process, where high molecular weight hydrocarbons are broken thermally into lower molecular weight ones, yielding products of low viscosity and low pour point.
- Petroleum residue is converted to small amount of light hydrocarbons such as LPG, naphtha, gasoline etc., heavy gas oil and residual part with reduced viscosity
- It has been developed to produce fuel oil resulting in saving the valuable lighter products called 'cutter stocks'. It is also used to prepare feed stocks for secondary units like FCC and Hydro Cracker.
- The mild operating conditions are essential because
  - Feedstocks are heavy and more susceptible to cracking
  - Allowable conversion to gasoline is lower in visbreaking due to fuel oil stability requirements

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And this process can give us hydrocarbons like LPG, naphtha, gasoline, heavy gas oil etcetera and by this method we are getting some lighter from the residual part. So if I think about our fuel oil so the blending of fuel oil is reduced. The oil which is produced through this process thus that can be used as fuel oil and the mild operating conditions as I have mentioned it is required because the materials which are available in the residue is susceptible to heat.

And in this method allowable conversion to gasoline is lower due to fuel oil stability requirements. So this is about the basics of visbreaking process. Now we will see the mechanism what actually happens. As we have discussed that visbreaking is the thermal treatment. So in this case cracking will take place. So the mechanism will be based on free radical just like the thermal cracking we have discussed in the previous classes.

So will be having here three steps: One is initiation another is propagation and then we have termination step.

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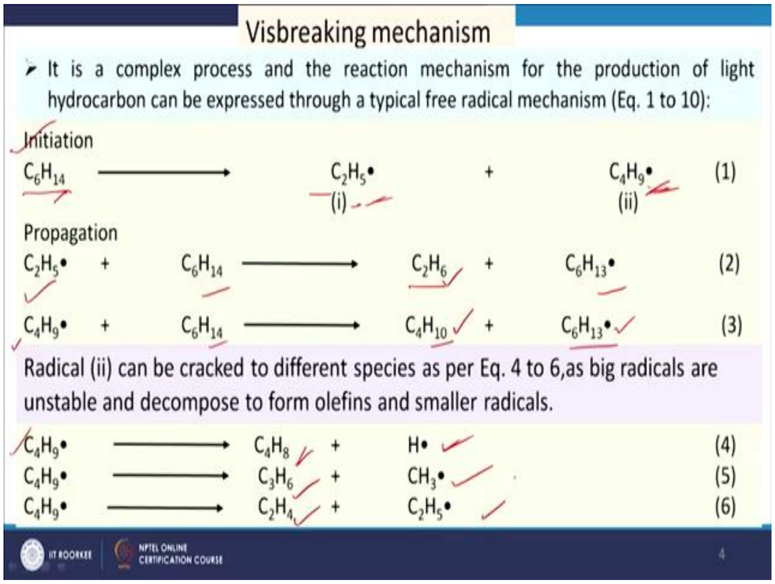

Visbreaking mechanism

- It is a complex process and the reaction mechanism for the production of light hydrocarbon can be expressed through a typical free radical mechanism (Eq. 1 to 10):

Initiation

$$C_6H_{14} \longrightarrow \underset{(i)}{C_2H_5\bullet} + \underset{(ii)}{C_4H_9\bullet} \quad (1)$$

Propagation

$$C_2H_5\bullet + C_6H_{14} \longrightarrow C_2H_6 + C_6H_{13}\bullet \quad (2)$$

$$C_4H_9\bullet + C_6H_{14} \longrightarrow C_4H_{10} + C_6H_{13}\bullet \quad (3)$$

Radical (ii) can be cracked to different species as per Eq. 4 to 6,as big radicals are unstable and decompose to form olefins and smaller radicals.

$$C_4H_9\bullet \longrightarrow C_4H_8 + H\bullet \quad (4)$$

$$C_4H_9\bullet \longrightarrow C_3H_6 + CH_3\bullet \quad (5)$$

$$C_4H_9\bullet \longrightarrow C_2H_4 + C_2H_5\bullet \quad (6)$$

So for example we have one initiation step if say C_6H_{14} so that will be producing C_2H_5 dot and $C_4H_9^*$. So these two radicals, free radicals are produced first one is lower molecular weight another is higher molecular weight with respect to this one. Now this is the initiation step then these free radical productions will propagate and more number of free radicals we will get and then ultimately those will combine and it will be terminated.

So $C_2H_5^*$ which you are getting here that can again react with C_6H_{14} and it can give us C_2H_6 hydrocarbon lower hydrocarbon and again $C_6H_{13}^*$ another bigger free radical. So this $C_4H_9^*$ free radical can give us again react with C_6H_{14} and give us $C_4H_{10} + C_6H_{13}^*$ free radical. So we are getting basically lower molecular weight hydrocarbon and the higher free radicals. So those $C_4H_9^*$ this can give us $C_4H_8 + H^*$ free radical.

So this free radical again giving us some hydrocarbon and giving us some free radical. In this case H in this case $C_3H_6 + CH_3^*$ and then C_2H_4 and $C_2H_5^*$. So there are possibilities of production of number of hydrocarbons, types of hydrocarbons and also the free radicals of lower size.

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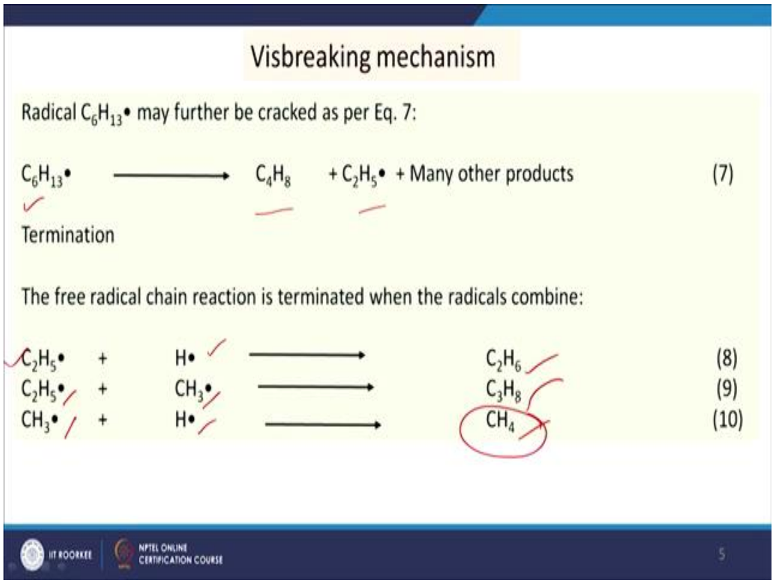

Visbreaking mechanism

Radical $C_6H_{13}\bullet$ may further be cracked as per Eq. 7:

$$C_6H_{13}\bullet \longrightarrow C_4H_8 + C_2H_5\bullet + \text{Many other products} \quad (7)$$

Termination

The free radical chain reaction is terminated when the radicals combine:

$$C_2H_5\bullet + H\bullet \longrightarrow C_2H_6 \quad (8)$$
$$C_2H_5\bullet + CH_3\bullet \longrightarrow C_3H_8 \quad (9)$$
$$CH_3\bullet + H\bullet \longrightarrow CH_4 \quad (10)$$

So this similarly $C_6H_{13}^*$ can give us C_4H_8 + $C_2H_5^*$ dot plus many other products. Then in termination the free radicals can add with H^* dot and then it will give up C_2H_6 so to another free radical $C_2H_5^*$ + CH_3^* dot it can give a C_3H_8 and it can CH_3^* dot + H^* dot gives CH_4. So we can get some gas also in this process. And these are all gas molecules in this. So LPG type of material we can get from the visbreaking process.

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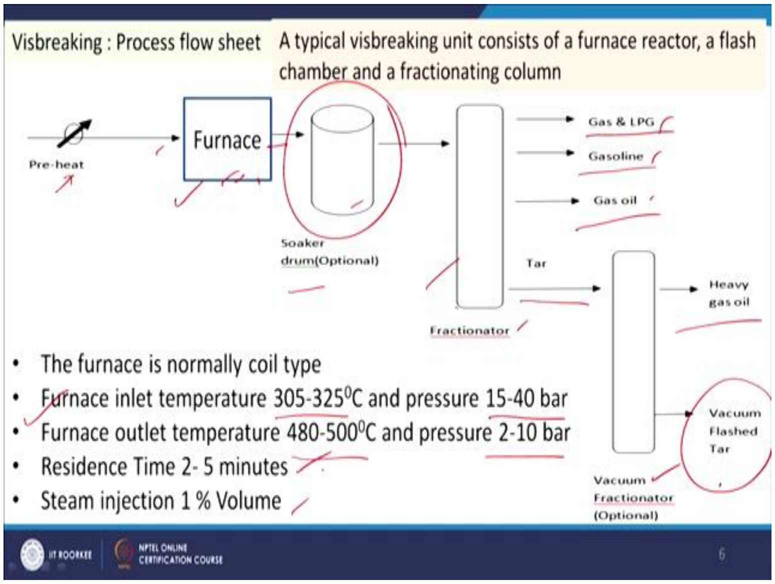

Visbreaking : Process flow sheet

A typical visbreaking unit consists of a furnace reactor, a flash chamber and a fractionating column

- The furnace is normally coil type
- Furnace inlet temperature 305-325⁰C and pressure 15-40 bar
- Furnace outlet temperature 480-500⁰C and pressure 2-10 bar
- Residence Time 2- 5 minutes
- Steam injection 1 % Volume

Now we will see the process flow sheet of the visbreaking process. So what we need? We have to apply heat. So what will be happening? In the previous class we have discussed that Maltane phase and asphaltene phase, resins and asphaltene are dispersed in the maltene phase. So by the application of heat the maltane phase will be broken and asphaltenes will settle, so that is the mechanism.

So you have to apply heat and we can apply heat in two mode. One for very small period and relatively high temperature and another is relatively lower temperature and for a longer period. But whatever may be the mode we apply but basically we need one furnace. We have to heat it here and then we have to flash it. So you have to flash it means we have to use this in high pressure.

So high pressure at furnace that the product pressure will be reduced and then it will go to flash chamber and from flash chamber it will go to the fractionator and from fractionator we will get different products, gas and liquid products here and ultimately the tar will come here for further distillation. And it is another vacuum fractionator you can it can come. So in the vacuum we will create some vacuum and we will get more heavy gas oil in this case.

And this will be vacuum flashed tar and this will be the feedstock for delayed coking. Now as I told that there will be two mode of operation one is very relatively longer period and the lower temperature. So in this case furnace and fractionator we put one soaker drum. So soaker gives some time at relatively lower temperature for the conversion process. So initially we preheat the feed here the initial ambient temperature to some preheated temperature.

Then it is coming to furnace so it is heated further and then for a very small time in the furnace it, it stays and then it goes to soaker. And relatively more longer period it stays here and then it is goes to flash drum fractionator and in this case the soaker drum is optional otherwise we can use here some coil visbreaking. There is no soaker coil visbreaking is there from furnace it is through the furnace coil for small span of time relatively higher temperature.

So that way also some fractionations will be there and we will get different products but will may, the products may vary in their quality and the relative amount may change to some extent. So in this case the furnace Inlet temperature is normally 305 to 325 degree centigrade here and then pressure is 15 to 40 bar and then outlet temperature it is coming here it is 480 to 500 degree centigrade and pressure reduction is there 2 to 10 bar.

So residence time is 2 to 5 minutes and steam injection is 1%. So 1% steam, steam is injected in this furnace. So this is the visbreaking process and as you have discussed that soaker drum helps to reduce the time in the furnace.

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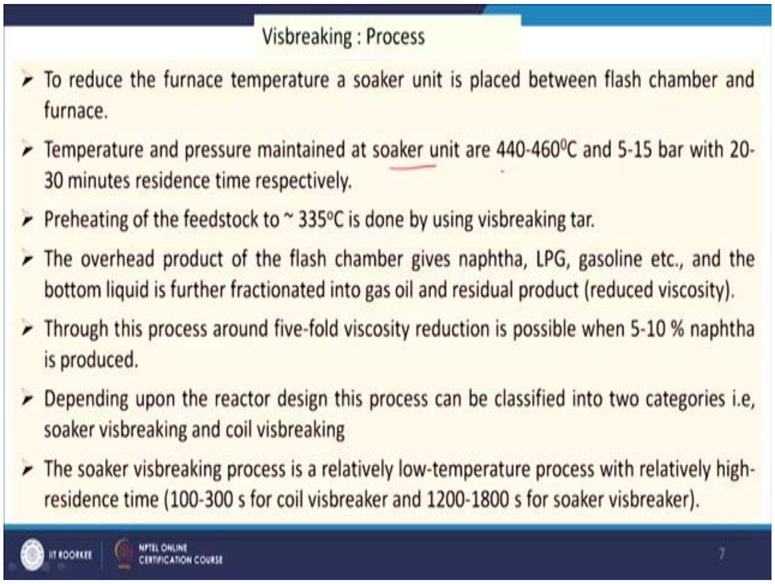

Visbreaking : Process

- To reduce the furnace temperature a soaker unit is placed between flash chamber and furnace.
- Temperature and pressure maintained at soaker unit are 440-460^{0}C and 5-15 bar with 20-30 minutes residence time respectively.
- Preheating of the feedstock to ~ 335^{0}C is done by using visbreaking tar.
- The overhead product of the flash chamber gives naphtha, LPG, gasoline etc., and the bottom liquid is further fractionated into gas oil and residual product (reduced viscosity).
- Through this process around five-fold viscosity reduction is possible when 5-10 % naphtha is produced.
- Depending upon the reactor design this process can be classified into two categories i.e, soaker visbreaking and coil visbreaking
- The soaker visbreaking process is a relatively low-temperature process with relatively high-residence time (100-300 s for coil visbreaker and 1200-1800 s for soaker visbreaker).

So temperature and pressure maintained at soaker unit is around 440 degree to 460 degree centigrade and 5 to 15 bar with 20 to 30 minutes residence time and preheating of the feedstock that 335 degree centigrade is done by using visbreaking tar. So this preheating which we are that is done basically this visbreaking tar which is obtained with some part of it is used for heating this.

And as I told that there are two mode one is soaker mode another is your we have your coil mode. So soaker mode visbreaking process is relatively low temperature process with high residence time. So here we have told that; 20 to 30 minutes. So it is around 1200 to 1800 second whereas in coil mode this is 100 to 300 seconds. So in the soaker mode of visbreaking 2 stages conversion we get, one minor degree of conversion of short period in the furnace and majority conversion takes place in the soaker unit for predetermined extended period that 20 to 30 minute.

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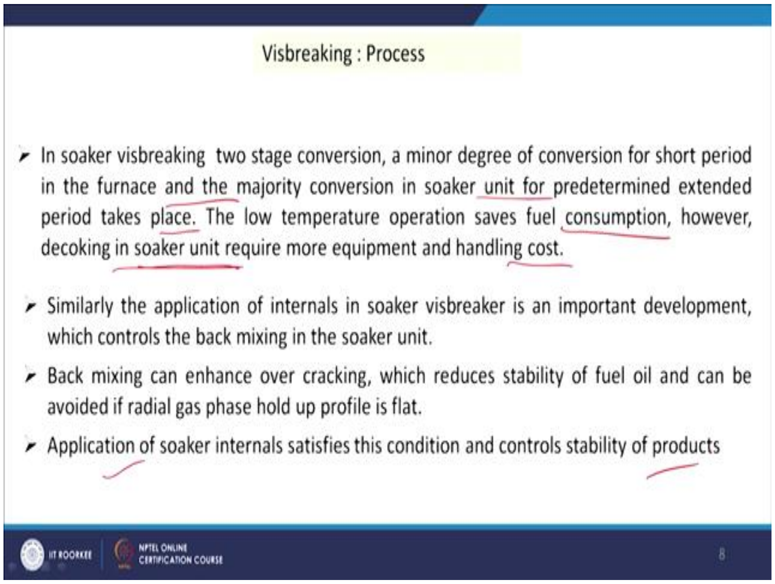

Visbreaking : Process

- In soaker visbreaking two stage conversion, a minor degree of conversion for short period in the furnace and the majority conversion in soaker unit for predetermined extended period takes place. The low temperature operation saves fuel consumption, however, decoking in soaker unit require more equipment and handling cost.
- Similarly the application of internals in soaker visbreaker is an important development, which controls the back mixing in the soaker unit.
- Back mixing can enhance over cracking, which reduces stability of fuel oil and can be avoided if radial gas phase hold up profile is flat.
- Application of soaker internals satisfies this condition and controls stability of products

As we are able to perform the conversion at lower temperature so we can save fuel consumption. However, decoking in soaker unit require more equipment and handling cost so one way we are using less energy but we are also passing other problem that decoking in soaker requires more equipment and handling cost. So this is that drawback and this drawback the coke formations in the unit that can be reduced by using some internals.

So if there is some back mixing in the soaker then there will be more coke formations. But if you can reduce the back mixing then the coke formations will be reduced so that way internals has been used. So internal helps to reduce the coke formations in the soaker. And application of soaker internals satisfies these conditions and control stability of products. Now we will compare the different soaker with internal and without internal.

What will be the difference between these two processes? So if we compare the temperature then we see 420 420.

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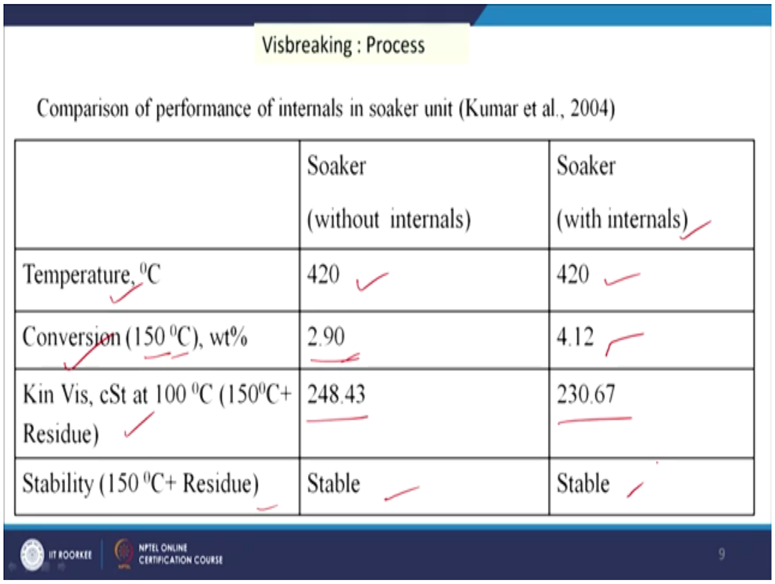

Visbreaking : Process

Comparison of performance of internals in soaker unit (Kumar et al., 2004)

	Soaker (without internals)	Soaker (with internals)
Temperature, ^{0}C	420	420
Conversion (150 ^{0}C), wt%	2.90	4.12
Kin Vis, cSt at 100 ^{0}C (150^{0}C+ Residue)	248.43	230.67
Stability (150 ^{0}C+ Residue)	Stable	Stable

In both the cases temperature is similar but if we are seeing about the conversion then we get 2.90% of the liquid fractions at 150 degree centigrade. So the liquid with the boiling point of 150 degree centigrade is 2.90% whether it is for internal it is 4.12 percent. So more liquid we are getting here in case of soaker internals, soaker with internals. And then kinetic viscosity if we take, then, it is 248.43 cSt whereas it is 230.67 cSt.

So viscosity is lower in case of soaker internal because it is it is preventing the coke formations and back mixing in a soaker unit. And then stability, both are stable. So that weight is very clear to us that if we use the soaker internals then the quality of the product will be improved. Next we will discuss on the delayed coking. So the term indicates that coking will take place and it will be delayed.

That means there will be some arrangement some more time will be given for the coke formation. So as we have discussed in the visbreaking part that application of it breaks the maltene phase and then we get the separation of the asphaltenes from the colloidal suspension of the vacuum residue or residual part. So here also the same mechanism will work if we apply heat then the Maltene phase will be broken and again the asphaltenes and resins will precipitate and they will get the coke.

If we get sufficient time so that part will give us coke. Another type may also be possible that when we are getting the at higher temperature if we increase the temperature we will be getting more vapors from it also and then that vapors may if contains more aromatics etcetera so those will be polymerized. And if some condition is maintained it can also give us coke. So coke formation by both ways by the first one that is cracking of the maltanes.

And then then the breaking of the emulsions and settling of the asphaltanes as well as the production of aromatics vapours and then the polymerization of those and then condensation and then then also give us some coke. And these two cokes which we can get by these two mechanisms the quality will be different the asphaltene and resins, which will produce the coke that will be amorphous in nature.

And not of that high quality but, when the aromatics are condensed and polymerized and condensed and gives this product, the coke that is crystalline in nature and having some good properties and it is considered as premium grade coke, coke or needle coke.

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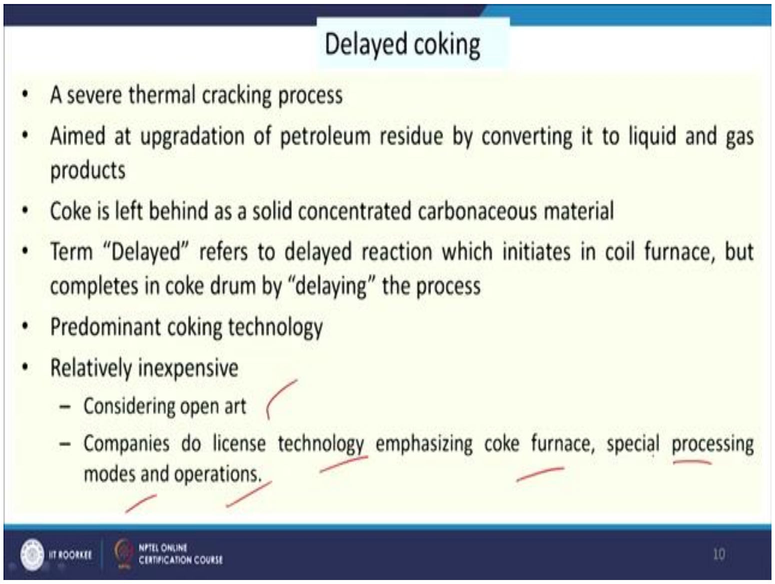

Delayed coking

- A severe thermal cracking process
- Aimed at upgradation of petroleum residue by converting it to liquid and gas products
- Coke is left behind as a solid concentrated carbonaceous material
- Term “Delayed” refers to delayed reaction which initiates in coil furnace, but completes in coke drum by “delaying” the process
- Predominant coking technology
- Relatively inexpensive
  - Considering open art
  - Companies do license technology emphasizing coke furnace, special processing modes and operations.

Now we will see how to get it. So this this delayed coking technology particularly, for the needle coke production is an, it is an art and the combination of art and technology. And already this delayed coke technology is an open art, it is known to everybody. But companies do license technology emphasizing coke furnace, special processing modes and operations. So these are the area when the company varies from one to others among the technology licenses.

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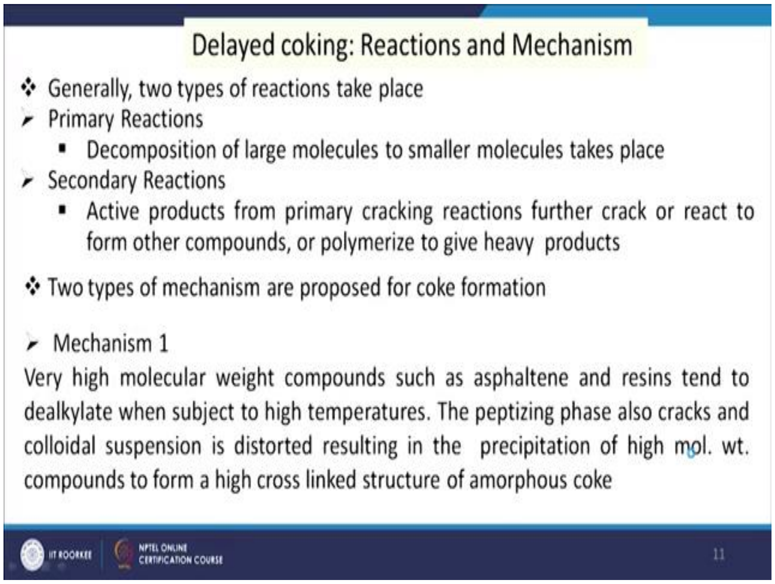

Delayed coking: Reactions and Mechanism

- Generally, two types of reactions take place
- Primary Reactions
  - Decomposition of large molecules to smaller molecules takes place
- Secondary Reactions
  - Active products from primary cracking reactions further crack or react to form other compounds, or polymerize to give heavy products
- Two types of mechanism are proposed for coke formation
- Mechanism 1

Very high molecular weight compounds such as asphaltene and resins tend to dealkylate when subject to high temperatures. The peptizing phase also cracks and colloidal suspension is distorted resulting in the precipitation of high mol. wt. compounds to form a high cross linked structure of amorphous coke

And they have more focus on these areas and in this case generally two types of reactions can take place one is your primary reactions and another is your secondary reactions. So primary reactions is your decomposition of large molecules into smaller molecules and then active compounds from the primary cracking reactions further crack or react to form other compounds or polymerized to give heavy products, already we have discussed.

And two types of mechanism also we have discussed that is one mechanism was for asphaltene precipitations and another was polymerization and condensation of parametric compounds. So it is very clear to us if our feedstocks has more aromatics then it will be giving better quality coke and this type of coke is called needle coke.

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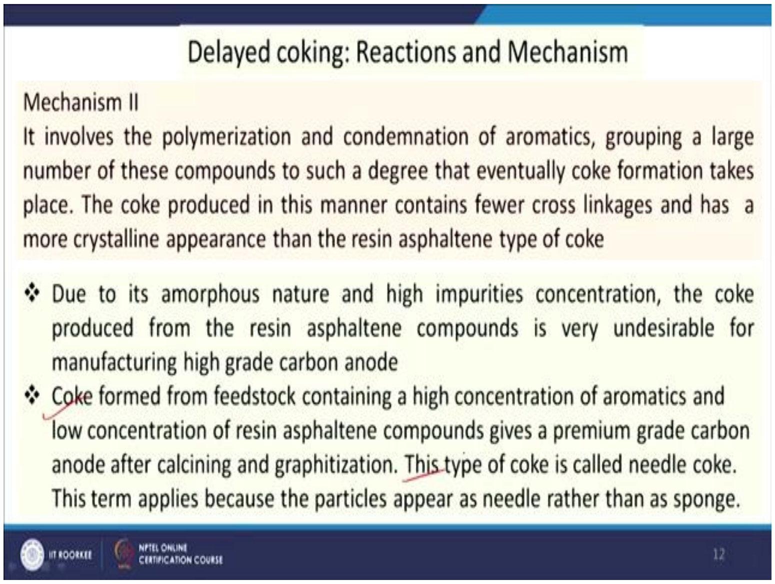

Delayed coking: Reactions and Mechanism

Mechanism II

It involves the polymerization and condemnation of aromatics, grouping a large number of these compounds to such a degree that eventually coke formation takes place. The coke produced in this manner contains fewer cross linkages and has a more crystalline appearance than the resin asphaltene type of coke

- ❖ Due to its amorphous nature and high impurities concentration, the coke produced from the resin asphaltene compounds is very undesirable for manufacturing high grade carbon anode
- ❖ Coke formed from feedstock containing a high concentration of aromatics and low concentration of resin asphaltene compounds gives a premium grade carbon anode after calcining and graphitization. This type of coke is called needle coke. This term applies because the particles appear as needle rather than as sponge.

This term applies because the particles appear in the form of needle in the; it is the crystal structure it has and the crystals are appeared like needles so that is why it is called needle coke. And we see what are the typical feedstock for this vacuum residue, delayed coking?

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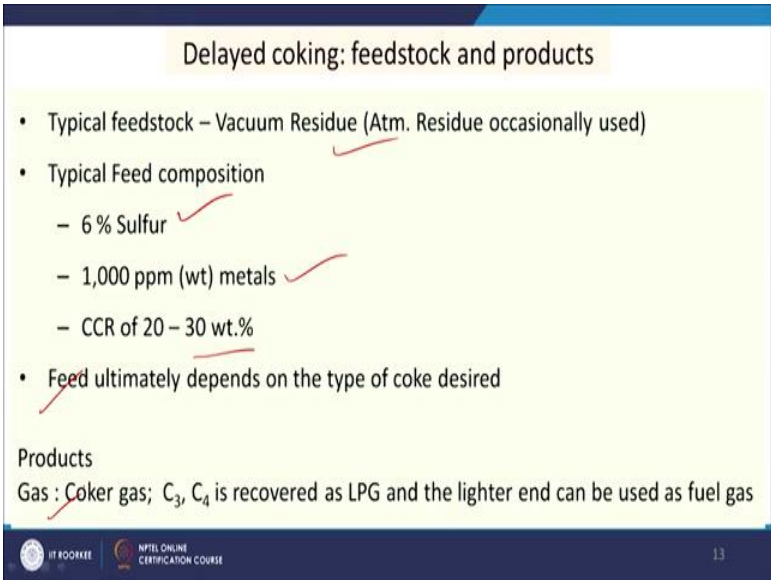

Delayed coking: feedstock and products

- Typical feedstock – Vacuum Residue (Atm. Residue occasionally used)
- Typical Feed composition
  - – 6 % Sulfur
  - – 1,000 ppm (wt) metals
  - – CCR of 20 – 30 wt.%
- Feed ultimately depends on the type of coke desired

Products

Gas : Coker gas; C_3, C_4 is recovered as LPG and the lighter end can be used as fuel gas

So for delayed coking the typical feedstock is vacuum residue. Atmospheric residue can also be used in some cases and typical feed composition if we see 6% sulphur it contains and 1000 ppm metals and CCR 20 to 30%. The CCR, Conradson carbon ratio higher the CCR value obviously we will get higher coke. And what type of feed we will use that will influence the product quality. And what type of products we can get for through these delayed coking?

We can get gaseous products, we can get liquid product and we can get solid product. So gas products which we can get that is a Coker gas that contains C_3, C_4 and this is recovered as LPG and lighter can be used as fuel gas.

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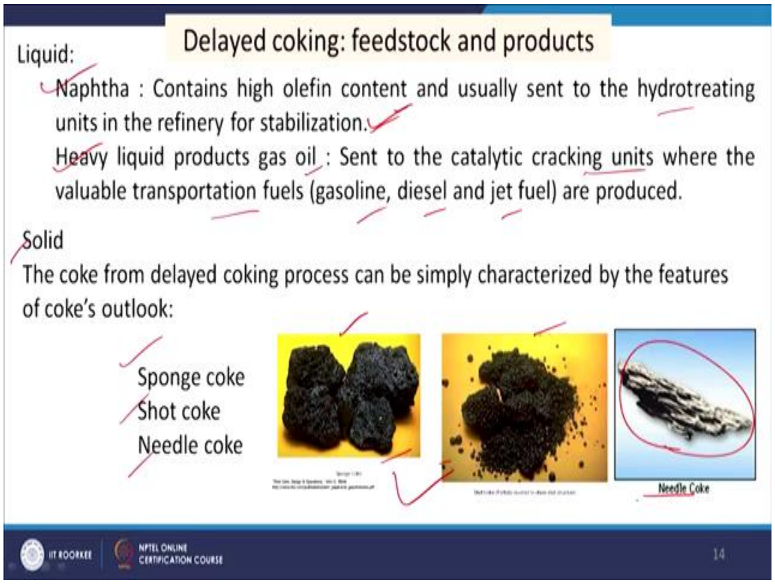

Delayed coking: feedstock and products

Liquid:

Naphtha : Contains high olefin content and usually sent to the hydrotreating units in the refinery for stabilization.

Heavy liquid products gas oil : Sent to the catalytic cracking units where the valuable transportation fuels (gasoline, diesel and jet fuel) are produced.

Solid

The coke from delayed coking process can be simply characterized by the features of coke's outlook:

- Sponge coke
- Shot coke
- Needle coke

And then liquid; liquid part can contain naphtha or heavy liquid products gas oil. So naphtha and gas oil, these two products we can get from this delayed coking and this naphtha contains high olefin content and usually sent to the hydrotreating units in the refinery for stabilizations. In the previous slides, we have discussed the mechanism and we have seen that olefins are formed. So those olefins are present in it.

So it requires more hydrogenation and sent to hydrotreating units in the refinery for its upgradation. And heavy liquid products that is gas oil we are getting from it that that is sent to catalytic cracking units where the valuable transportation fuels like gasoline, diesel and jet fuel can be produced. So, this is our liquid product and solid product we can get different types of coke.

So coke may be a sponge coke it may be of shot coke and it may be of needle coke. So here, we see needle coke. So this is a crystalline structure whereas this shot cook and your sponge coke we are not getting any crystal structure. Here this is a spongy sponge coke spongy appearance and this very small particles we are getting here for shot coke. So these among these three types of coke through these two cokes that is your sponge coke and short coke those are not of that high quality.

And those can be used for the production of electricity in combustion or in gasification plant. And then this needle coke is superior quality premiere grade coke and it apart from these thermal applications it has more attractive applications that is as electrode. So it can be used as electrode because of its some specific properties. So you see the characteristics of needle coke.

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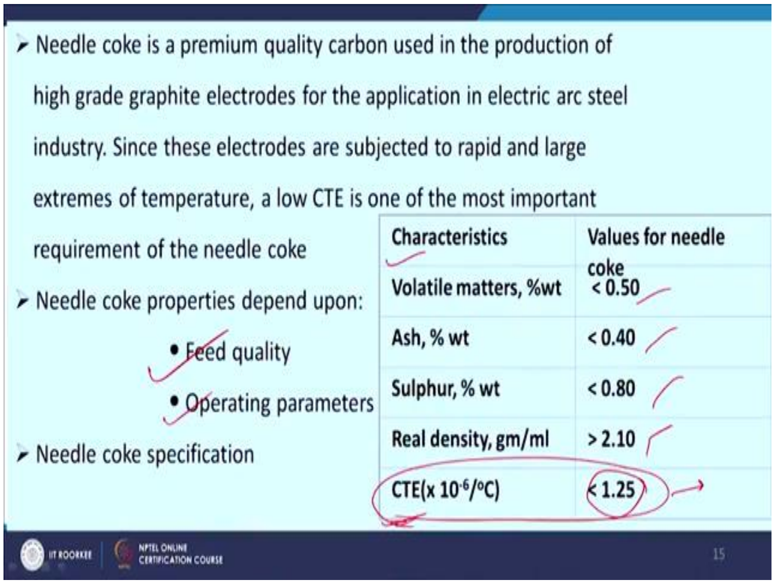

- Needle coke is a premium quality carbon used in the production of high grade graphite electrodes for the application in electric arc steel industry. Since these electrodes are subjected to rapid and large extremes of temperature, a low CTE is one of the most important requirement of the needle coke
- Needle coke properties depend upon:
  - Feed quality
  - Operating parameters
- Needle coke specification

Characteristics	Values for needle coke
Volatile matters, %wt	< 0.50
Ash, % wt	< 0.40
Sulphur, % wt	< 0.80
Real density, gm/ml	> 2.10
CTE(x 10^{-6}/°C)	< 1.25

So volatile matter is less than 0.50 percent and then ash content is less than 4% and sulfur is less than 0.8 percent and density is greater than 2 the densities around 2.1 gram per ml. But this is the property which is most important for needle coke that is CTE coefficient of thermal expansion into 10 to the minus 6 per degree centigrade it is 1.25 so that is 1.25 x 10 to the power of minus six per degree centigrade, because of this low CTE value it is used as electrode.

And needle coke production whether the needle coke will be produced or other type of coal will produce will be produced during delayed coking process that will depend upon some factors. One is your feed quality and other is your operating parameters. So more the aromatic contents in the feed we it is expected that the needle coke will get and the quality will also improve.

And operating condition is also very, very important as I told that delayed coking is also a blend of art and technology. So in this case also, needle coke can, quality needle coke quality can be improved by the practice or maintaining the operating parameters.

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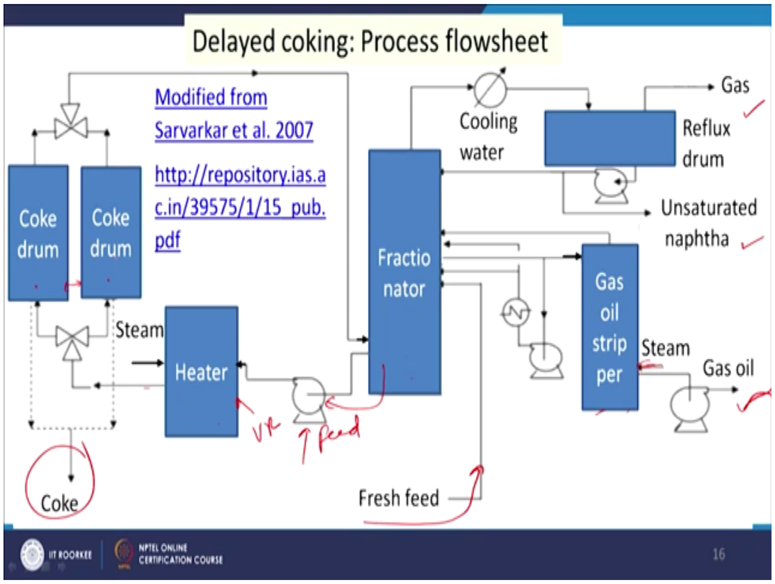

Delayed coking: Process flowsheet

Modified from Sarvarkar et al. 2007

http://repository.ias.ac.in/39575/1/15_pub.pdf

Now we will see the delayed coking process flows sheet. So here we have some feed so you are giving some feed here. So this feed it is going to heater it is heated up so it will be taking the cracking will take place here where we are putting heat here. So heat it up then it is going to coke drum. So in this heater also we add some amount of steam. So steam is also added here.

So steam and a small amount of steam and then residue this is equal to VR so VR and this it is heated and then it is going to coke drum. So, high temperature here and here pressure is applied and then longer period the coke stays here that is it is called coke drum, so when it is after heating the VR and steam it is going to this the coke drum. It is remaining here under high pressure at high temperature, then, vapours are going out then it is going for the fractionation.

So after fractionation we will get different products we can get gas, we can get unsaturated naphtha here and we can get some middle product also. So gas oil, stripper and then we will get steam and we like we will send steam here for its heating and then we will get gas oil. So that we are getting gas oil here and we are getting some Fresh feed also we are adding in this case. So fresh feed and this vapour which is coming it is fractionated and the bottom part is again taken here.

So this is the feed mixed feed actually it is taken and sent into the heater and then it is going to Coke drum. And then it is the vapour pass and it is condensed and then we are getting different products. This is for liquid and gas recovery from this but we getting coke from this coke drum will get the coke after certain time will collect the coke from the coke drum. So this is the process for the delayed coking where we can get coke we can get gas and we can get different types of liquid.

Now how we can change the distribution of this product? Because unlike visbreaking, in visbreaking our main focus was to get more liquid and here our focus is also positively to get liquid and gas as well as that coke also of premiere quality coke that is of needle coke. If we can get needle coke then this process will be more economic so that is the one of the main objective of the delayed coking unit.

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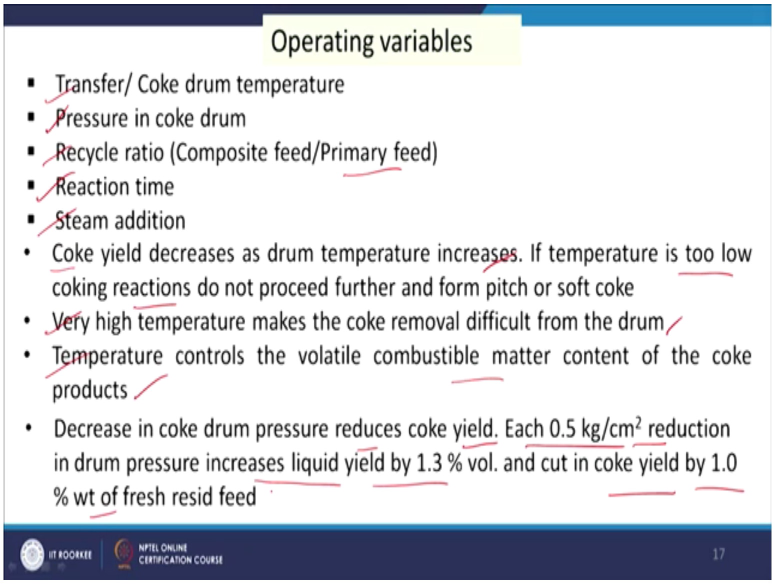

Operating variables

- Transfer/ Coke drum temperature
- Pressure in coke drum
- Recycle ratio (Composite feed/Primary feed)
- Reaction time
- Steam addition
- Coke yield decreases as drum temperature increases. If temperature is too low coking reactions do not proceed further and form pitch or soft coke
- Very high temperature makes the coke removal difficult from the drum
- Temperature controls the volatile combustible matter content of the coke products
- Decrease in coke drum pressure reduces coke yield. Each 0.5 kg/cm^2 reduction in drum pressure increases liquid yield by 1.3 % vol. and cut in coke yield by 1.0 % wt of fresh resid feed

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So what are the factors that will influence the quality of different products and its relative distribution of the products? That is the some operating variables are transfer of coke drum temperature, what is the coke drum temperature? I am maintaining that will influence how much gas is produced how much coke is produced how much liquid is produced and what is the pressure that also influence.

And recycle ratio that means that I have shown you that we are adding some free fresh feed and then we are taking this one so fresh feed and VR how we are taking that composite feed and primary feed that is the ratio is called your recycle ratio so that also influence the quality of the products and the reaction time. How much time I am giving in the furnace and how much steam is added. It has been shown that if we increase the drum temperature then, coke yield decreases;

Because more cracking takes place and the more lighter parts goes off and if temperature is too low then coking reaction do not happen. So we have to select an optimum temperature in coke drum. And then very high temperature makes the coke removal difficult from the drum and temperature controls the volatile combustible metal content of the coke products. And then if we change the pressure of the coke drum.

If we increase the pressure then, we may get more condensation of the vapours into the coke, so coke yield will increase but we reduce the pressure then we will get more liquid product. So decreasing coke drum pressure reduces coke yield. So some data is given here each 0.5 kg per centimetre square pressure reduction in drum increases liquid yield by 1.3% by volume and cut in Coke or coke yield by 1.0 weight percent of fresh resid feed. So this is some data which is available in literature.

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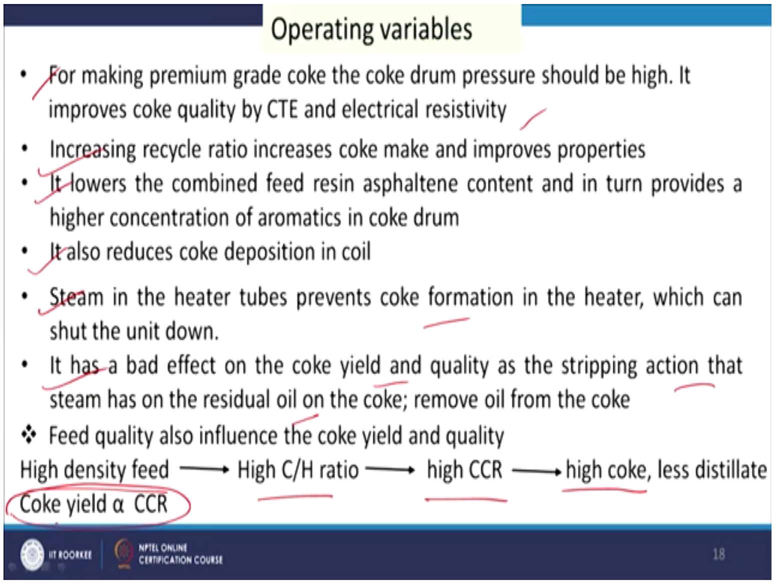

Operating variables

- For making premium grade coke the coke drum pressure should be high. It improves coke quality by CTE and electrical resistivity
- Increasing recycle ratio increases coke make and improves properties
- It lowers the combined feed resin asphaltene content and in turn provides a higher concentration of aromatics in coke drum
- It also reduces coke deposition in coil
- Steam in the heater tubes prevents coke formation in the heater, which can shut the unit down.
- It has a bad effect on the coke yield and quality as the stripping action that steam has on the residual oil on the coke; remove oil from the coke

❖ Feed quality also influence the coke yield and quality

High density feed → High C/H ratio → high CCR → high coke, less distillate

Coke yield α CCR

Then for making the premium grade coke, the coke drum pressure should be high. It improves coke quality and CTE and electrical resistivity. So, when we are increasing the pressure one way we are getting the more coke as well as the quality of premium grade coke is also better. And increasing recycle ratio increases coke make and improves properties because it lowers the asphaltene in the feed. More fresh feed we are using that means the asphaltene concentration is reduced.

So that is why quality of the product improves it also reduces coke deposition in coil. Now we use some steam. What is the role of steam? Steam in the heated tubes prevents coke formation, so coke formation does not take place. Otherwise you have to shut down the plant very frequently so that way the steam helps. But steam does not help to get good quality coke it has some negative impact on it.

It has a bad effect on the coke yield and quality as the stripping action that steam has on the residual oil on the coke. So we can summarize that high-density feed then it will give us high carbon by hydrogen ratio, it will give high CCR, it will give high coke, less distillate and less gas and coke yield is proportional to CCR.

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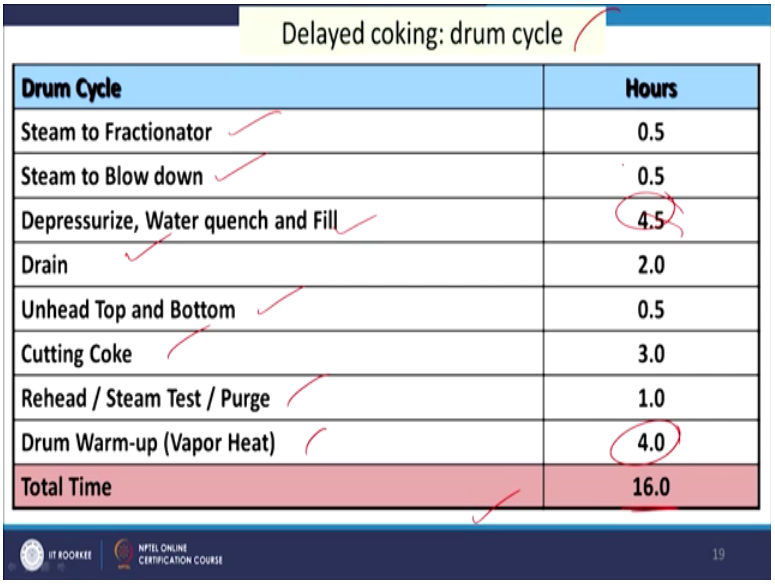

Delayed coking: drum cycle

Drum Cycle	Hours
Steam to Fractionator	0.5
Steam to Blow down	0.5
Depressurize, Water quench and Fill	4.5
Drain	2.0
Unhead Top and Bottom	0.5
Cutting Coke	3.0
Rehead / Steam Test / Purge	1.0
Drum Warm-up (Vapor Heat)	4.0
Total Time	16.0

Now delayed coking if we think that first it is heated in the furnace then you go to coke drum and then coke drum to vapour goes for fractionation the upper part and bottom part is we are getting them from the coke drum as a coke. So this is a cycle coke drum once it will fill then we have to replace the coke from the drum and again new drum has to be added. So if we think about the whole process it is it will require some time.

And in one drum cycle the time distribution is provided in this table. You see it has steam to fractionator then steam to blow down then depressurize then water quench and fill and drain unhead top and bottom and cutting coke and rehead, steam test, purge, drum warm-up. So we see the drum warm-up requires around 4:00 hour out of 16 hour. Then major part is here. Depressurize water quench and fill filling of the coke drum.

And the gradually it fills at a time the coke drum is not filled, it takes some time to fill. Then, we give some time for cutting of the coke. Coke cutting also takes some time and then other times as already say drain times also takes some two hours and others are given. Now, there are some empirical relationship to determine the coke yield. So if we know the properties of the feedstock then we can guess what will be the coke, amount of coke produced during the delayed coking process.

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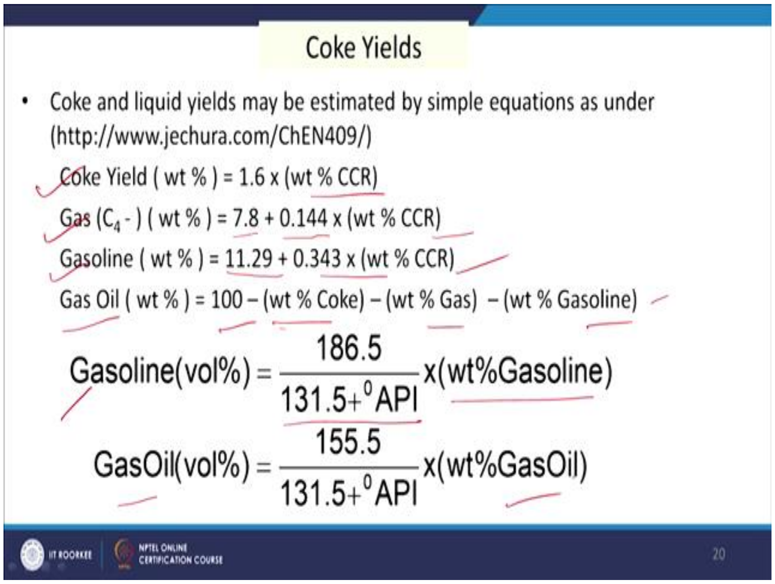

Coke Yields

- Coke and liquid yields may be estimated by simple equations as under (http://www.jechura.com/ChEN409/)

Coke Yield (wt %) = 1.6 x (wt % CCR)

Gas (C_4 -) (wt %) = 7.8 + 0.144 x (wt % CCR)

Gasoline (wt %) = 11.29 + 0.343 x (wt % CCR)

Gas Oil (wt %) = 100 – (wt % Coke) – (wt % Gas) – (wt % Gasoline)

$$\text{Gasoline(vol\%)} = \frac{186.5}{131.5+{}^{0}\text{API}} \text{x(wt\%Gasoline)}$$

$$\text{GasOil(vol\%)} = \frac{155.5}{131.5+{}^{0}\text{API}} \text{x(wt\%GasOil)}$$

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So coke yield in percentage basis =1.6 x CCR value in weight percent what is the CCR then 1.6 into that that will be the coke yield and gas that will be there is LPG, the 7.80 + 0.144 x CCR value and gasoline we can get this one 11.29 + 0.343 x CCR value in weight percent and gas oil will be 100 - this coke - gas - gasoline. That way we can calculate by mass balance.

Another formula gasoline, how much we can get 186.5/131.5 + degree API x weight percent of gasoline and then gas oil 155.5/131.5 + degree API x wt. percentage of gas oil. So, these are some expressions empirical expressions which are available in literature for the predictions of different types of products of the delayed coking unit. Now we are coming to gasification.

Already you have discussed many thing about the gasification in the previous classes and we have we have discussed that there are four types of gasifier basically 3, one is fluidized based and then fixed bed and entrained bed and the transfer reactor in between entrained and fledged weight. We have already discussed and we have also discussed that entrained bed gasifier is more suitable for feedstocks which is less reactive.

So what pet coke residue all those are not of that high reactive because it is coming the bottom product after high thermal treatment. So these products if we want to gasify we need a reactor like entrained bed gasifiers to handle this less reactive feedstock.

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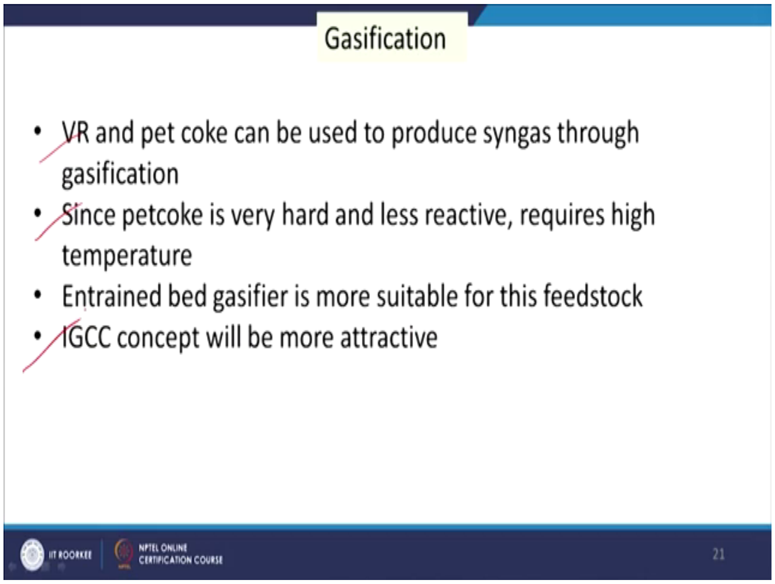

Gasification

- VR and pet coke can be used to produce syngas through gasification
- Since petcoke is very hard and less reactive, requires high temperature
- Entrained bed gasifier is more suitable for this feedstock
- IGCC concept will be more attractive

So now we see here VR and Pet coke can be used to produce in syngas through gasification and in entrained bed gasifiers will be most, more preferable and IGCC concept will be more attractive for the utilisation of this coke produced through the delayed coking unit. Now we will see some example of gasification plants based on this VR and pet coke. So around the world there are number of plants.

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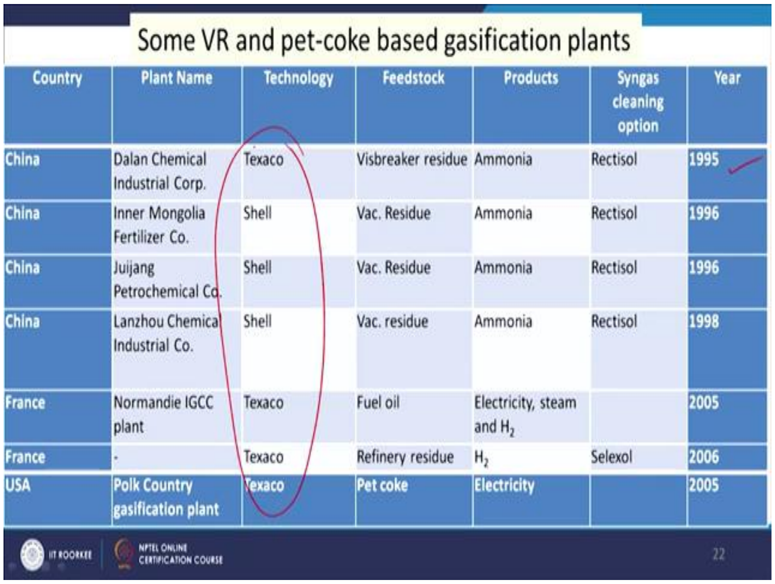

Some VR and pet-coke based gasification plants

Country	Plant Name	Technology	Feedstock	Products	Syngas cleaning option	Year
China	Dalan Chemical Industrial Corp.	Texaco	Visbreaker residue	Ammonia	Rectisol	1995
China	Inner Mongolia Fertilizer Co.	Shell	Vac. Residue	Ammonia	Rectisol	1996
China	Juijang Petrochemical Co.	Shell	Vac. Residue	Ammonia	Rectisol	1996
China	Lanzhou Chemical Industrial Co.	Shell	Vac. residue	Ammonia	Rectisol	1998
France	Normandie IGCC plant	Texaco	Fuel oil	Electricity, steam and H_2		2005
France	-	Texaco	Refinery residue	H_2	Selexol	2006
USA	Polk Country gasification plant	Texaco	Pet coke	Electricity		2005

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But these these technology gasification technology is not pretty old one for pet coke. You see it is started from 1995 and 2005 like this and most of the 5, 6 like this 1995.

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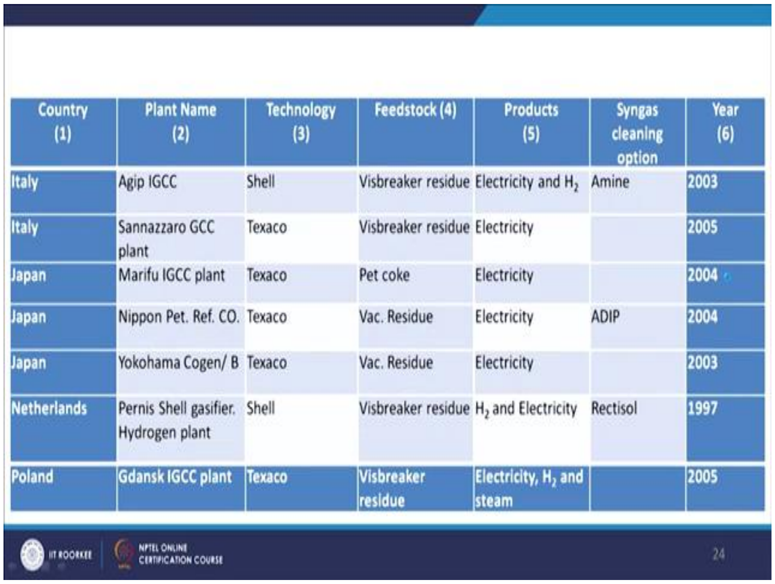

Country (1)	Plant Name (2)	Technology (3)	Feedstock (4)	Products (5)	Syngas cleaning option	Year (6)
Italy	Agip IGCC	Shell	Visbreaker residue	Electricity and H_2	Amine	2003
Italy	Sannazzaro GCC plant	Texaco	Visbreaker residue	Electricity		2005
Japan	Marifu IGCC plant	Texaco	Pet coke	Electricity		2004
Japan	Nippon Pet. Ref. CO.	Texaco	Vac. Residue	Electricity	ADIP	2004
Japan	Yokohama Cogen/ B	Texaco	Vac. Residue	Electricity		2003
Netherlands	Pernis Shell gasifier. Hydrogen plant	Shell	Visbreaker residue	H_2 and Electricity	Rectisol	1997
Poland	Gdansk IGCC plant	Texaco	Visbreaker residue	Electricity, H_2 and steam		2005

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And around the globe in many countries the gasification of vacuum residue and pet coke is implemented and applied. And if we see that all the reactors are basically Texaco and shell. So Texaco and shell means entrain bed reactors for all the cases.

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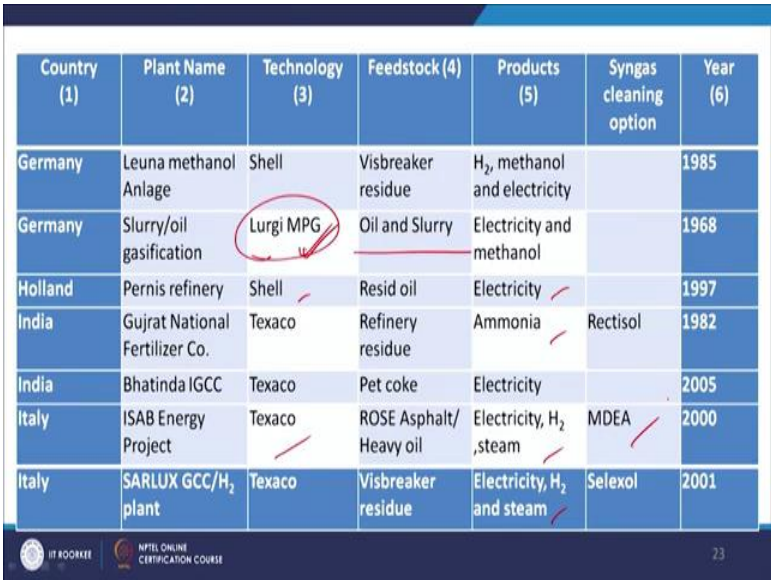

Country (1)	Plant Name (2)	Technology (3)	Feedstock (4)	Products (5)	Syngas cleaning option	Year (6)
Germany	Leuna methanol Anlage	Shell	Visbreaker residue	H_2, methanol and electricity		1985
Germany	Slurry/oil gasification	Lurgi MPG	Oil and Slurry	Electricity and methanol		1968
Holland	Pernis refinery	Shell	Resid oil	Electricity		1997
India	Gujrat National Fertilizer Co.	Texaco	Refinery residue	Ammonia	Rectisol	1982
India	Bhatinda IGCC	Texaco	Pet coke	Electricity		2005
Italy	ISAB Energy Project	Texaco	ROSE Asphalt/ Heavy oil	Electricity, H_2 ,steam	MDEA	2000
Italy	SARLUX GCC/H_2 plant	Texaco	Visbreaker residue	Electricity, H_2 and steam	Selexol	2001

Here only Lurgi MGP used but here it is oil and slurry. So Oil and slurry it is relatively reactive than the pet coke and residue. So that is your Lurgi reactor is applied but all other cases Texaco and Shell. And here we see electricity, ammonia, hydrogen, steam, methanol, synthesis all have been implemented and different types of syngas cleaning rectisol, selexol, MDEAs are used and Rectisol is mostly used.

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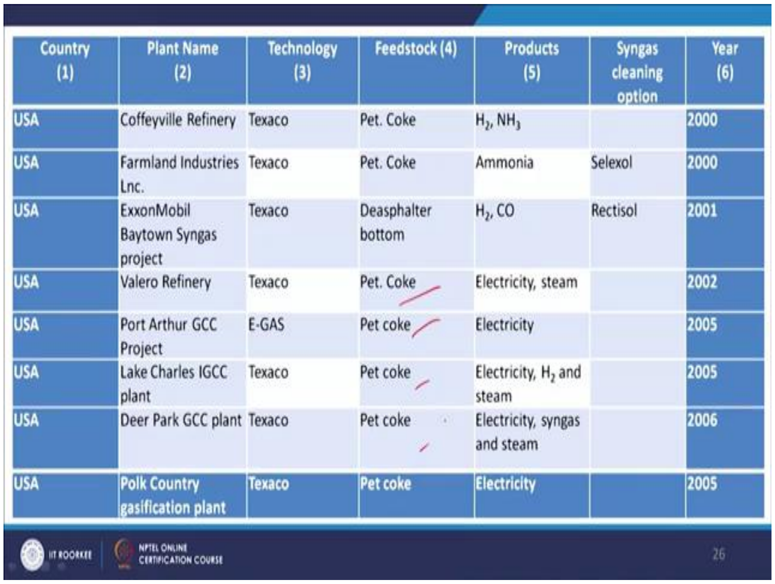

Country (1)	Plant Name (2)	Technology (3)	Feedstock (4)	Products (5)	Syngas cleaning option	Year (6)
USA	Coffeyville Refinery	Texaco	Pet. Coke	H_2, NH_3		2000
USA	Farmland Industries Lnc.	Texaco	Pet. Coke	Ammonia	Selexol	2000
USA	ExxonMobil Baytown Syngas project	Texaco	Deasphalter bottom	H_2, CO	Rectisol	2001
USA	Valero Refinery	Texaco	Pet. Coke	Electricity, steam		2002
USA	Port Arthur GCC Project	E-GAS	Pet coke	Electricity		2005
USA	Lake Charles IGCC plant	Texaco	Pet coke	Electricity, H_2 and steam		2005
USA	Deer Park GCC plant	Texaco	Pet coke	Electricity, syngas and steam		2006
USA	Polk Country gasification plant	Texaco	Pet coke	Electricity		2005

So, here else you see all the pet coke so pet coke has been used widely for the production of electricity. But those are of sponge coke and shot coke type of coke. But needle coke is not processed through this route. It has better applications as electrode so that way in this part we have seen how the vacuum residue can be converted to different liquid parts and the solid part also that we will be having more value than the conventional petroleum coke so up to this in this class. Thank you very much for your patience.