Chemical Technology
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Module - 6
Petroleum Refinery
Lecture - 4
Thermal Cracking Visbreaking and Delayed Coking

We are discussing the module 6 of the organic chemical technology course and in this we are discussing about the petroleum refining. The total 8 lectures are there in petroleum refining and already we have discussed 3 lectures. Today I will be discussing about the thermal cracking, vis breaking and delayed coking, that is one of the very important operations that are being done at petroleum refining industry.

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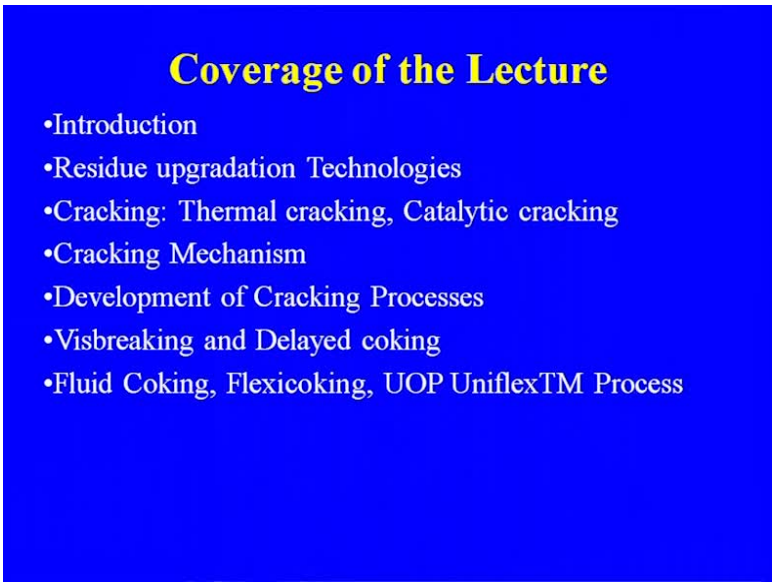

This will be the coverage of the lecture introduction, residue upgradation technology, cracking- thermal and catalytic cracking, where the brief of the about the process that will be given not in detail about the catalytic cracking, cracking mechanism, development of the cracking processes, vis breaking and delayed coking, which is now the most of the refining they are using, one of them and so we will be discussing in more detail about the vis breaking and delayed coking. Another about because there is lot of the development in case of the thermal cracking processes, so the fluid, flexi coking, U O

P uniflex process that has come and so we will be discussing just brief introduction about these processes also.

Let us come to already we had discuss about the distillation of the crude oil and the some introductive part of the petrol refining. So, as I discuss in the lecture 1 that we have the two major processes in the refining; one is the primary processes unit and the secondary process unit.

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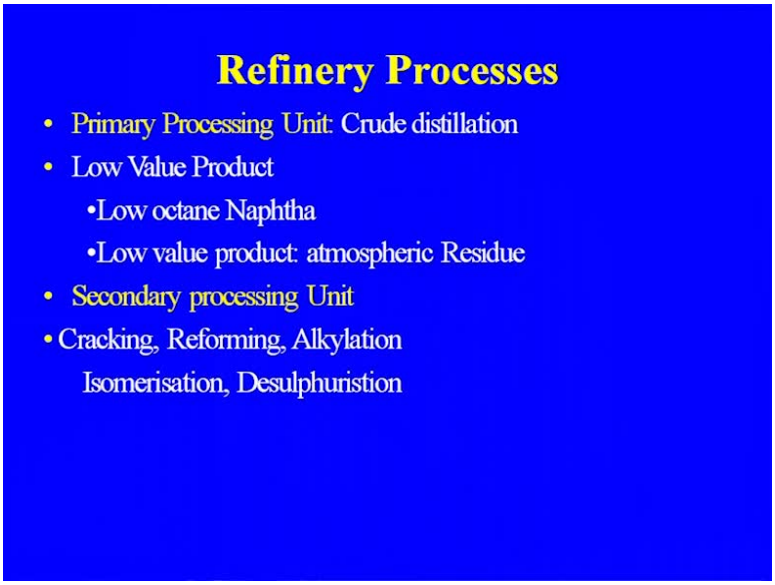

In the primary process unit what we are doing, we are doing the crude distillation, crude oil distillation and what is happening in case of the crude oil distillation? We are getting a number of the low value product which we cannot use as such and so the just to increase their importance or the value, what we are doing? We are going for the secondary conversion process. So, what is the low value product from the primary processing that is the low octane naphtha? This is not suitable and so, earlier it was going to the fertilizer plant and the, but some, but now the, because in most of the fertilizer plant they have shifted to natural gas.

So, the a naphtha, the low octane naphtha especially the light naphtha that we have, that is going for further processing to improve the octane number or some of the refinery they have gone for isomerization of low octane naphtha, low value product, which we are getting from the atmospheric column and the vacuum column also the vacuum distillation, we are getting the light vacuum oil and another stream of the (( )) vacuum oil

or the heavy vacuum oil. So, data has to be cracked, further that has to be processed to make it more value added. So, what are the secondary processes we are using in refinery that is the cracking?

Cracking of the heavy residue that may be thermal or catalytic cracking, reforming of the low octane naphtha to gasoline, so that the octane number will increase, alkylation, isomerization and desulphurization is just to remove the sulphur compound and sometimes the hydrodesulphurization that is being done just to improve the impurity. So, that the sulphur compound and nitrogen compound which are present there, then that may not poison the catalyst. So, these are some of the process.

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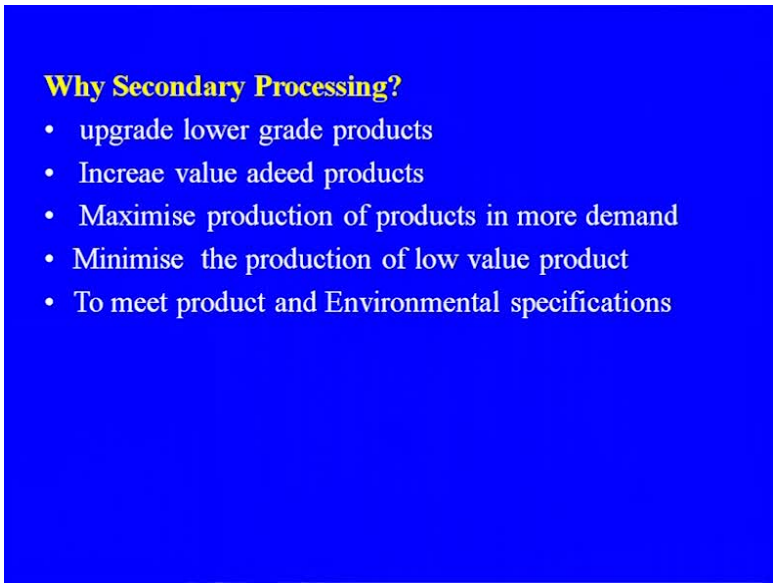

Let us now discuss about the thermal cracking, why secondary process? Why we are going for the thermal or catalytic cracking or reforming? Just to upgrade the lower grade product, increase the value added product, maximize the production of the products in more demand, and minimize the production of the low value product, because this is the earlier we started with only thermal cracking.

So, huge amount of the product that was available which was not having that was mostly just like as a fuel oil and so just to minimize the production of the low value product and as we know that we are more interested in the light distillation and middle distillate. So, our interest is to produce more and more, light distillation, middle distillate which is being used in some or other form to meet the product and the environmental

displacement specifications. Because you see the, as I told you earlier also that the octane number requirement that is increasing, so we have to further process the low octane naphtha.

Similar to the environmental constants are also there our environmental extenders are becoming more and more stringent, so removal of the sulphur that is important. So, that is the requirement to give the more value added product to meet the requirement from the environment point of view. So, some of the secondary process that is being done in we are having in the refinery.

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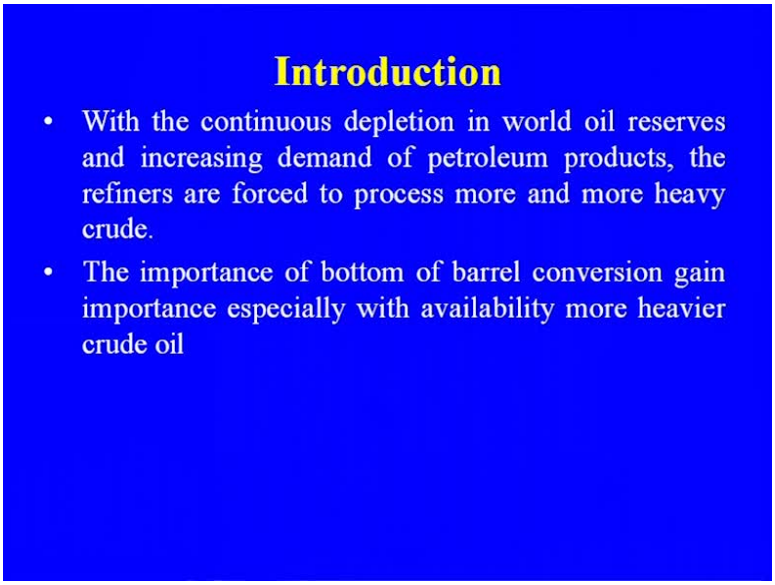

Now, let us come to the thermal cracking, with the continuous depletion in the world oil reserve and increasing demand of the petroleum products, the refiners are forced to process more and more, heavy crude, because I discuss earlier also that, now we are left with the more heavy crude, opportunity crude and we will have to process this. So, the importance of the bottom of barrel conversion gains importance especially with the availability of heavier crude oil and the opportunity crude oil.

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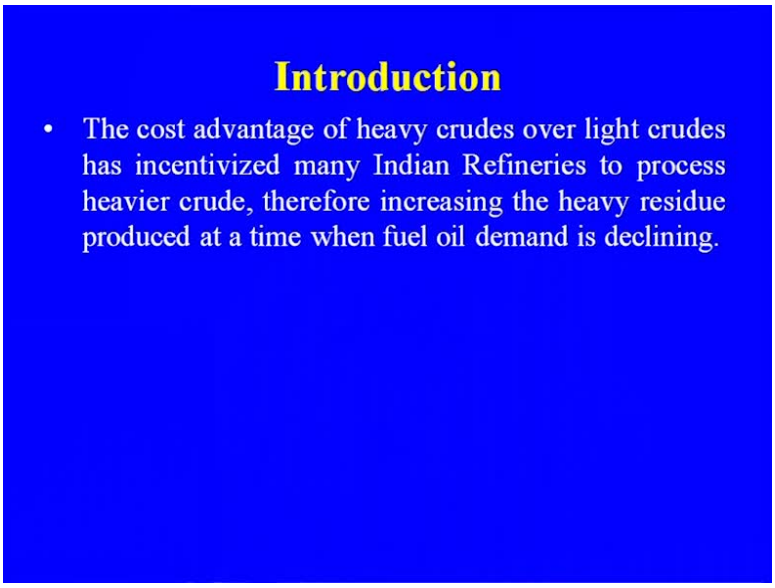

The cost of advantage of the heavy crudes over light crude has incentivized the many Indian refineries to process heavier crude, therefore because what is the cost of the heavier crude is much cheaper than the light crude or sweat crude. Therefore, increasing the heavy residue produced at a time when fuel oil demand is declining. So, this is the reason why we are going for more and more heavy crude oil.

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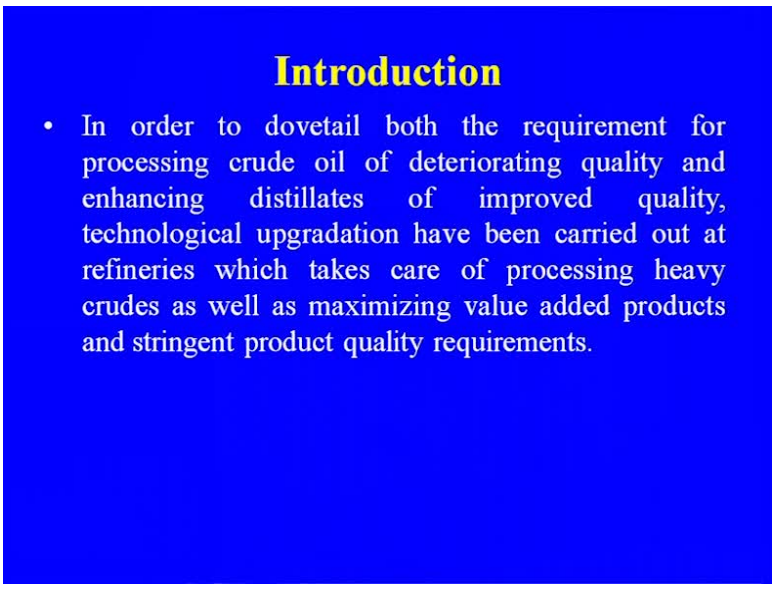

In order to dovetail both the requirement of processing crude oil of deteriorating quality and enhancing the distillates of the improve quality, technological up-gradation have

been carried out at refinery which takes care of the processing heavy crudes as well as the maximize the value added product and stringent product quality requirement. Let, us now discuss the cracking. Cracking means as you know cracking of heavy residue, what we are in refinery the term that the cracking of the heavy residue is most to the lighter product.

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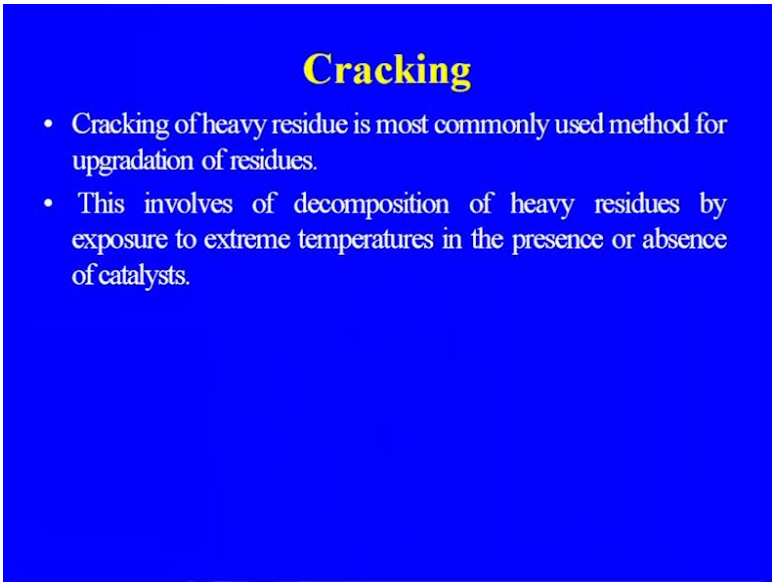

So, the cracking of the heavy residue is most commonly used method for up-gradation of the residue which are low value product in the refinery, this involve the decomposition of the heavy residue by exposure to extreme temperature in the presence or absence of the catalyst. So, some of the thermal cracking process are there where we do not use the catalyst, but other process that has been developed where the advantage, because that will be discussing in the next lecture about the when we will be discussing about the F C C in a presence of the catalyst we are doing the cracking.

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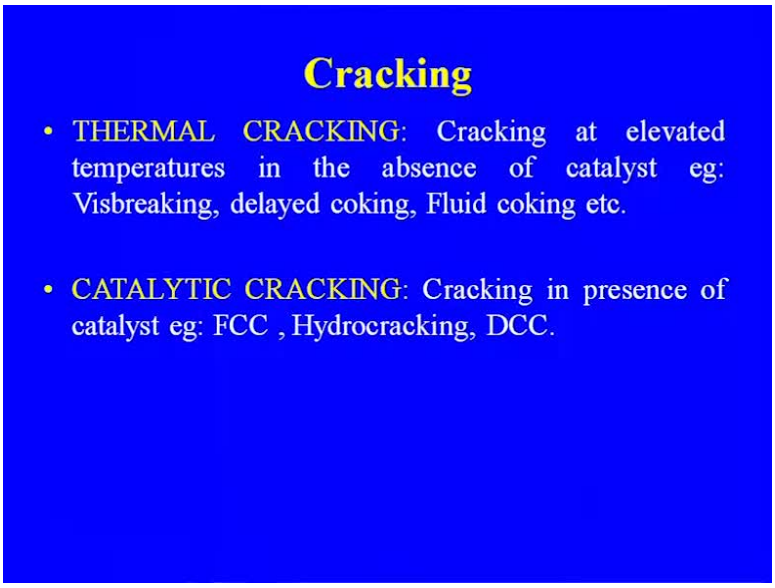

Thermal cracking, cracking at elevated temperature in the absence of catalyst, these are some of the actually the processes that is being used in refinery, vis breaking, delayed coking, fluid coking. These are the some of the process thermal cracking process. Catalytic cracking; cracking in presence of catalyst, fluid catalytic cracking, hydro cracking, deep catalytic cracking. So, these are the some of the technology and in most, another some of the technology that has been developed by the Indian oil corporation also, the catalytic cracking that I will be discussing, while discussing the catalytic cracking, what are the residue up-gradation technology?

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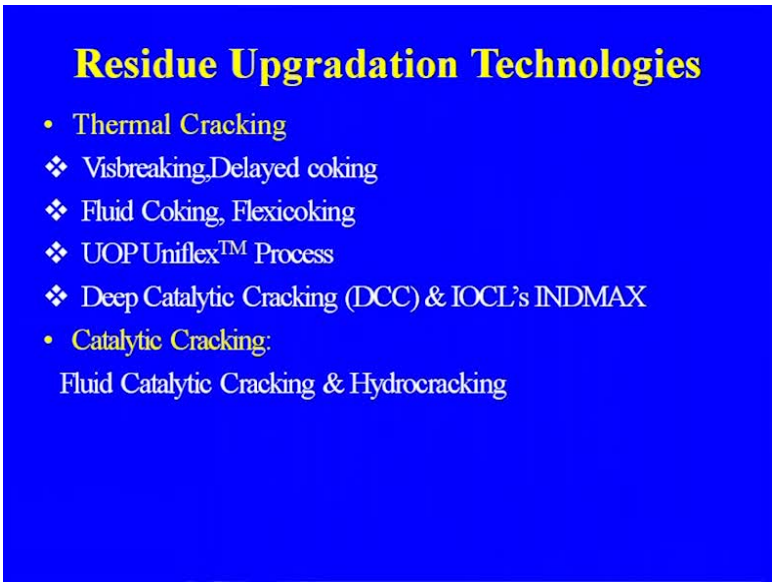

Thermal cracking, already I told you the vis breaking and delayed coking that is one of the very commonly used processes in refinery, fluid coking and flexi coking process that has been developed to improve the thermal cracking processes, U O P uniflex T M process, deep catalytic cracking and the I O C L INDMAX technology that is actually coming in the part of the catalytic cracking, so in the catalytic cracking fluid, catalytic cracking and the hydro-cracking.

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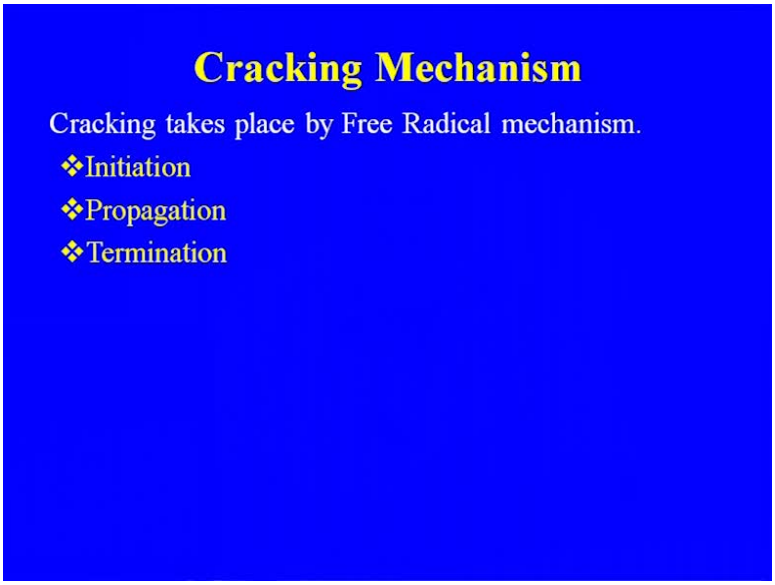

So, the cracking mechanism, so whatever the cracking reaction that is taking place as the free radical mechanism, initiation, propagation and the termination. So, these are the steps that are taking place during the cracking process.

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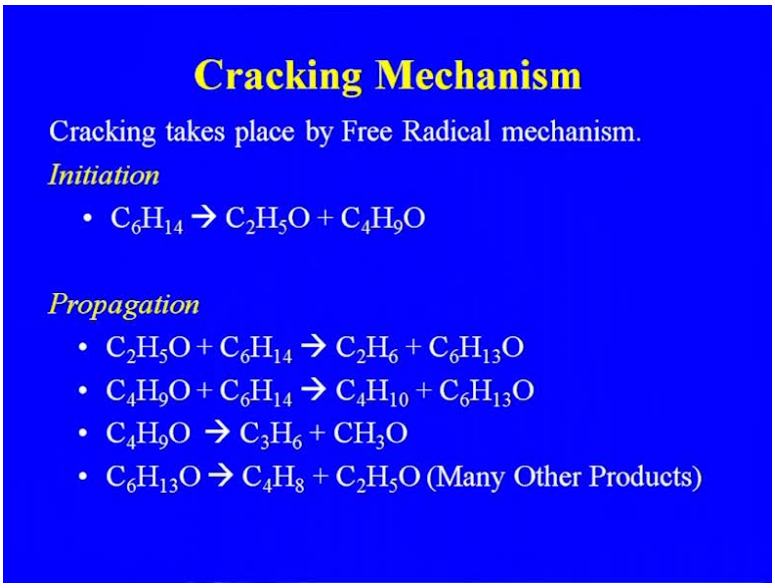

Initiation, this is the reaction that is taking place in the initiation and the lighter product we are getting and again from the propagation, this is converted too much other large number of the product, finally the termination where we are getting some of the lower molecular weight hydro carbons.

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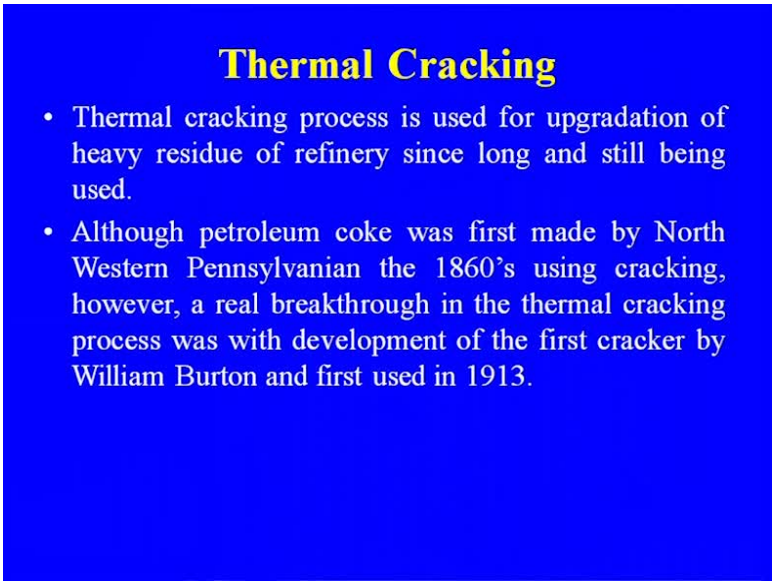

Now, let us come to the thermal cracking, thermal cracking process is used for up-gradation of heavy residue of refinery, since long and still being used, because you see with the coming of the more and more, heavier crude. Now, thermal cracking using the

vis breaking or the delayed coking that has become important operation in the refinery, because in the what is happening in the various processes like the crude oil, distillation or even in case of the cracking process also catalytic cracking? We are producing the heavy residue, so that can be or further that has to be cracked to more value added products and that is the reason why the importance of the visbreaker or the delayed coking is there.

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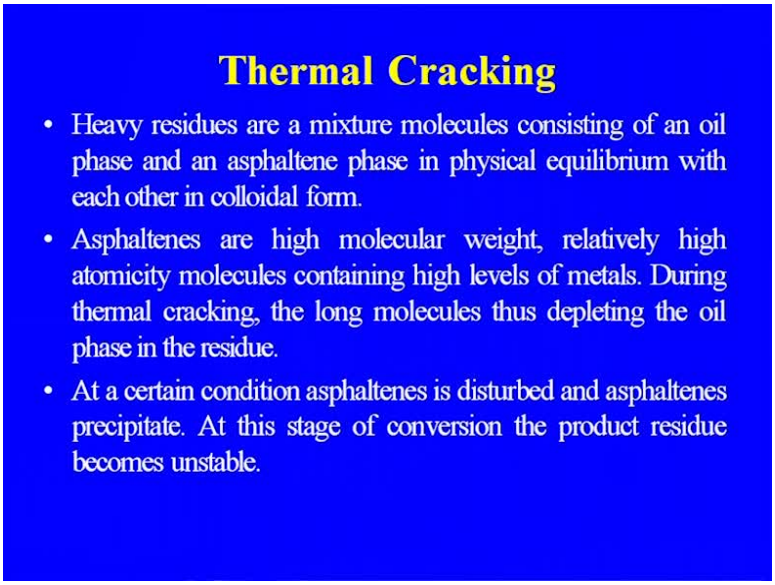

Although the petroleum coke was first made by north western Pennsylvanian in the eighteen sixties using cracking, however a real breakthrough in the thermal cracking process was the development of the cracker by William Burton and the first used in 1913. Thermal cracking; heavy residue or a mixture molecules consisting of an oil phase and asphaltene phase in physical equilibrium with each other in colloidal form. The asphaltenes are high molecular weight, relatively high atomicity molecules containing high level of the metals.

During the thermal cracking, the long molecules thus depleting the oil phase in the residue. At a certain condition the asphaltenes is distributed and asphaltenes precipitate. At this stage of conversion the product residue becomes unstable.

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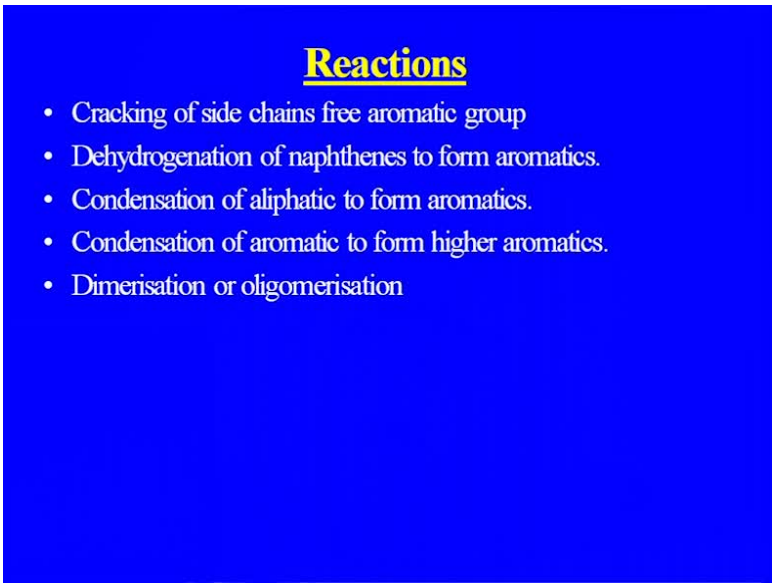

Thermal cracking reaction, cracking of the side chains free aromatic group, dehydrogenation of naphthenes to form aromatics, condensation of aliphatic to form aromatics, condensation of the aromatic to form higher aromatics and dimerisation or oilgomerisation process. These are the some of the reaction that is taking place and one of the problems in case of the formation of the coke during the process which is the unavailable process in case of the thermal cracking or even in the catalytic cracking, where the high temperature that is there.

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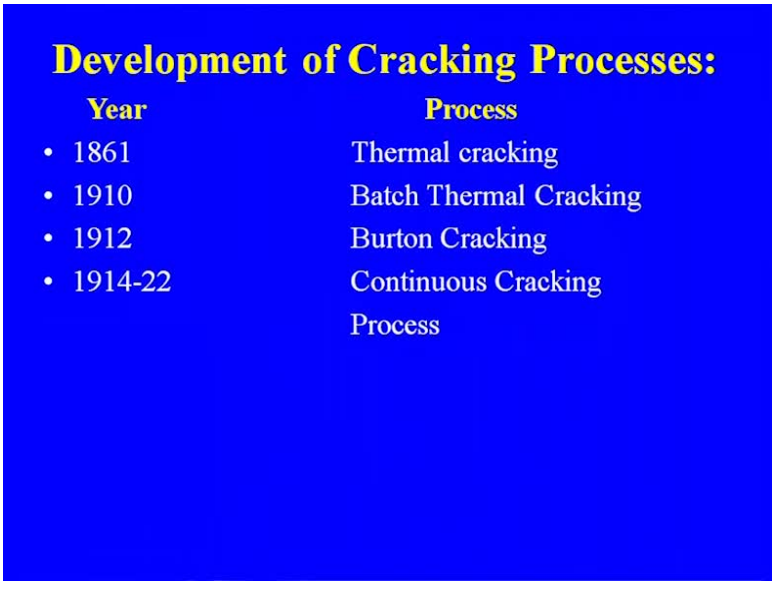

This is the development of the cracking processes 1860 thermal cracking, 1910 batch thermal cracking 1912 that is burton cracking and the 1914 to 1922 that was the continuous cracking process that was developed. In case of the thermal cracking what are the process variables? Feedstock property, because that will play important role on what type of the product that we are going to get after the cracking, cracking temperature residence time pressure.

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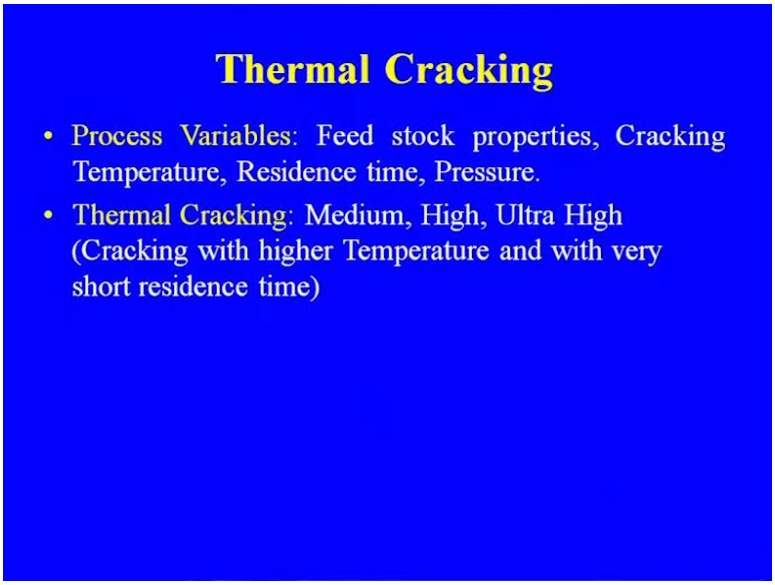

Thermal cracking that may be medium, high, ultra cracking with ultra high cracking means the cracking with higher temperature with very short residence time, because the residence time that is playing very important role in the cracking processes in the formation of the coke.

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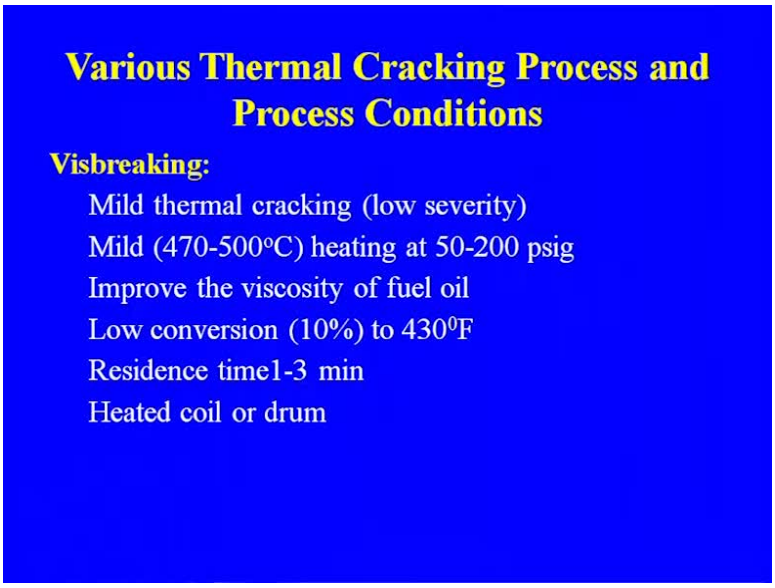

Now, let us discuss some of the important thermal cracking processes and the process condition then we will go in detail about the individual process. This is the condition we are using in case of the vis breaking, mild thermal cracking, low severity, temperature is 470 to 500 centigrade at 50 to 200 P S I G, improve the viscosity of the fuel oil, low conversion residence time 1 to 3 minute heated coil or drum that we are using.

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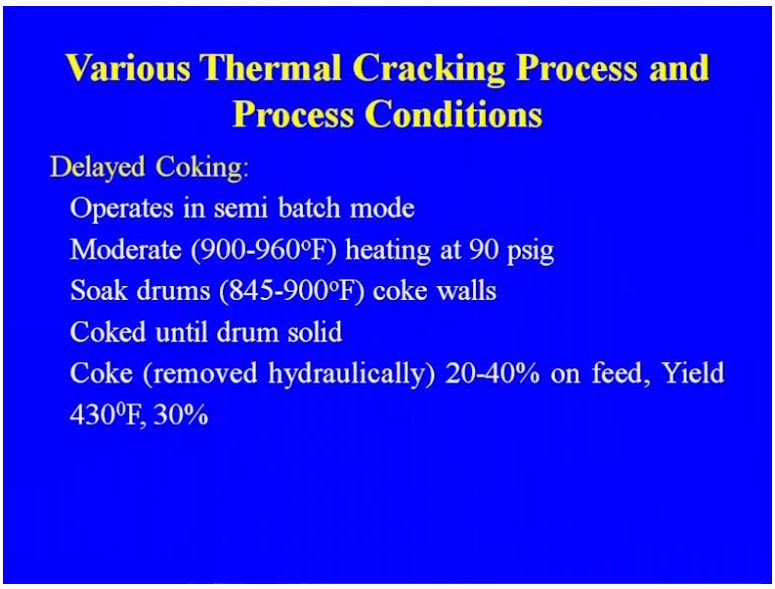

Delayed coking operates in semi batch mode, moderate temperature heating at 90 P S I G, soak drums are used coked until drum solid that is separated, there coke removed

hydraulically 20 to 40 percent on feed, yield is 30 to 20 to 40 percent at temperature 430 degree centigrade the yield slightly go higher 30 percent, this is the 30 percent is that particular temperature.

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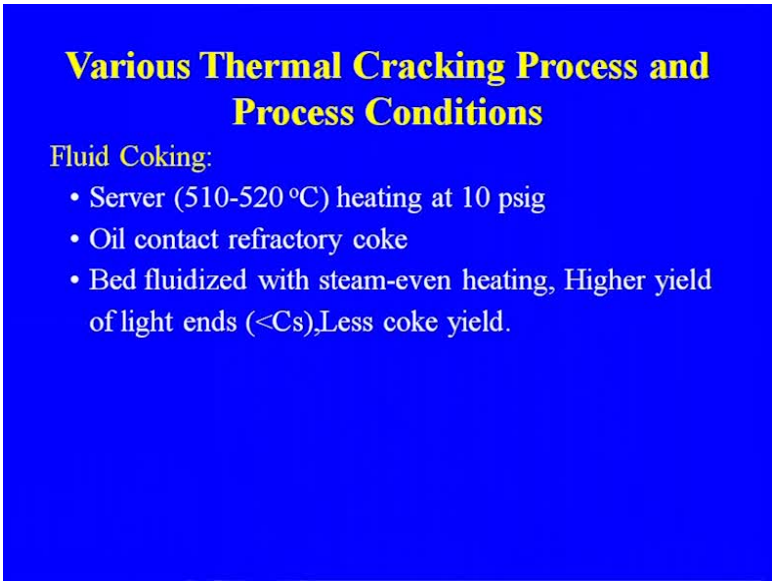

Fluid coking we are having the severe higher temperature severe condition and so 500 to 520 oil content and the refractory coke, fluidized bed we are using with steam even heating higher yield of the light ends less coke yield is there in this process. Let, us now discuss the vis breaking process, the detail of the vis breaking, because this is one of the important unit in refinery as I told you earlier also.

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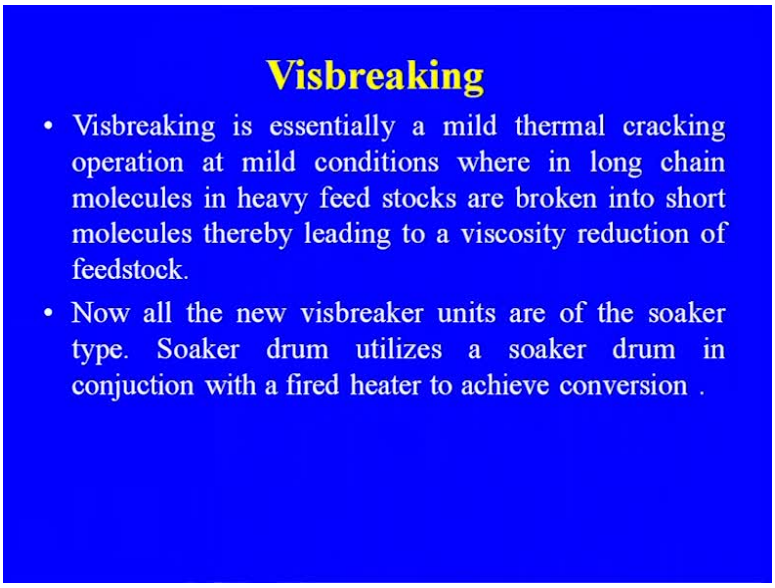

Vis breaking essentially a mild thermal cracking operation at mild condition, where in long chain molecules in heavy feed stocks are broken into short molecules, there by leading to a viscosity reduction of the feed stock. So, this is what is happening, how we are getting the lighter products and because the lighter products it will be less viscous. So, now all the new visbreaker units are of the soaker type, because the soaker drums that has been provided with the oil cracking where the visbreaker, if the coming of the soak drum we are leaving the additional reaction that is taking place in the soaker drum and so it is avoiding the formation of more and more coke. Soaker drum utilizes a soaker drum in conjunction with a fire heater to achieve the conversion. So, higher conversion is there less coke formation is there.

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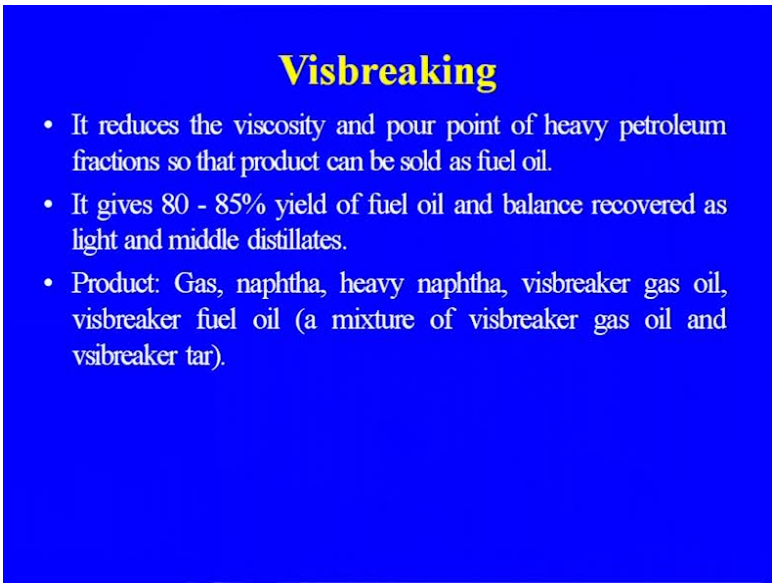

It reduces the viscosity and the pour point of the heavy petroleum fraction. So, that the product can be sold as a fuel oil, it gives eighty to 80 to 85 percent yield of fuel oil and balance recovered as light and middle distillate. So, again still the major courses in fuel oil and rest is this, because in all the vis breaking process or the delayed coking we are getting the light and middle distillates and again the some of the heavier fraction. Product which we are getting from the vis breaking, gas, naphtha, heavy naphtha, visbreaker gas oil, visbreaker fuel oil and the mixture of visbreaker gas oil and the visbreaker tar.

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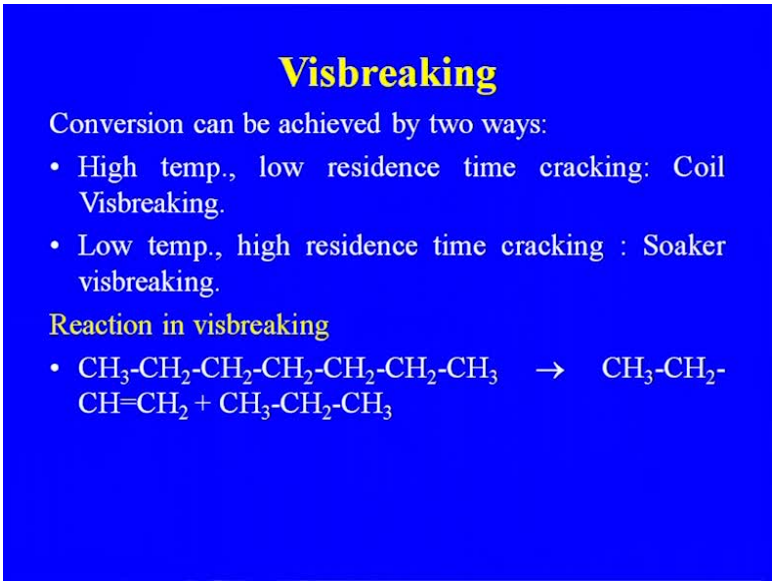

Conversion can be achieved by two ways high temperature, low residence time cracking that is the coil vis breaking we are doing low temperature, high residence time cracking soaker vis breaking. In the both the cases our objective is just to break the heavier fraction into lighter fraction, only the changing residence time and the temperature, the type of the product which we are getting that will vary.

The reaction involved is the reaction that is taking place in case of the vis breaking, the reaction in the cracking process due to it is very complex in nature and depending upon the operating condition temperature, pressure type of feed stock, the product which we are getting after the vis breaking that will vary.

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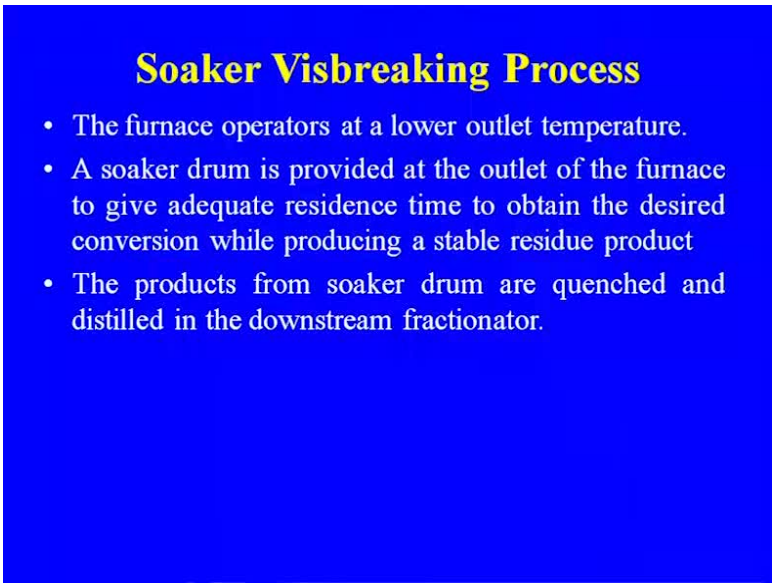

Soaker vis breaking process, the furnace operates at a lower outlet temperature. A soaker drum is provided at the outlet of the furnace to give adequate residence time to obtain the desired conversion while producing a stable residue product. The products from the soaker drum are quenched and distilled in the downstream fractionators.

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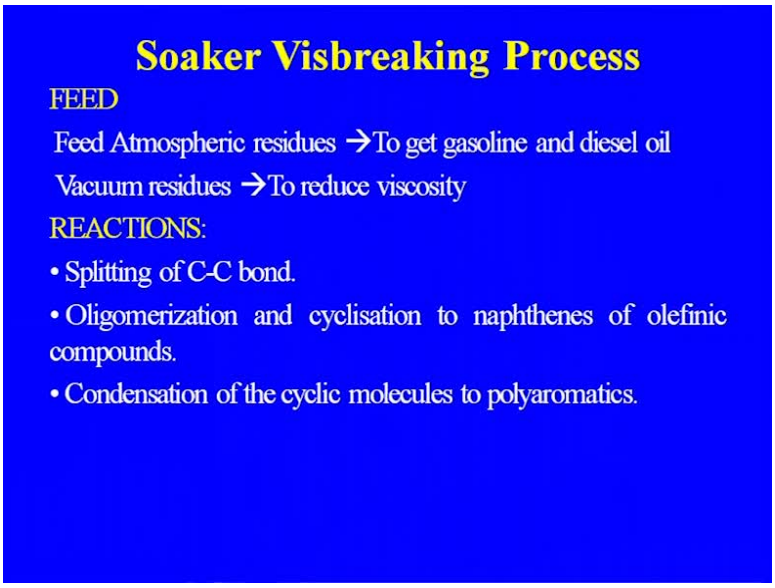

Feed to the soaker or atmospheric residue to get gasoline and diesel oil vacuum residue to reduce the viscosity. So, depending upon the feed which we are using in case of the visbreaker, the type of the product which is getting that will vary. Reaction; these are the reaction, already we have discussed everything oligomerization and cyclisation of the naphthenes condensation of the cyclic molecules. So, the different reactions are taking place.

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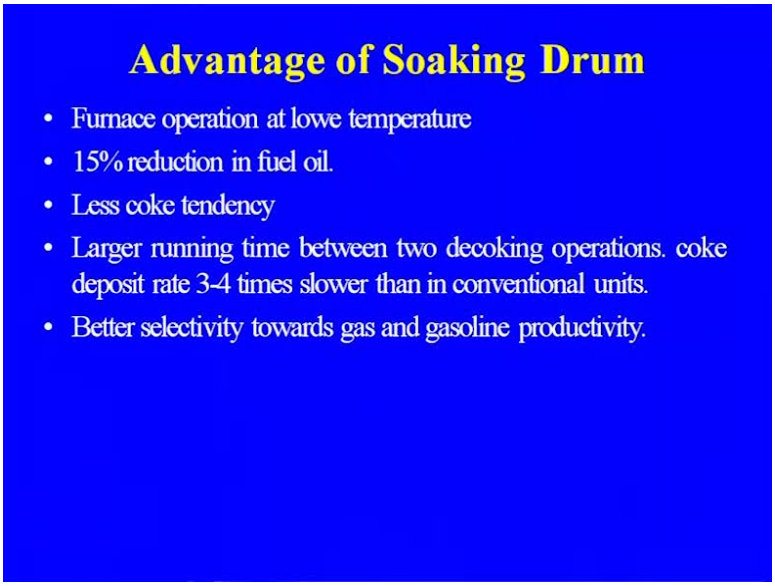

Advantage of why we are having the soaking term in the visbreaker, that is the furnace operation at a lower temperature 15 percent reduction in the fuel oil, less coke tendency which I told you that, because we are giving more reaction time at a lower temperature in the soaker drum, larger running time between two decoking operations, coke deposit rate 3 to 4 times slower than in conventional units. Better selectivity towards gas and gasoline productivity. These are the vis breaking condition again that will vary with the type of the feed stock you are processing. This is the temperature with the soaking drum if you are using.

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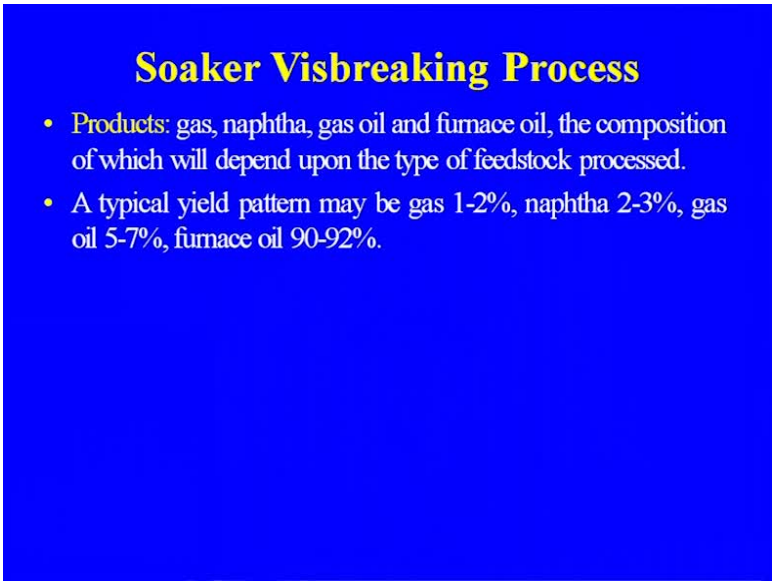

Soaker vis breaking process; the products which we are getting from this are gas, naphtha, gas oil and furnace oil the composition which will depend upon the type of the feed stock process, which I told you depending upon the feed stock the whole product range which we are getting about the cracking that will vary. A typical yield pattern may be gas 1 to 2 percent, naphtha 2 to 3 percent, gas oil 5 to 7 percent, furnace oil that is 90 to 92 percent.

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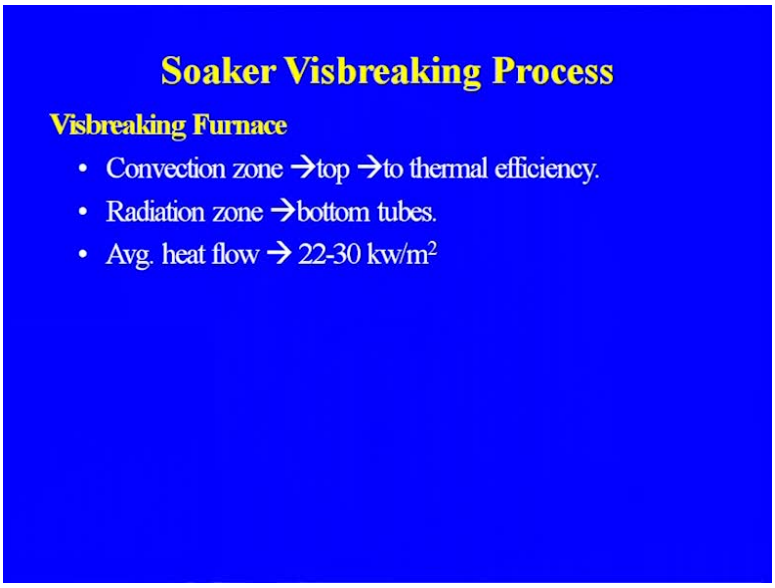

Vis breaking furnace in the furnace we are having the convection zone that is top to thermal to increase the thermal efficiency radiation zone, bottom tubes where actually the cracking is taking place, average heat flow this is for a particular case, 22 to 30 kilo watt per meter square.

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Variables, in case of the soaker vis breaking process, what are the variables? Feed rate, furnace transfer temperature, visbreaker tar quench to transfer line, fractionation pressure, fractionation top temperature, circulation, reflux flow, visbreaker tar quench to

fractionator bottom, vibreaker tar quench to visbreaker tar stripper bottom, stabilizer temperature and pressure . These are the some of the operating variables in case of the vis breaking.

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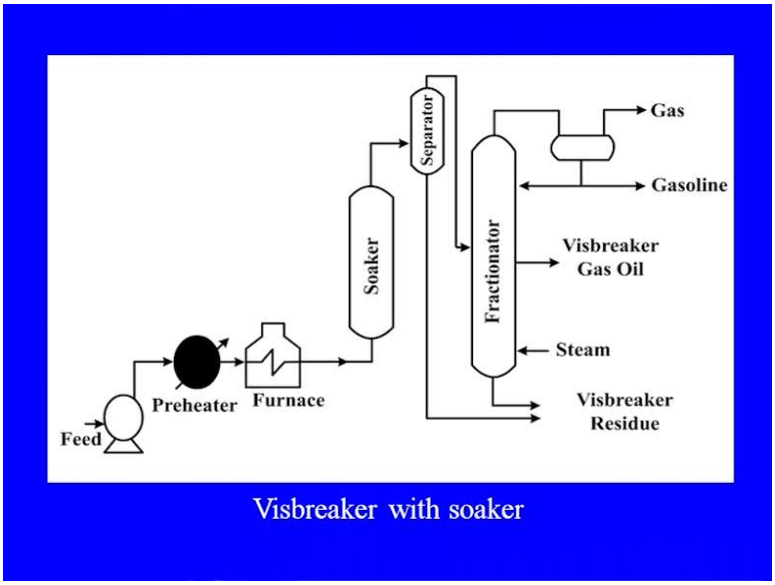

This is the flow diagram at typical visbreaker which is not having any soaker, so the feed that will go to the pre heater from the pre heater, it will go to the furnace where the cracking that will take place. Then the cracked product that will go to the separator from the separator the product the heavier part that will be getting as a residue and the lighter product that will go for further fractionation of the lighter and middle distillate and the heavier residue. So, this is the separation of the gas, gasoline, visbreaker that is the distillate middle distillate that will be getting. So, here it maybe the light distillate, middles distillate that will be getting and then the visbreaker residue, finally we will be getting. These are the products we will get after the fractionation of the product which we are getting from the after the cracking from the furnace.

Now, let us discuss the base faker with the soaker, because slightly difference in, here we are providing a soaker. The purpose of the soaker is to give the more residence time here and reduce temperature is there that discuss their, feed is going to pre heater, pre heater to furnace and from the furnace it is going to the soaker and from the soaker again rest of the process is same, because the product again from the soaker. Here actually, we are giving more residence time for the reaction and after soaker of the product that is

going to the separator, from the separator again, as I told u sorry, the residue which we are getting that the visbreaker residue and these are the some middle distillates, gas, gasoline and the string that we are that we are adding here.

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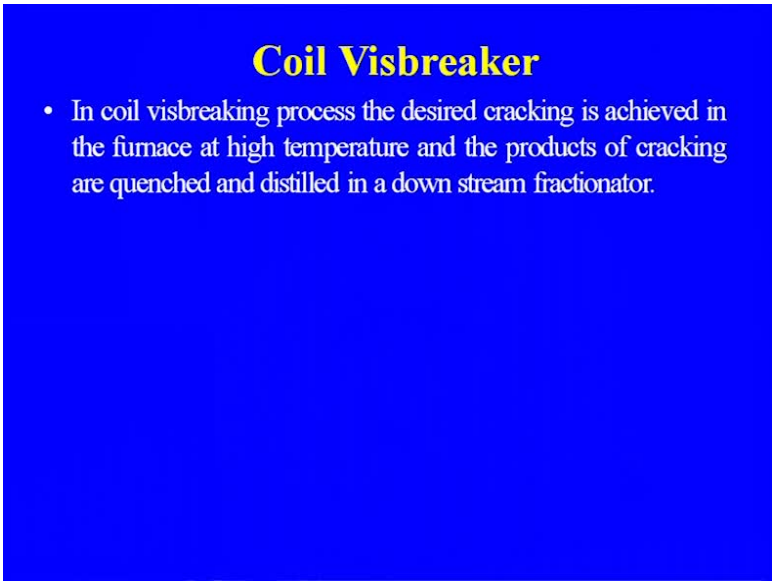

Now, actually the coil visbreaker which is without soaker, the coil visbreaker process, the desired cracking is achieved in the furnace at high temperature and the products of cracking are quenched and distilled in downstream process. Here no soaker is provided directly, whatever the cracking reaction is taking place that is taking place in the furnace. One of the important problem in case of the furnace is that the coke formation. We are using the actually the efficiency of the furnace and sometime the higher pressure drop and the higher fuel consumption that is resulting. So, frequently we will have to clean depending up on the type of the crude oil the residence you are getting from the crude oil.

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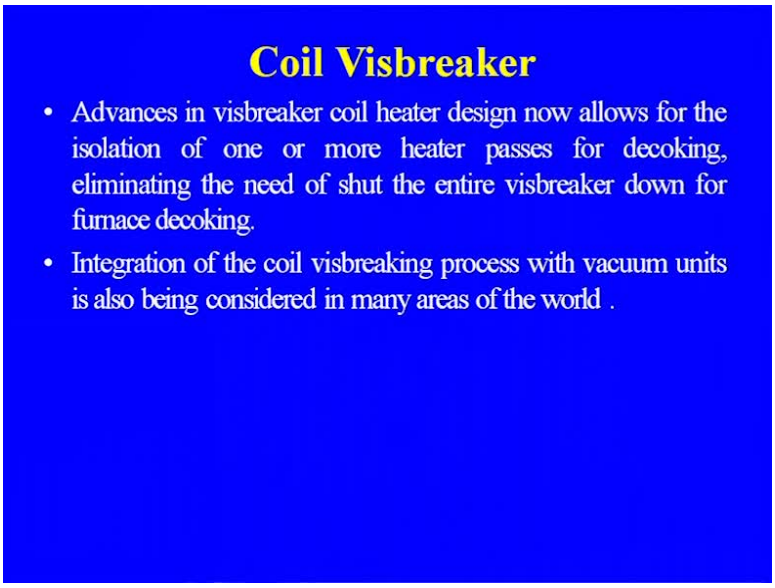

Advance in the visbreaker coil heater design now allows for the isolation of one or more heater passes for decoking, because decoking is the removal of the coke during the process, which is because the coke formation will be always there. Only you can reduce the amount of coke that is form eliminating the need for this shutdown and the entire visbreaker down for the furnace decoking. Integration of the coil visbreaker with vacuum units is also being considered in many areas of the world, because the vacuum residue that will go to the coil visbreaker and the breaking or the cracking that will take place.

So, this is another development coking. Now we have discussed about the vis breaking, because you see the name itself, in one process we are telling that the vis breaking means the reduction in the viscosity. Another process which we are using for the processing of the heavy residue is the coking process.

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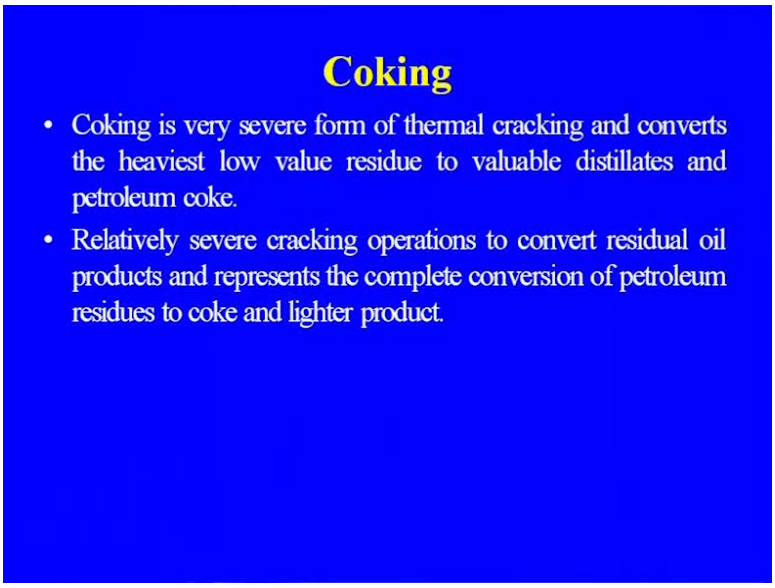

Coking is very severe form of thermal cracking and converts the heaviest low value residue to valuable distillates and petroleum coke. So, this is the actually the process we are getting a petroleum coke which I discuss also, while discussing the raw material and the gasification part. Petro coke gasification now some of the refinery just like jam in the refinery, where they are going to they are processing more and more average. They are going for the petro coke gasification and that is just to for the generation of the hydrogen through the partial oxidation or the gasification process.

Relatively severe cracking operation to convert residual oil products and represent the complete conversion of the petroleum residue to coke and lighter product, because the residue which you are getting here coke and the lighter products you are getting. So, coke again that, because many of the similar plant they are using this petro coke as their fuel.

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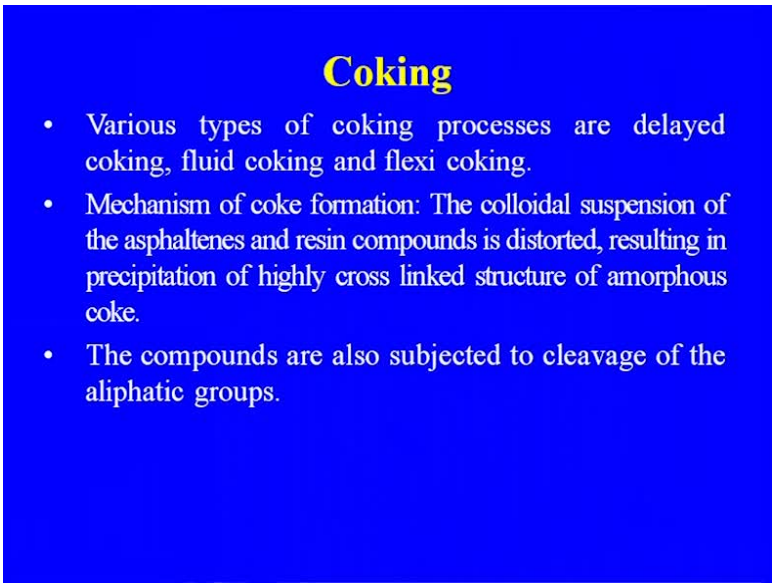

Various type of the coking process are delayed coking, fluid coking or the flexi coking. Mechanism of the coke formation; the colloidal suspension of the asphaltene and the resin compounds is distorted, resulting in the precipitating of highly cross link structure of the amorphous coke. The compounds are also subjected to cleavage of the aliphatic groups.

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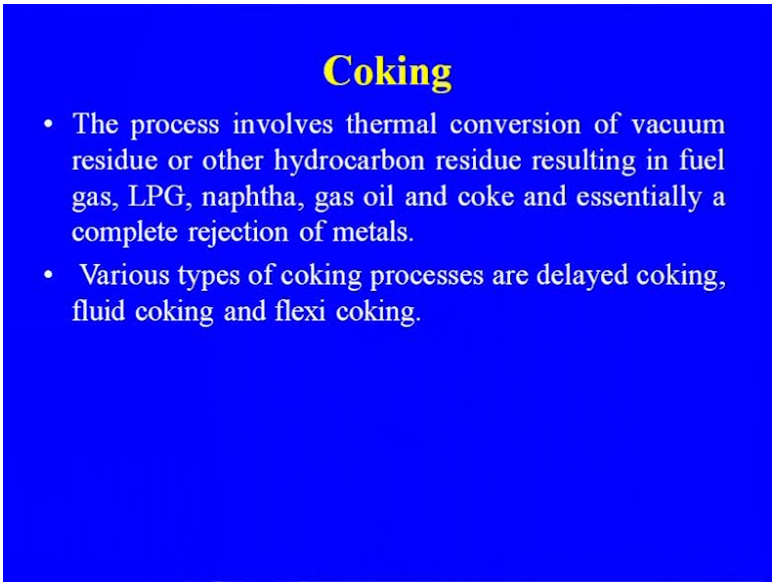

The process involves thermal conversion of vacuum residue or other hydrocarbon residue resulting in, these are the products fuel gas, L P G, naphtha, which called is the

crack naphtha, gas oil and coke and essentially a complete rejection of the metals. Various types of the coking process already I told you we are having the delayed coking, fluid coking and the flexi coking.

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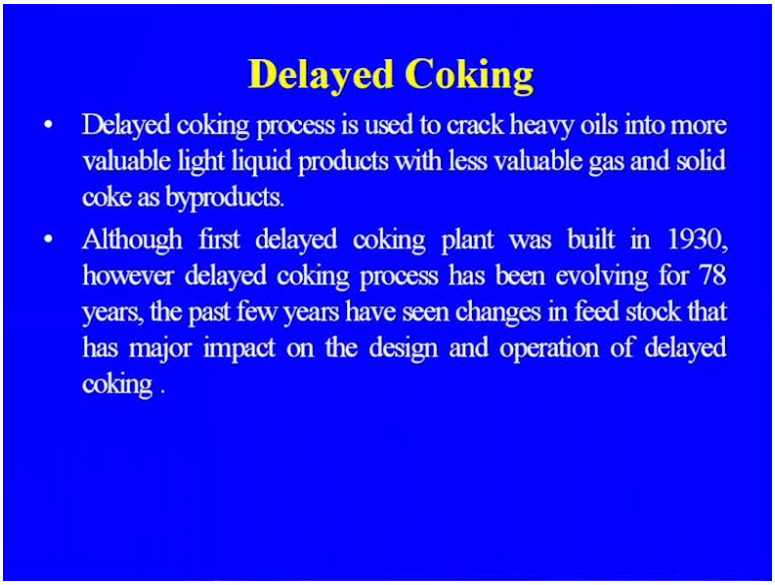

Now, let us discuss in more detail about the delayed coking. Delayed coking process is used to crack heavy oils into more valuable light liquid products with less valuable gas and solid coke as by products. Although the first delayed coking plant was built in 1930, however delayed coking process has been evolving for the last 70 80 years, the past few years have been changes in feed stock and has major impact on the design and operation of the delayed coking.

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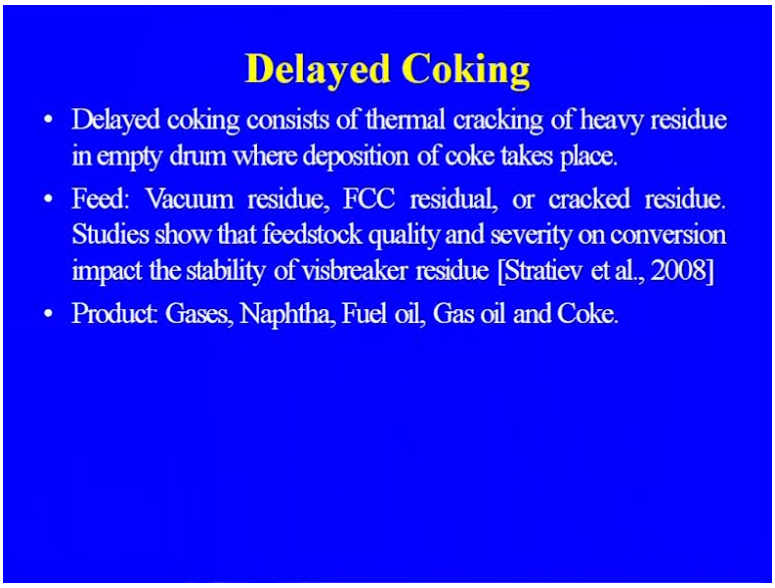

Delayed coking consists of the thermal cracking of the heavy residue in empty drum where deposition of the coke takes place. Feed is feed to the delayed coking is normally we are using vacuum residue which we are getting from the vacuum distillation column F C C, fluid catalytic cracking residual or the cracked residue. Studies show that the feed stock quality and severity on the conversion impact the stability of the visbreaker residue. Product here we are getting in case of the delayed coking or the gases, naphtha, fuel oil, gas oil and the coke.

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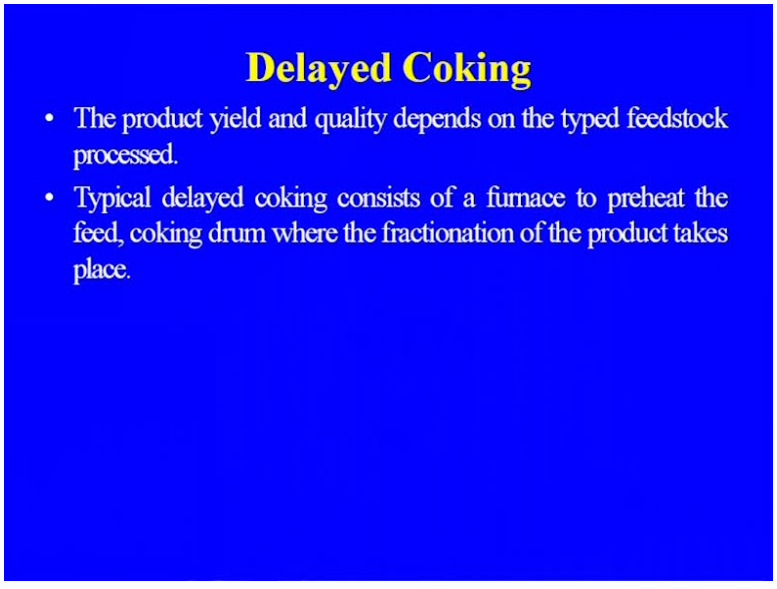

So, already I told you in case of the vis breaking or here also in case of the delayed coking, the product yield and the quality depends on the type of the feedstock being processed. Because all the product yield totally that will depend upon more heavier than what about the products we will be getting that will be different in quality and then what we are if you are cracking some of the lighter residue. So, typical delayed coking consists of a furnace to preheat the feed, coking drum, where the fractionation of the product takes place, separation not the fractionation exactly it is separation of the products takes place and the coke is separated from the reaction part.

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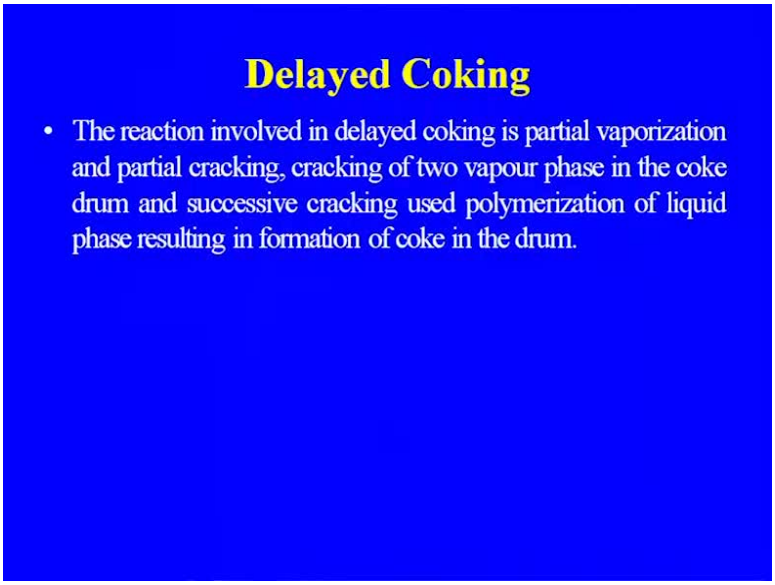

The reaction involved in delayed coking is partially vaporization and partial cracking, cracking of two vapour phase in the coke drum and successive cracking used polymerization of liquid phase resulting in the formation, because always the formation of the coke is because of the polymerization reaction that is taking place in any furnace or any process.

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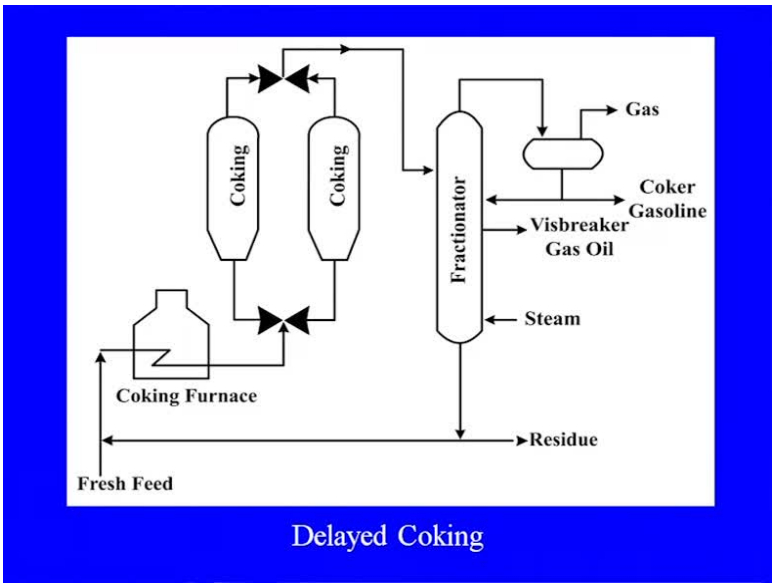

This is about the delayed coking, here the feed is going to the coking furnace a temperature is raise here and then it is going to the coking drum and from the coking drums it is going to the fractionators, again from the fractionator we are getting the different product the gas, coker gasoline that may be there, coker gas oil we are getting and the residue from the fractionator and from the coking process, so that will be the residue that will be getting.

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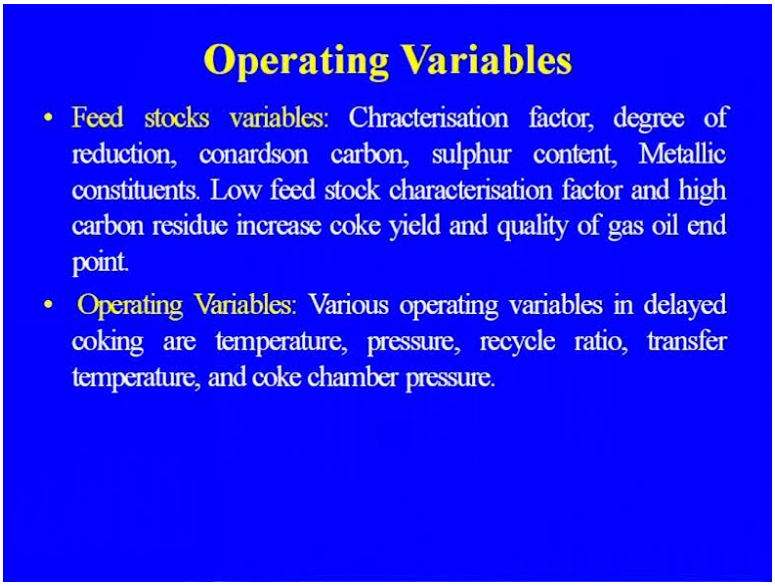

Operating variables in case of the here, the operating variables are characterization factor. Already we discuss how the characterization factor, you can that is the whether this paraffinic, naphthenic or the intermediate way, degree of reduction, conardson carbon, sulphur content, metallic constituent. Low feed stock characterization factor and high carbon residue increase coke yield and quality of gas oil and end point. Operating variables; as I told you the in case of many furnaces, the temperature that is one of the very important variables. So, various operating variables in delayed coking are temperature, pressure, recycle ratio, transfer temperature, and coke chamber pressure. These are the major variables in case of the delayed coking.

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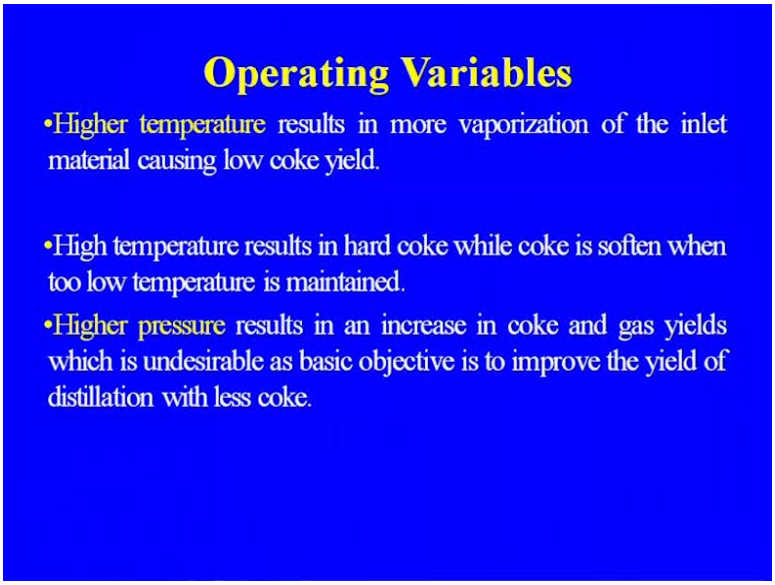

Now, let us discuss about the effect of the some of the important variables which are having in case of the delayed coking. Higher temperature results in more vaporization of the inlet material causing low coke yield. High temperature results in hard coke while the coke is soften when too low temperature is maintained. So, the coke quality also, because the whatever the petro coke we are getting from the refinery that is also varying in the properties depending upon the process also, because the coke quality which we are getting from the catalytic cracking is different than what you are getting from the vis breaking or the delayed coking.

Higher pressure result in an increase in the coke and gas yields which is undesirable as basic objective is to improve the yield of distillation with less coke formation. Because

coke is not, to make coke is not a main objective, our objective is to get the more light middle distillate or some of the more valuated product. Now, let us discuss about some other development which has taking place in a thermal cracking process that is the fluid coking process.

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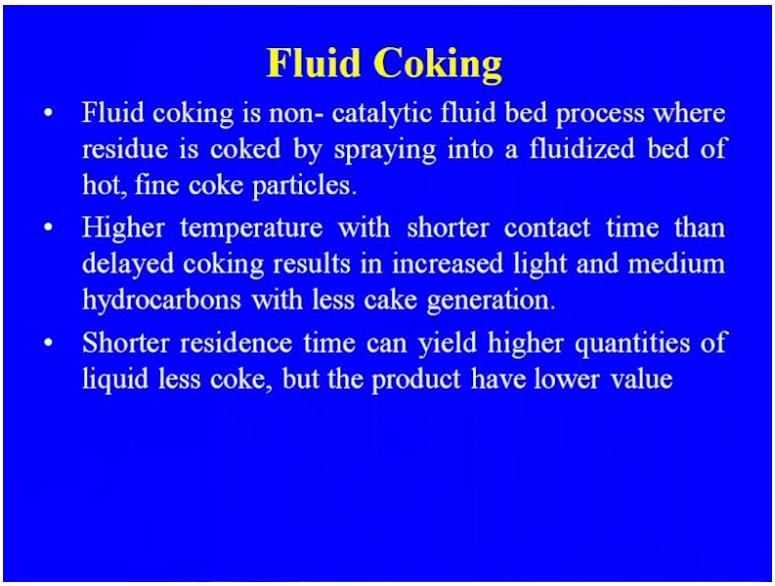

Fluid coking is non-catalytic fluidized bed process where residue is coked by spraying into a fluidized bed of hot fine coke particles. Here we are using the fluidization phenomena for the cracking process and so definitely as you know in the case of the fluidization definitely the improvement in the quality of the product is there and similarly other parameters are also getting operated better operation is there.

So, higher temperature with shorter contact time than the delayed coking results in increased light and medium hydrocarbon with less coke generation. Shorter residence time can yield higher quantity of liquid less coke, but the products have lower value. So, we will have to provide the optimum residence time. Another development that has been in case of the coking process that is the flexi coking.

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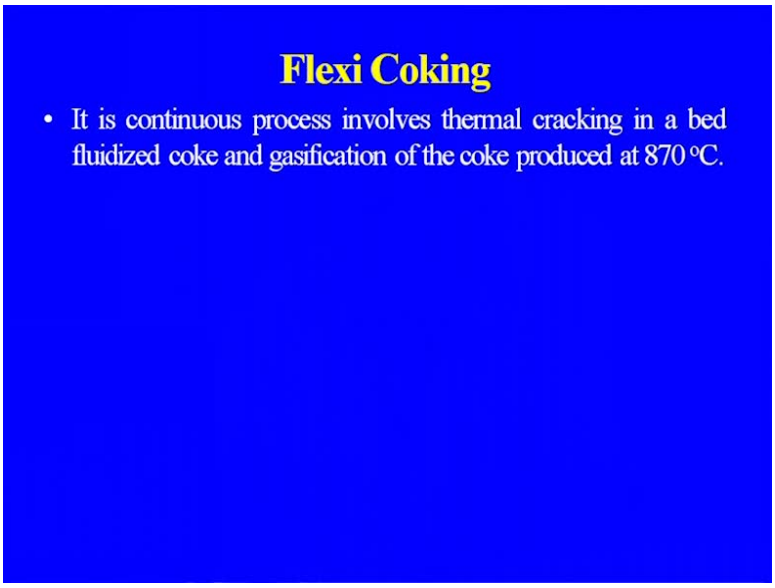

It is continuous process which involves the thermal cracking in a bed fluidized coke and gasification of the coke produced at 870 degree centigrade. So, this is the flexi coking.

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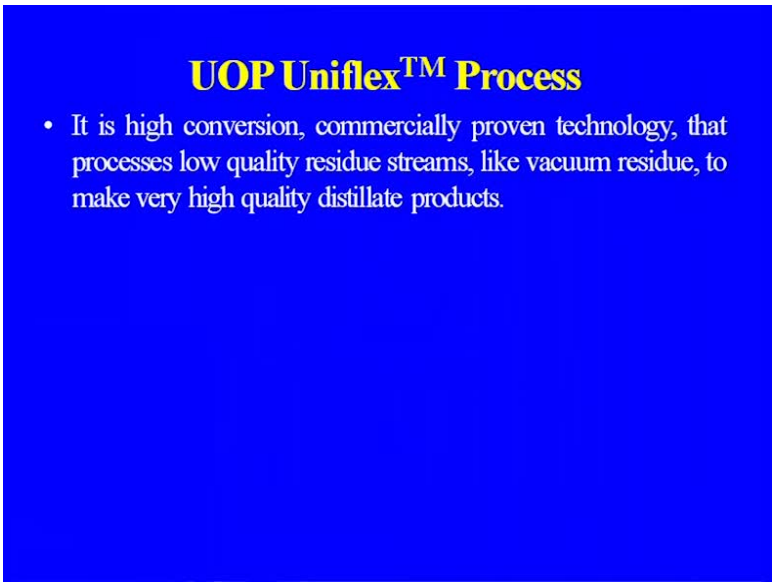

Again the U O P, because you see the we are using more and more heavier pool, so there has been continuous development in the thermal cracking process also, so the U O P uniflex T M process which is now available. So, it is a high conversion, commercially proven technology that process low quality residue stream, like vacuum residue, to make very high quality distillate products. So, this was about the thermal cracking process

which we are using in the refinery, but you see the all refinery they are having the both catalytic cracking and the thermal cracking, because some of the during the catalytic cracking process also, it may be F C C or the hydro cracking, we are producing some heavy residue and which is further cracked along with the residence we are getting from the vacuum distillation column.

So, in the next lecture we will be discussing about the catalytic cracking and where the two major processes that will be discussing that is the fluid catalytic cracking and the hydro cracking, so these are the two processes that has become integral part of the refinery, we will be discussing in detail. Only in case of the thermal cracking, because all the refinery along with the catalytic cracking they are also having the thermal cracking, because now we are processing more and more heavier crude and so because of that the generation of the heavy residue is more and so the processing of the heavy residue to get more value added product through the middle distillate or the even some other fuel oil product. So, that has become very important.