Chemical Technology
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Module - 6
Petroleum Refinery
Lecture - 8
Desulphurisation Process and Recovery of Sulphur

We are discussing the organic chemical technology core. We have discussed the various processes which have been done in petroleum refining. And today we will be discussing one of the very important topics in case of petroleum refining because the importance of increasing of stringent environmental standards have been imposed and at the same time sensitivity of the catalyst. So, desulphurization process and the recovery of the sulphur.

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This is difficult sulphur recovery plant of the IOC Panipat.

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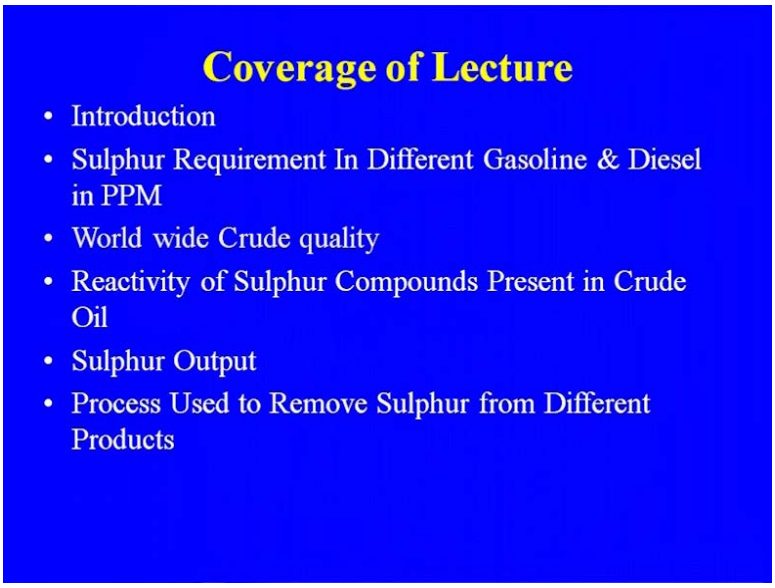

Coverage of the lecture, the lecture contain about that will continue as introduction, sulphur requirement in different gasoline and diesel. This is one of the driving force which is requiring the desulphurization process, and at the same time the requirement of the catalyst because the catalyst which we are using in various process they are very sensitive. So, we need the desulphurization process. So, that is the second driving force apart from the sulphur requirement in the gasoline and diesel. Worldwide crude oil quality, because you see the crude oil quality is very earlier we used to get seat crude and low sulphuric crude, but now for the coming of the heavier crude containing the sulphur content that is increasing, even the crude which we have got in Rajasthan that is the high time crude and with high sulphur.

Reactivity of the sulphur compound because what is happening during the treatment process, the reactivity of the various sulphur compounds which are present that also process problem in removal. So, that is the will be discussing in the reactivity of various sulphur compounds, which are mercaptained to therapy that are present. So, how they are reacting in the during diesel sulphur output because there are various processes of the why we need the desulphurization. Why we need the sulphur recovery bond? Because huge amount of the sulphur SO2 gas or S2S gas or the other gasses that is as we generated.

What are the various sources of this? Because in all the processes as we discussed earlier in the previous lecture, whether it was the cathartic reforming or the FCC or the hydro cracking. In all the process the pre requisite for treatment of the feed stock before it was going to the main process. Because this sulphur that is one of the highly poisoned cartelize poisoned material, removal of that it is very important. And so the various sources bought up process used to remove sulphur from the different products.

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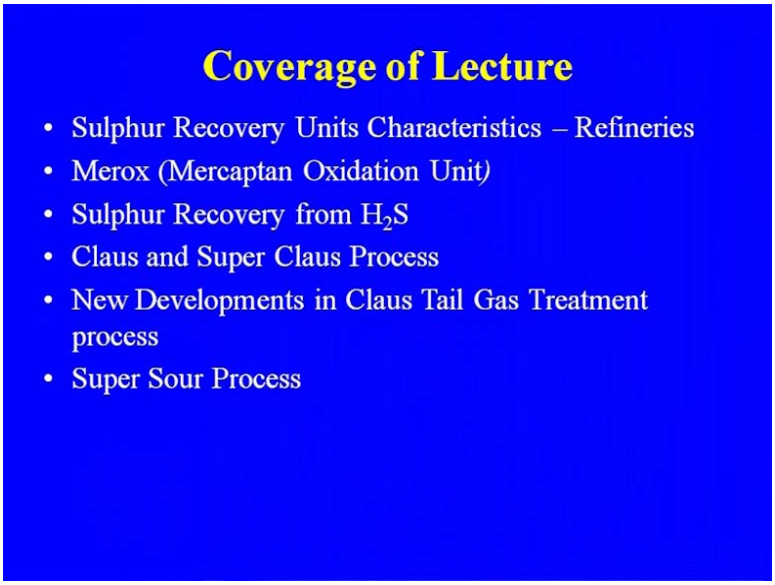

Sulphur recovery characteristics, merox process, merox sulphur recovery from H2S; because there have been continuous development in case of the sulphur recovery processes because, what has happened? The conventional process still the emission of the sulphur compounds. So, how to minimize that emission that super caught then that new development that is taken place in the because the close steel gas continuing how to steel gas.

So, we will be discussing about class steel gas process some of the other development which are taken place that is the super process that are taken place have been developed by Indian all (( )) position that is in business technology that we are having. Introduction about the why we need this one the desulphurization process the recovery why it has been involved important.

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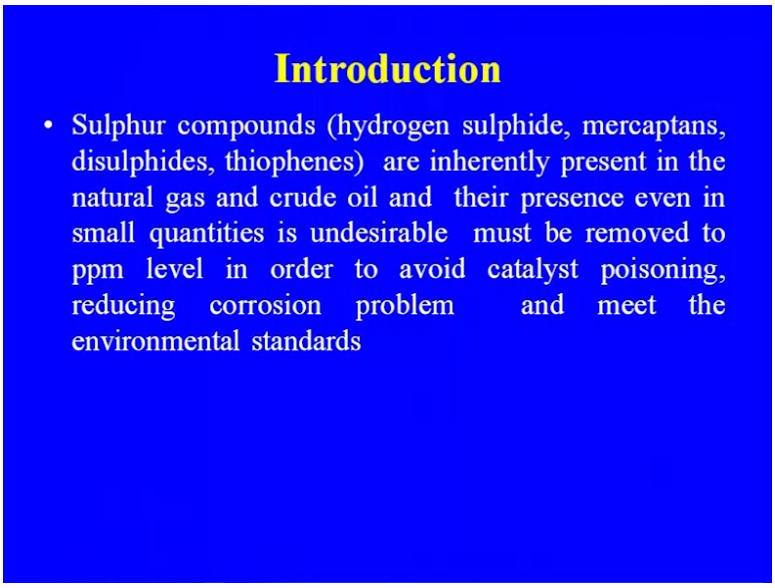

Sulphur components, hydrogen sulphide, mercaptans, disulphates, thiophenes are inherently present in the natural gas and crude oil. And their presence even in their small quantities is undesirable must be removed to ppm level in order to avoid catalyst poisoning, reducing corrosion problem and meet the environmental standards. Because the corrosion problem is also one of the severe problem because of the coming of the high ten crude oil and at the same time high sulphur crude oil.

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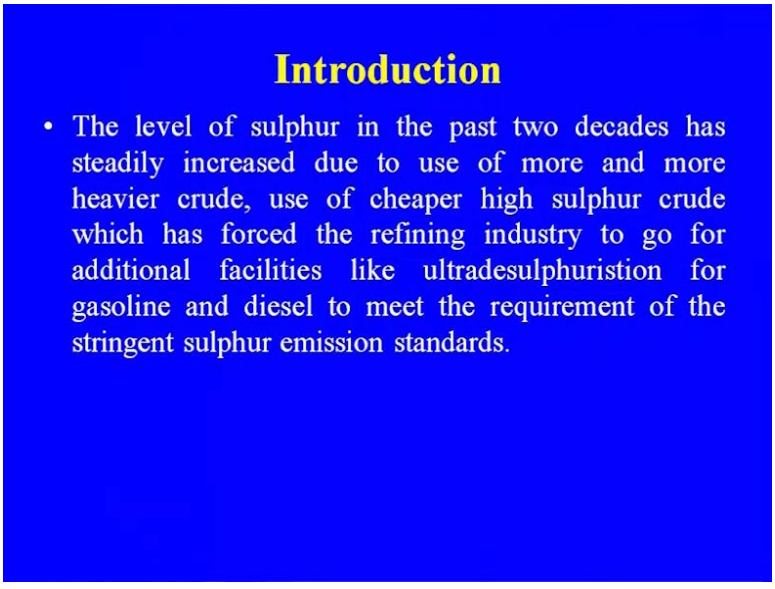

The level of the sulphur as I told you it is been increasing so, the level of the sulphur in the past 2 decades has steadily increased due to use of more and heavier crude. Use of cheaper high sulphur crude, which has forced refining industry to go for additional facilities like ultradesulphurization for gasoline and diesel to meet the requirement of the stringent sulphur emission standards. Because, whatever the products we are getting is the diesel, kerosene or gasoline that has to be desulphorised before it is going for the end use. So, these are some of the driving force, which as laid to development of the various sulphur recovery process or the desulphorision process.

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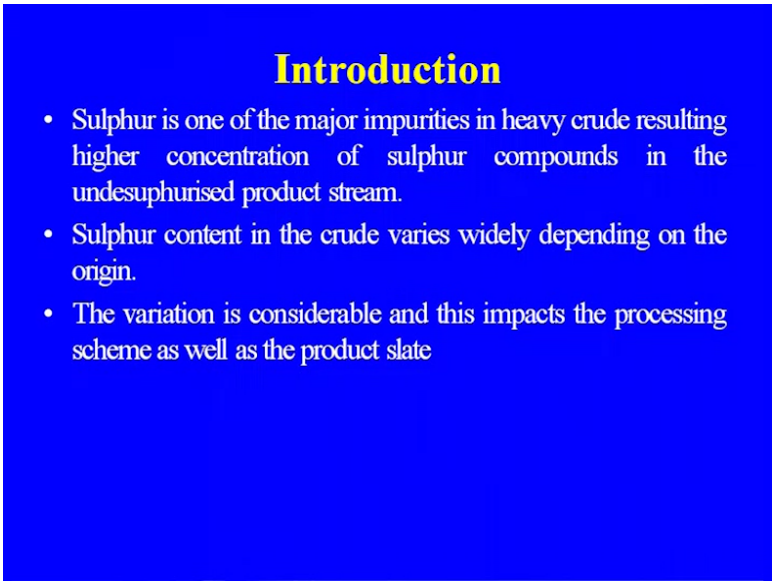

Sulphur is one of the major impurities in heavy crude resulting higher concentration of sulphur compounds in the undesulphurised product stream. Product streams are not the final product, but also the feady stock to the various processes like FCC, hydro cracking and catalyze forming. Already we have discussed what are because before it is going to main reactor the feed is pre treated

And then even after the products, which you are getting the make containing the forces of the sulphur compounds and to meet the environment standards of the 50 from differently the product has to be detailed. Sulphur contained in the crude oil widely depending on the origin because, this also varying from one place to another and from one reason to another so, the wide variation we found in the crude oil quality is also with

respect to sulphur. The variation is considerable and this impacts the processing scheme, as well as, the product slate.

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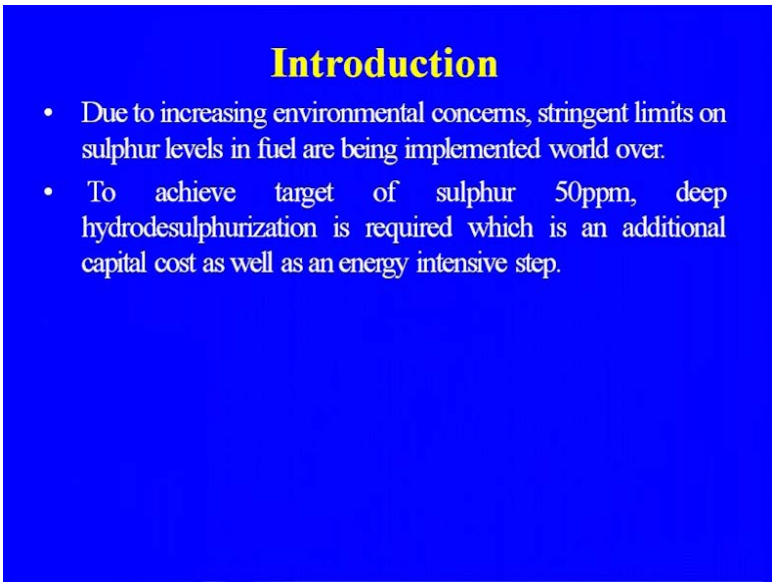

Due to increasing environmental concerns stringent limits on sulphur levels in fuel implemented world over, whether you take the continuously reduction in the SO2 mission as per the euro norm, euro 1, euro 2, euro 3, euro 4, and now to achieve the 50 ppm that is the big challenge for the refining to achieve target of sulphur 50 ppm diesel hydro desulphurization. So, ultra desulphurization deep desulphurization, hydro desulphurization is required, which is an additional capital cost, as well as, an energy intensive step and some time the loss of the hydro carbon also there. This is why I was telling why we are going for the desulphurization process.

If you see this figure from the 2000 to the changes which is taking place, now the BIS standard 1000 was earlier bharat 2 it was 500 euro 2, euro 3 150, euro 4 50. So, that is the level SO2 that has to be maintained in the gasoline or the diesel. So, definitely you see that there is lots of changes in this standards also, this is one of the reason why we are going for the recovery of sulphur, when at the same time the sulphur also, one of the very important feed stock of the various chemical compound. Only problem of that the generalization of sulphur it is not huge as it is required whether, it is sulphuric acid or the other part.

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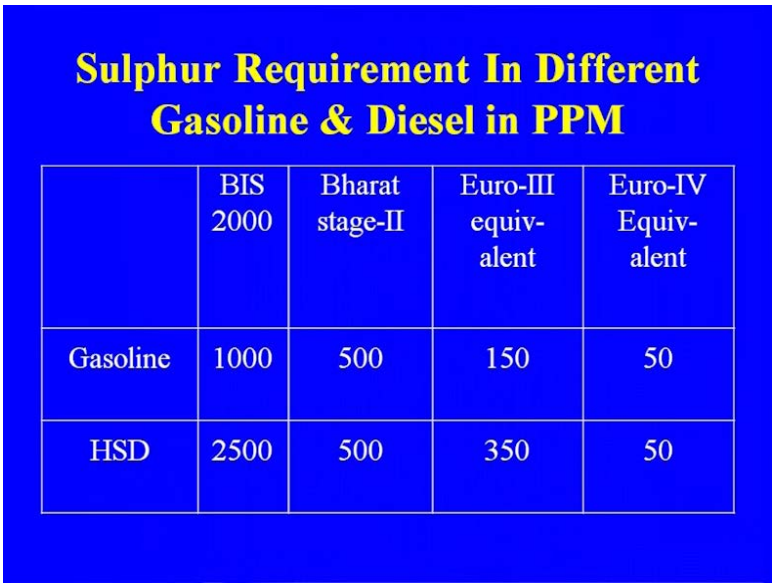

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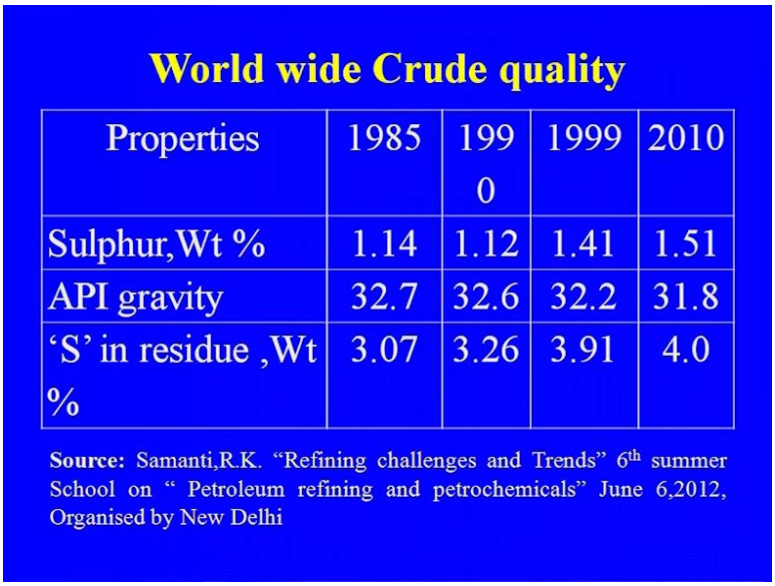

This is the worldwide crude quality how it is changing. If you see the 1985 to 2010 is sulphur contained crude oil variety from lighter to heaver sulphur in the ratio, that is also increasing. So, these are some of the problems which need desulphurization of the product disulphidation of the feed stock to the various process. And During the process from various schemes we are getting because one of the major source of the sulphur in this refining is the FCC. If you see, the FCC because the feed stocks is going to deduct. So, one of the major sources of the sulphur is FCC.

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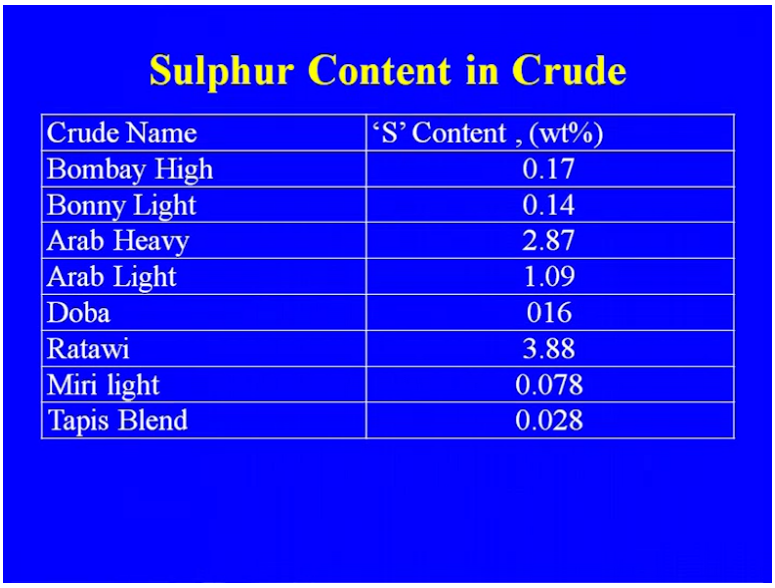

This is the sulphur content of the various crude, indigenous crude and other crude. Here it is the Bombay 0.1 bonny 0.1, or heavy 2.8. So, you can see that wide variation is there in case of the sulphur content in the crude.

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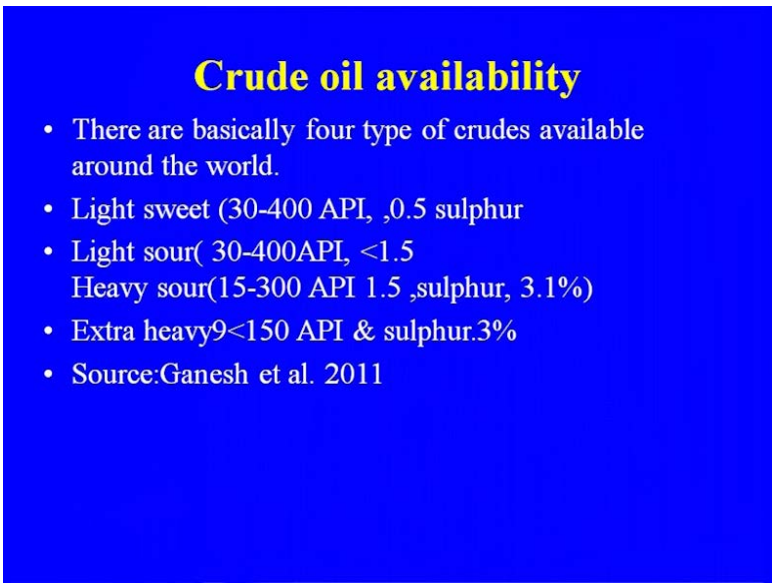

There are basically four types of crudes available around the world that already we have discussed that we are having the light sweet and light sour, heavy sour, extra heavy sulphur. So, this is how that sulphur content that is varying, gravity that is varying or in case of light that is 30 to 40 light sour. But in case of the heavy sour it is more heavier

stock is there. So, this is how the changes is taking place in crude availability in the future it is expected at more and more heavier crude oil that will be available.

And you will have to adjust your processing scheme in the required refining accordingly just to meet the environmental standards. Because definitely now we will have to supply the fuel of euro 4 norms even in India. Some refining already they are ready to supply the fuel of the euro 4 norms. So, definitely these are the changes that is will be taking place in the refinery process of the coming of the heavier crude or the high sulphur crude.

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Reactivity of Sulphur Compounds Present in Crude Oil

Sulphur compound	Relative reaction rate	Boiling points
Thiophene	100	185
Benzothiphene	50	430
Dibenzothiophene	30	590
Dimethyldib-nzothiophene	5	600-620
trimethyldibenzothiophene	-	630-680

These are I was telling reactivity of sulphur compound relative reaction rate, boiling points of the various component which is creating lots of problems in case of the. So, depending upon the removal of the mercaptans sulphide is more easier than the thiophenes and the benzothiophene. Now, let us discuss what are the sources from where the sulphur is living in this scheme.

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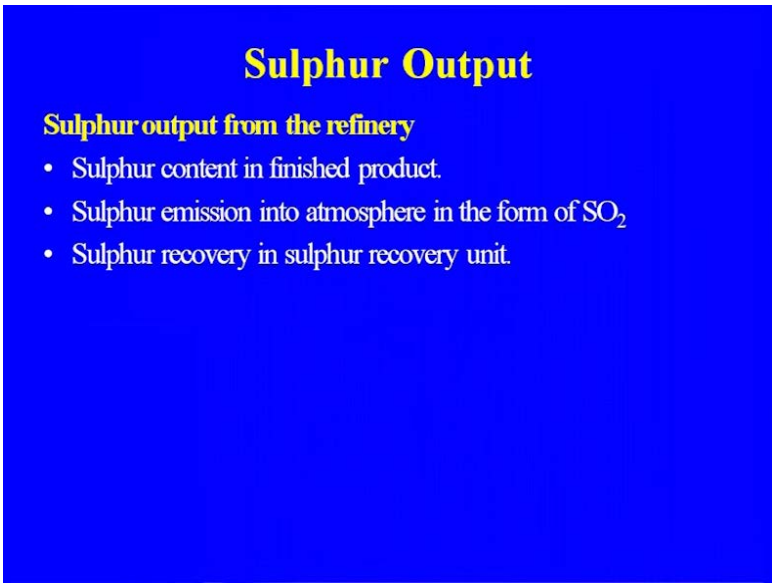

So, the sulphur content in finished product sulphur emission into atmosphere in form of SO2. This is coming to the because we are speaking about the sulphur output from the refinery. Sulphur recovery- in sulphur recovery unit there are nearly the clause process or modify process been up to 97percent. Some of the sulphuric compound is still remaining, so because of that reason now we are going for the has been development in the sulphuric units to achieve maximum sulphur compound.

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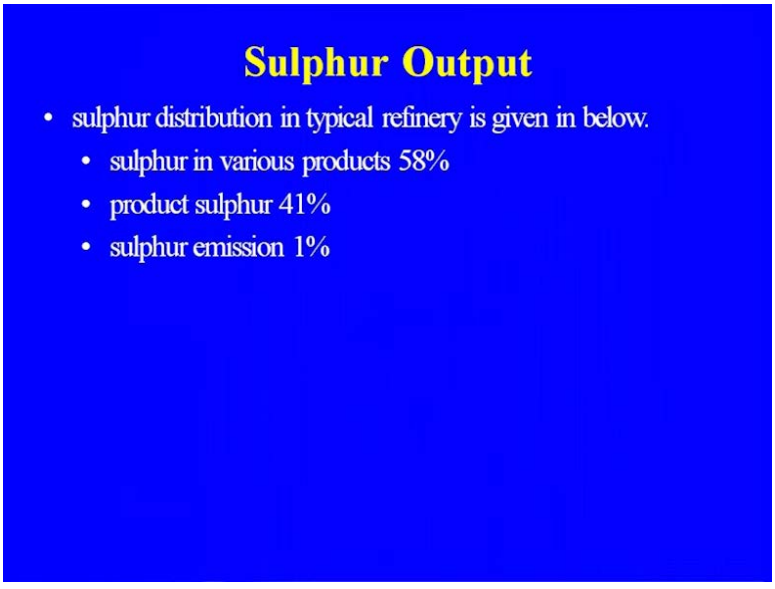

Sulphur distribution typical to find a sulphur in the various products 58 percent, product sulphur 41 percent and sulphur emission 1 percent.

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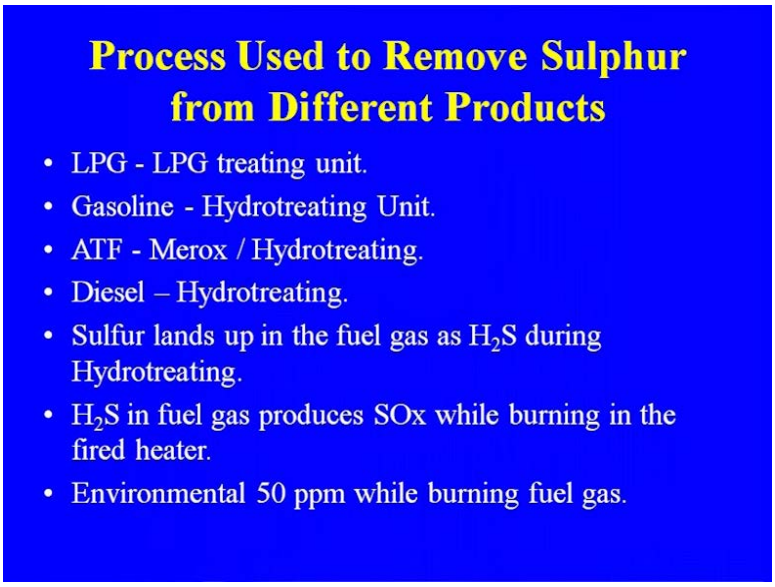

You see the user contributor or the product and the various products, which are getting from the refinery operation. These are the some of the sources, which need the removal of the sulphur and we are doing the desulphurization for removing the sulphur. LPG treating unit where we are removing force, because these are all which are removable and they are going further processing, for the removal of this gases from the gaseous stream. And finally, this going to the recovery of the sulphur by class, modify class or, any other modification.

So, the gasoline treating hydro treating is also again the hydro sulphur process emission merox process and so on hydro treating has been there, hydro treating- hydro sulphate is there. Sulphur lands up in the fuel as H2S during the hydro treating processes. H2S of the of the fuel gas Sox while burning in the fired heater. Environment 50 ppm, while burning the fuel gas this is the environmental standard of the emission.

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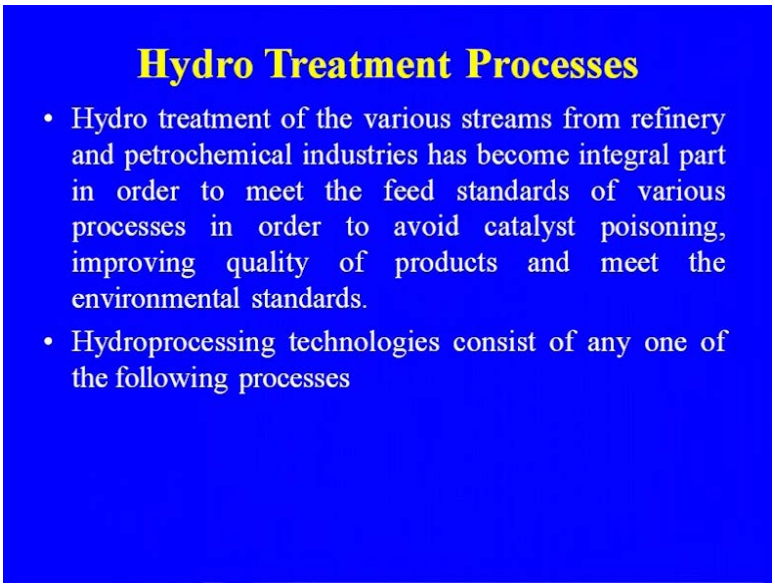

Hydro treatment processes are the various streams from refinery and petro chemical industries, it has become integral part in order to meet the feed of standards of various processes. In order to avoid catalyst poisoning, improving quality of products and meet the environmental standards. Hydro processing technologies consist of any one of the process that we are using.

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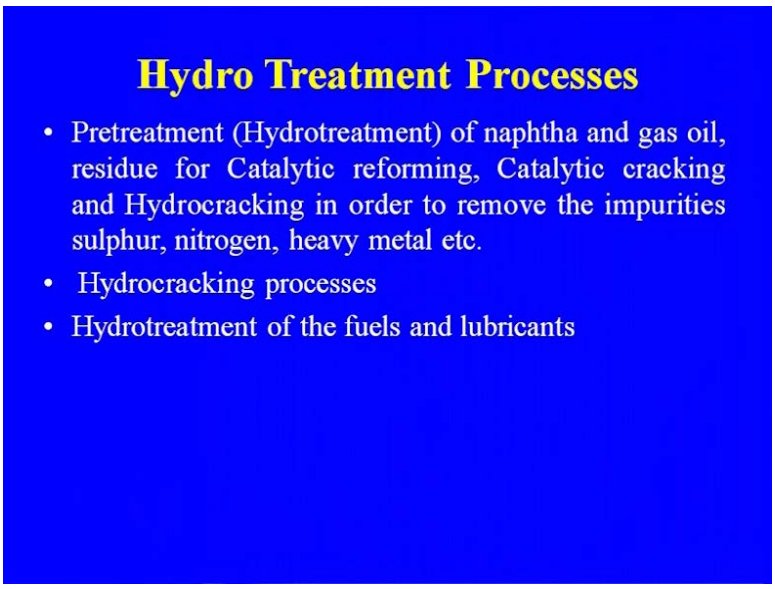

That may be the pretreatment, it may be the hydro cracking processes, hydro treatment of the fuels and lubricants. These are some of hydro treatment process. Pretreatment of the

hydro treatment of naphtha and gas oil, residue for the catalytic, residue from the catalytic reforming, catalytic cracking. Hydrocracking in order to remove the impurities of sulphur, nitrogen, heavy metal extra. Hydro cracking processes, hydro treatment of the fuels and lubricants.

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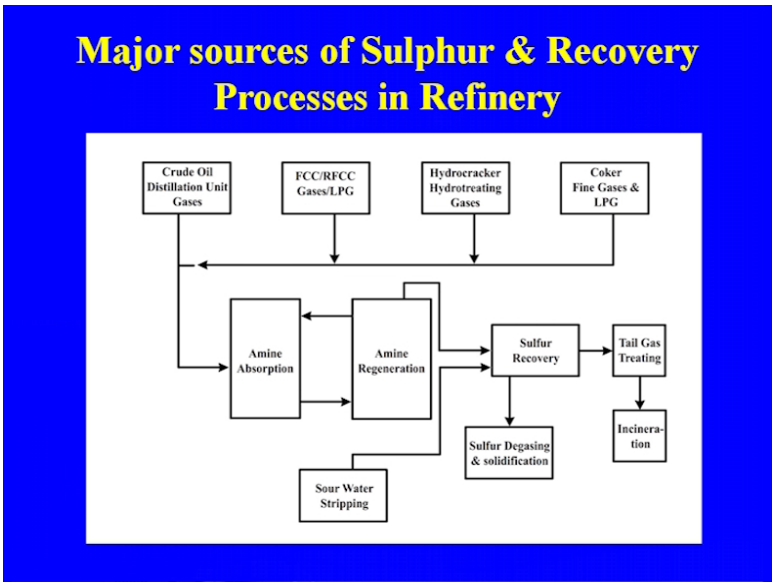

This is actually the if you see the major sources of sulphur and recovery process in refinery to find the crude oil distillation in unit, FCC are the residue fluid catalytic cracking, gases LPG hydrocracker, and hydro treating gases is a cooker, refine gases and the LPG. So, these are some of the sources which normally from the gases we are having the mean absorption. And then, the amine regeneration gases after the refinery removal that is going to the sulphur recovery, we are getting sulphur it is when the tail gas is which are there that is going for further removal.

And the Finally, it is going to installation and have definitely one or the other source finding, because of the processing sour crude, that is sour water from the various stream. So, the sour water is gaseous from the source, water that is removed and again it is going to the sulphur recovery plant. This is same process that we discussed.

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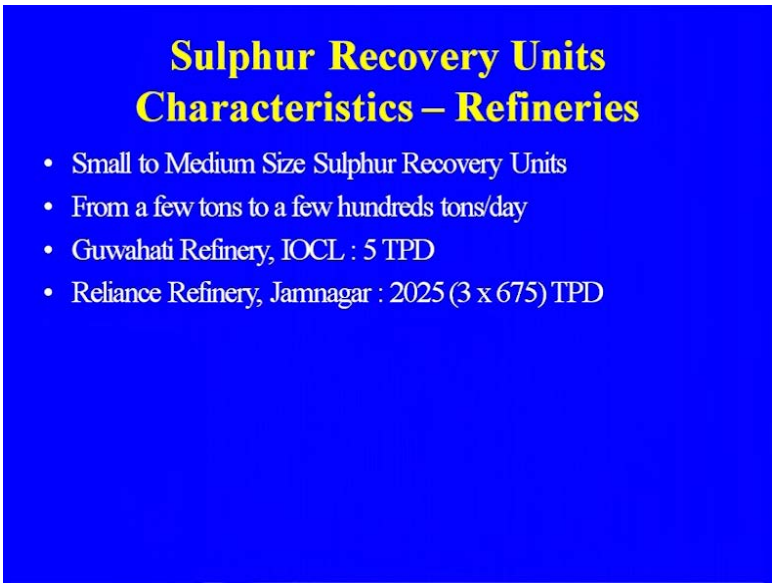

Sulphur recovery units characteristics small to medium size sulphur recovery units and from a few tons to a few 100 tons per day Guwahati refining, because of the sulphur content is low, the sulphur production is less. But, in case of the Reliance Jamnagar processing where they are processing more heavier fluid stock production of the sulphur is high.

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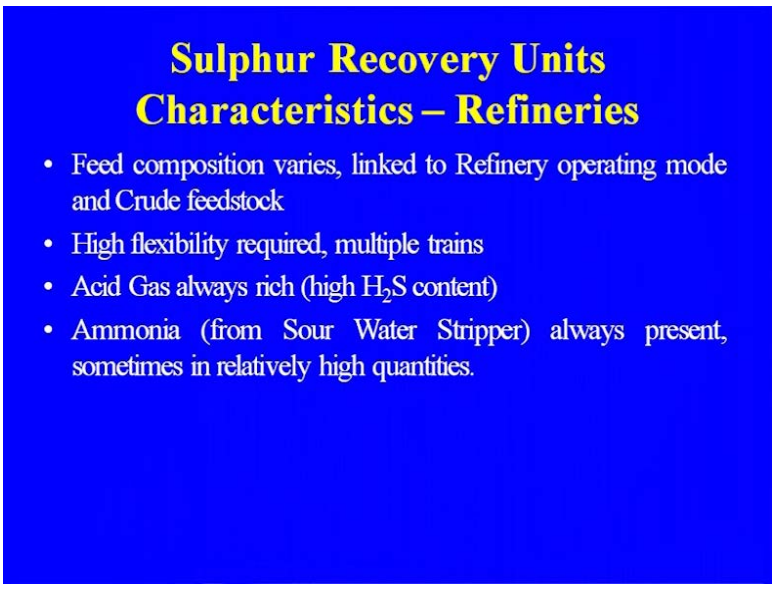

Sulphur recovery units, feed composition varies linked to refinery operating mode and crude feedbacks. High flexibility is required, multiple trains, acid gas always rich high

H2S content. Ammonia from sour water always present, sometimes in relatively high quantities because the ammonia that we are using in case of the distillation column from crude distillation call or remaining case of the FCC also (( )) to get rid of the corrosion problem. So, these were the some of the sources about from the actually the sour gases are the sulphur gas that is coming. And now, let us discuss about the sulphur recovering unit.

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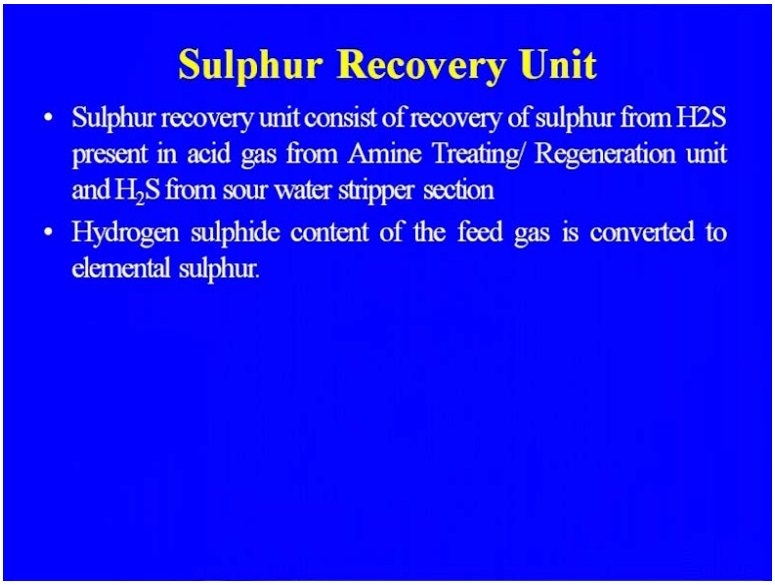

Sulphur recovery unit consist of recovery of sulphur from H2S present in acid gas from amine treating regeneration unit, and H2S from sour water stripping section, which I had told you, there are two sources. One the all gasses that is going to amine absorption and after the amine absorption again the after re-generation of the amine the gas is steam that is going for the treatment. And other source of the sour where H2S, that may be from water deeper section from the sour water. Hydrogen sulphide content of the feed gas is converted to elemental sulphur because this is how we can get rid of the sulphur compound.

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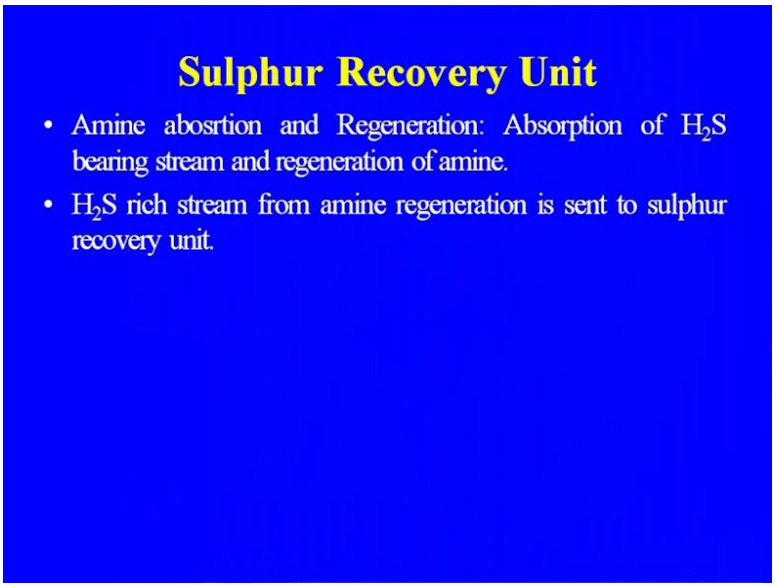

So, amine absorption and regeneration, it is the process which I told you absorption of the H2S, where H2S is bearing stream, and regeneration of amine. H2S rich from amine regeneration is sent to sulphur recovery unit for recovery of the sulphur from the gas. Now, let us discuss the merox process, that is the integral part of the refinery, and all the refinery they are having merox process.

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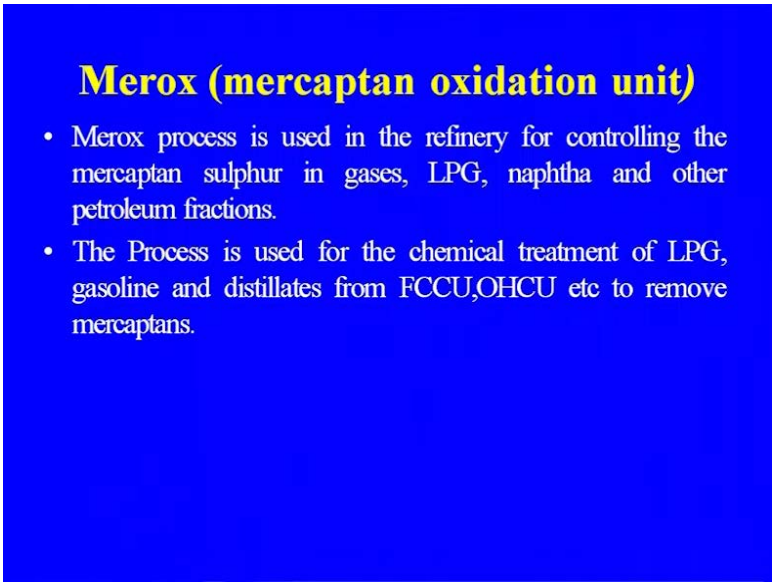

Merox process is used in the refinery for controlling the mercaptan sulphur in gases LPG, naphtha and other petroleum fraction. The process is used for the chemical

treatment of LPG gasoline and distillates from FCC or the hydro clerical or the (( )) the OHCU joins through and FCC will be fluid catalytic craking to remove the mercaptans.

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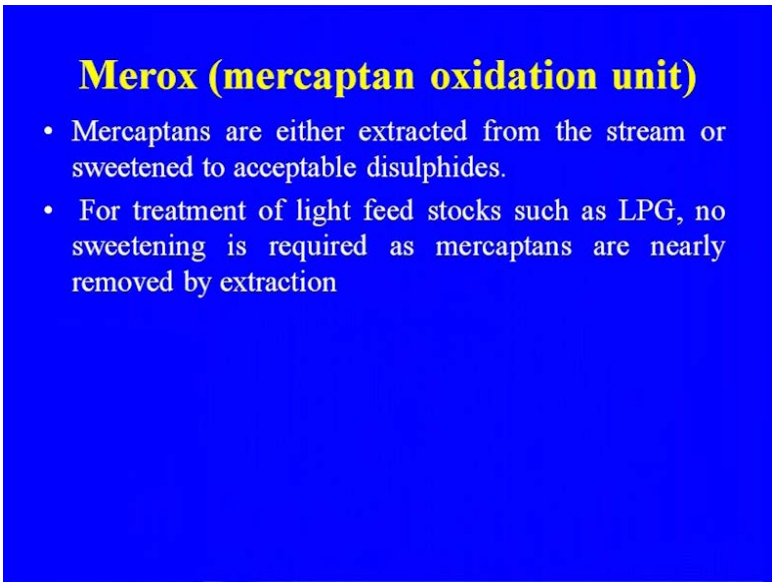

Mercaptans are either extracted from the stream, or sweetened to acceptable disulphides because the disulphides may or may not be present, but the removal of the both part sulphides and disulphides, or, it has to be removed for treatment of the light feed stocks, such as, LPG no sweetening is required as mercaptans are removed by extraction. So, that is the two types of the measure to do the sweetening, by which you can remove the mercaptan from the gaseous stream. However, feed containing higher molecular weight mercaptans may require a combination of merox extraction and sweetening using catalyst. Because the process catalyst promote the oxidation of mercaptans to disulphide using air as the source of oxygen.

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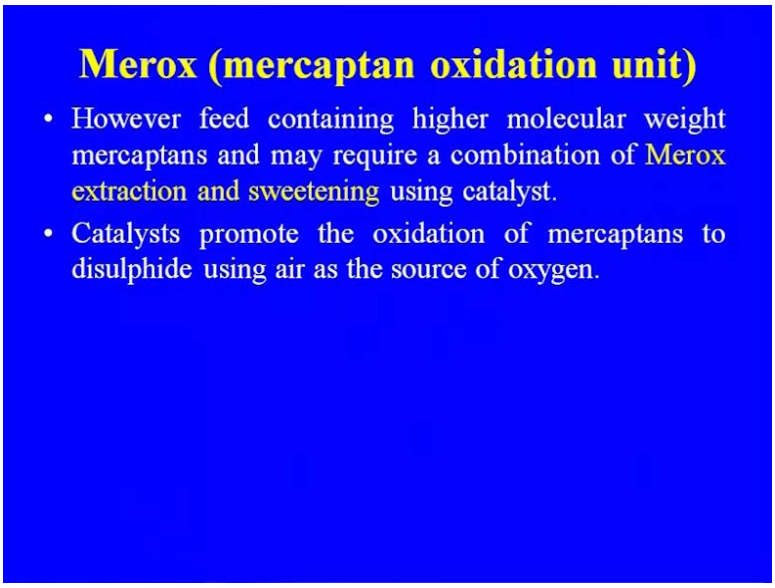

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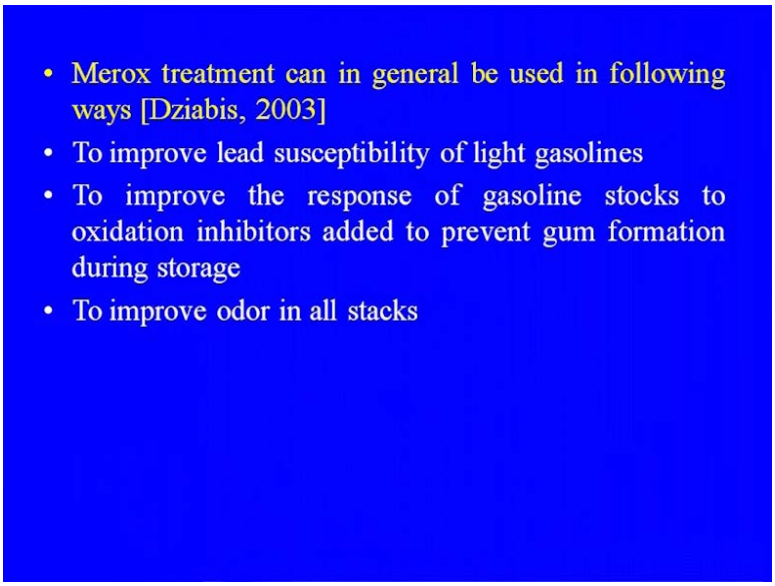

Merox treatment can, in general be used in following ways to improve lead susceptibility of light gasolines. But, that problem is not there to improve the response of gasoline because you already read as free zone to improve the response of gasoline stocks to oxidation inhibitors added to prevent gum formation during storage to improve odor in all stocks.

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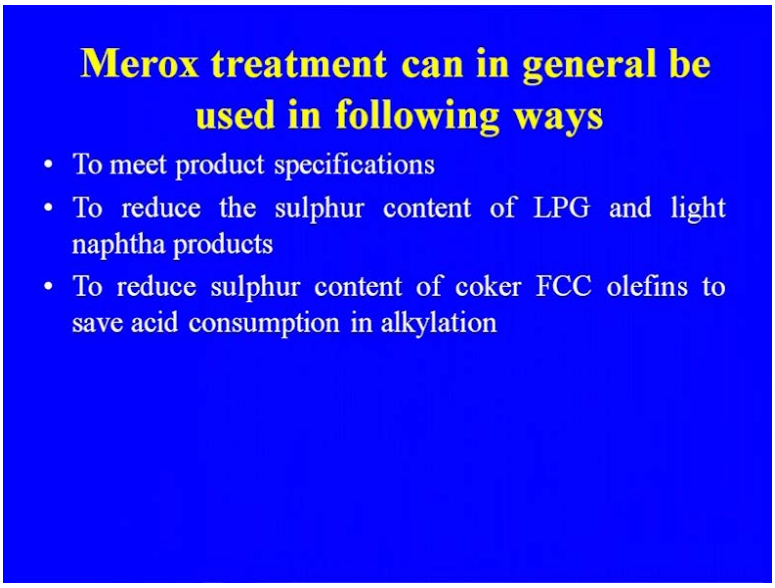

Merox treatment can in general be used to meet the product specifications to reduce the sulphur content of the cooker FCC, olefins to save acid consumption in alkylation process.

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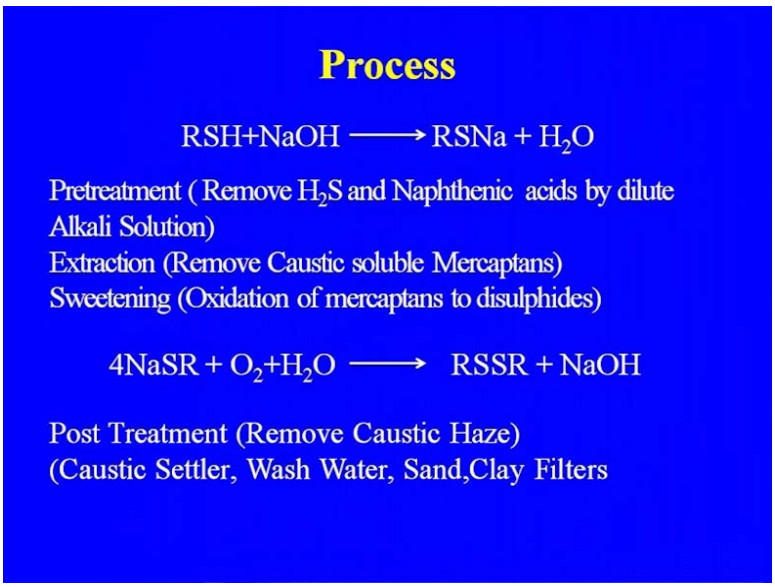

This is the process that we are using in pretreatment extraction and the sweetening. So, this is the method that the reaction is taking place. You are treating with the NaOH, sweetening oxidation mercaptans to disulphides that is taking place. So, these are some of the reaction that are taking place in the extraction and this is the cost sheet we are

using for the extraction. So, in the extraction of the sweetening process. Sulphur recovery from H2S, what about this H2S that we are getting, the conversion of the H2S are mercaptans of the sulphur that is important.

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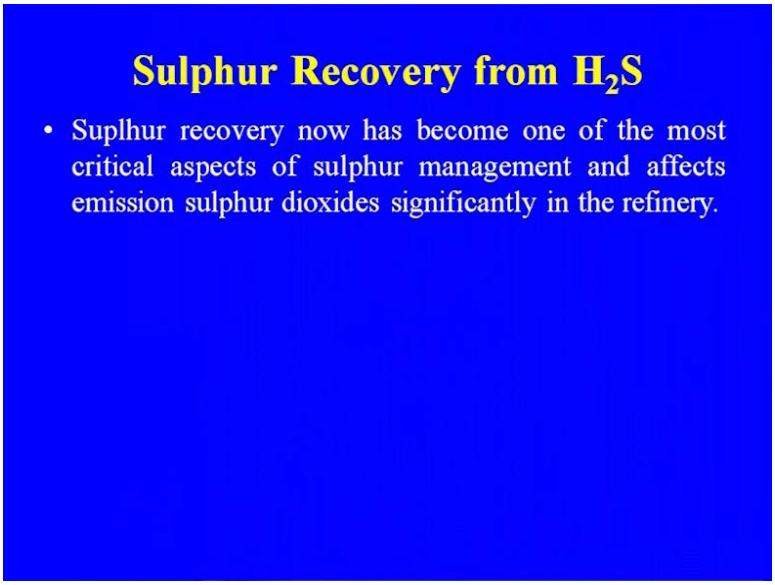

Sulphur recovery now has become the most critical aspects of sulphur management and effects emission sulphur dioxides significantly in refinery because, if you are not properly removing. So, this SO2 emission data will be at and even it is not at requirement of the fuel only it is required at the requirement of the refining stage emission and also to have the close sulphur dioxide in the stage they are, of course, the emission of SO2 or the particular matter from the FCC and one of the main sources that is available in the standards given by the central portion control port.

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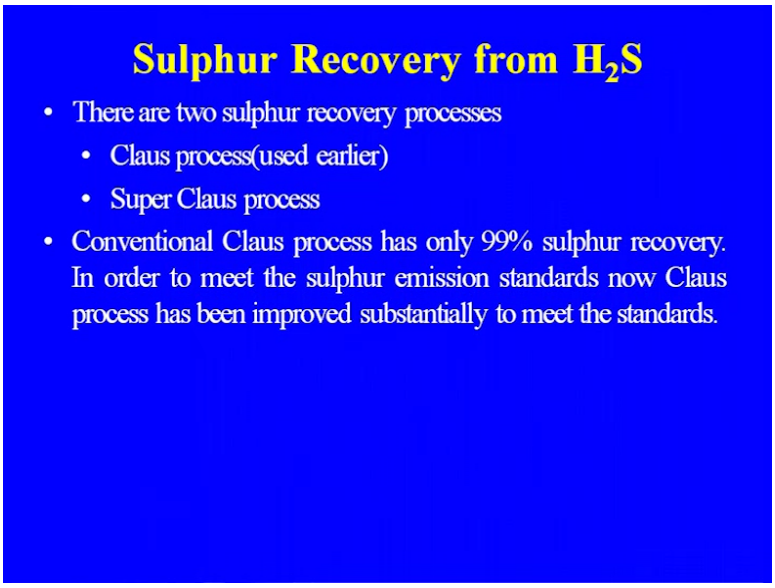

Now, let us discuss about the sulphuric recovery in more detail, there are two recovery processes that is, the class process and the conventional claus process used as earlier, now we are talking about super claus process. Because you see in claus process the removal of the sulphur compound that was less, and the recovery part that was less, and this still gets continue to form lot of the sulphur compound and just to minimize that emission again the conventional claus for process that has been modified.

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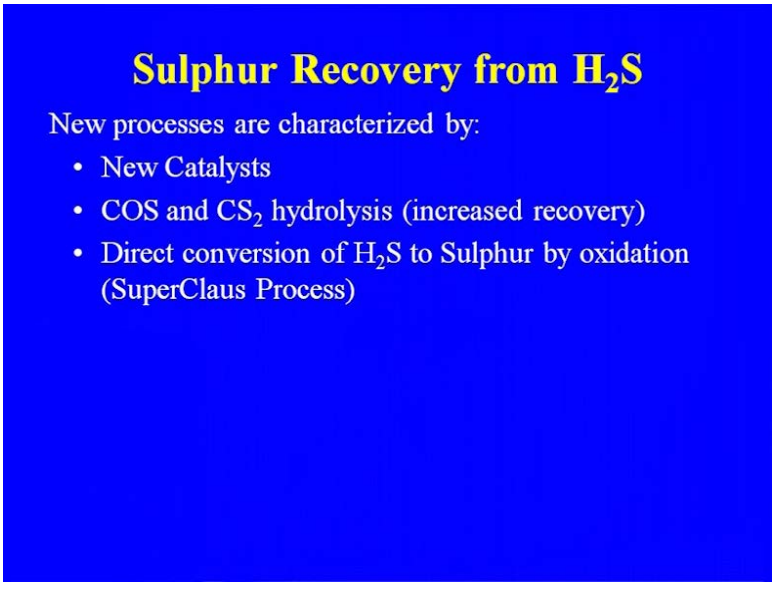

The conventional claus process is only even 99 or 97 to 99 percent sulphur recovery. In order to meet the sulphuric emission standards now claus process has been improved substantially to meet the standards. New processes are characterized by new catalysts like COS and carbon sulphide hydrolysis increased recovery direct conversion of H2S sulphur by oxidation. That is what we are doing in case of the super claus process.

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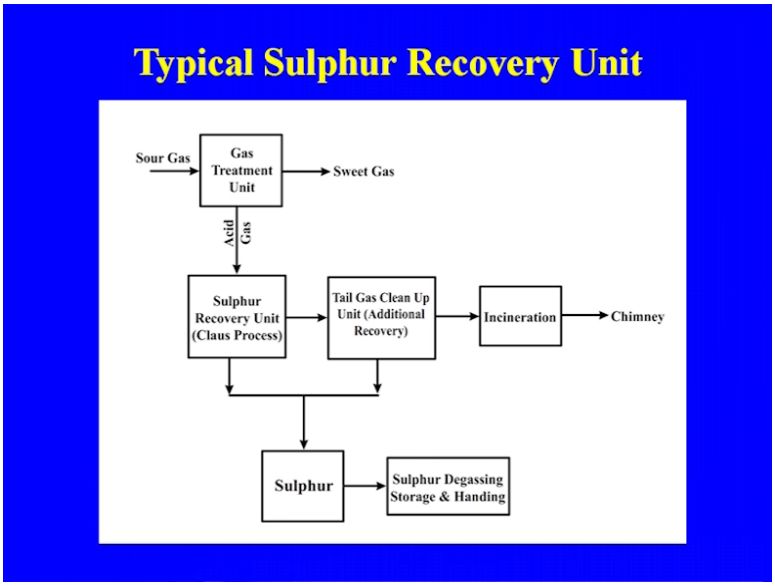

This is the typical sulphur recovery unit, this is sour gas that is going to gas treatment unit sweet gas, then acid gas is that will go to recovery unit claus process. Then the tail gases in claus process again that will go to further treatment. So, tail gas clean up unit additional recovery. Then, finally we are getting the sulphur and gas, that will go of incineration and they enter the chimney. So, this is the process that we are having in case of the typical sulphur recovery unit. Here you see the steel gasses because this was the additional modification that has been done with the coming of the stringent standards and the sulphur recovery, tail gas that is treated and finally, the sulphur compounds that can be used in the various processes.

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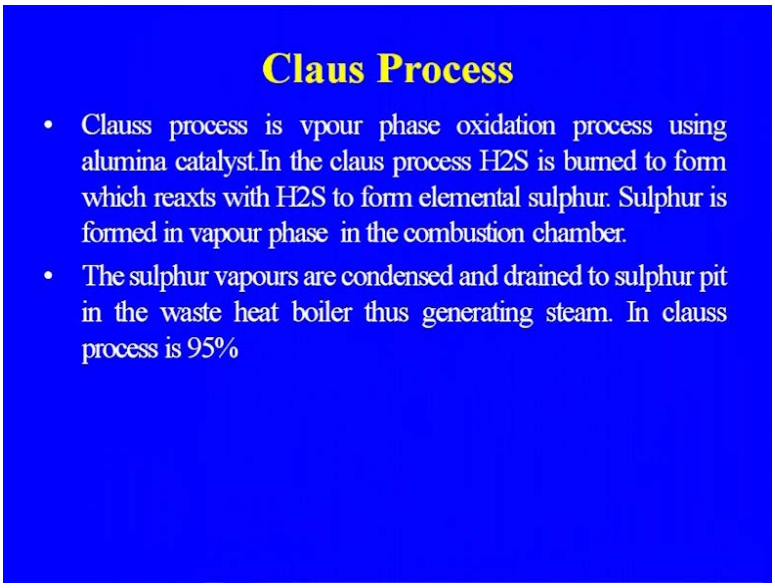

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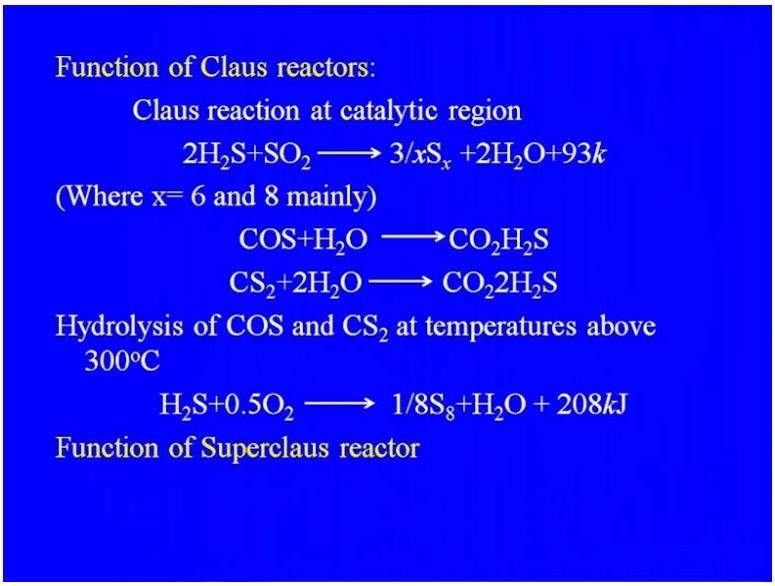

Let us now discuss claus process is vapor phase oxidation process using alumina catalyst. In the claus process, H2S is burned to form which reacts with H2S to form elemental sulphur. Sulphur is formed in vapour phase in the combustion chamber. The sulphur vapours are condensed and drained to sulphur pit in the waste heat boiler, thus generating steam in Claus process for about 95 to 97 percent. If you have super claus then the heated is high.

So, the function of the claus reactors these are the some of the reaction at the catalytic reason hydrolysis part, which I was telling was the COS. CS2 finally and the part is oxidized to element sulphur, this is the burning function of the superclaus reactor that we are generating the sulphur compound.

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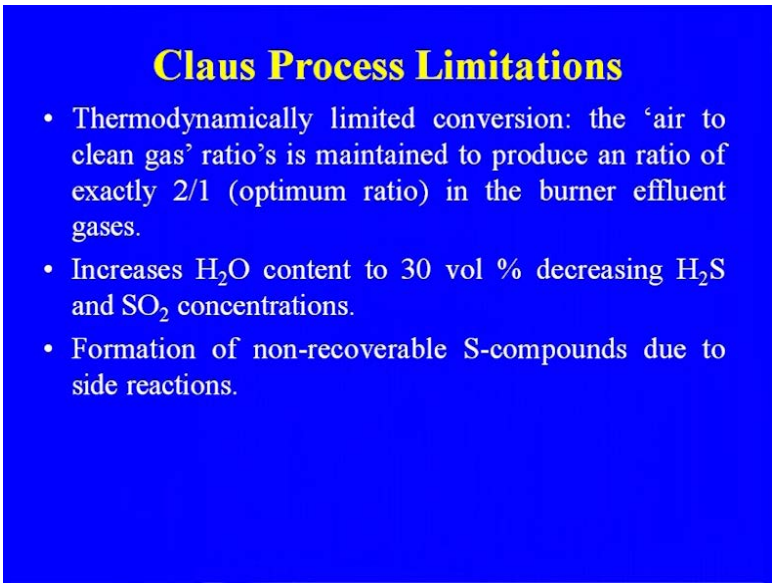

Claus process limitations, thermodynamically limited conversion the air to clean gas ratio's is maintained to produce an ratio of exactly 2 by 1 optimum ratio in the burner effluent gases. Increases H2O content to 30 volume percent decreasing H2S and SO2 concentrations. Formation of the non-recoverable sulphur compounds due to side reactions. So, these are the some of the limitation in case of the claus processes. So, let us now discuss the super claus process as I told you because, the problem in case of the claus process is removal efficiency around 95 to 96 we can say. And the further removal that can say the necessities and that can again removal of the sulphur compounds that are in carbon.

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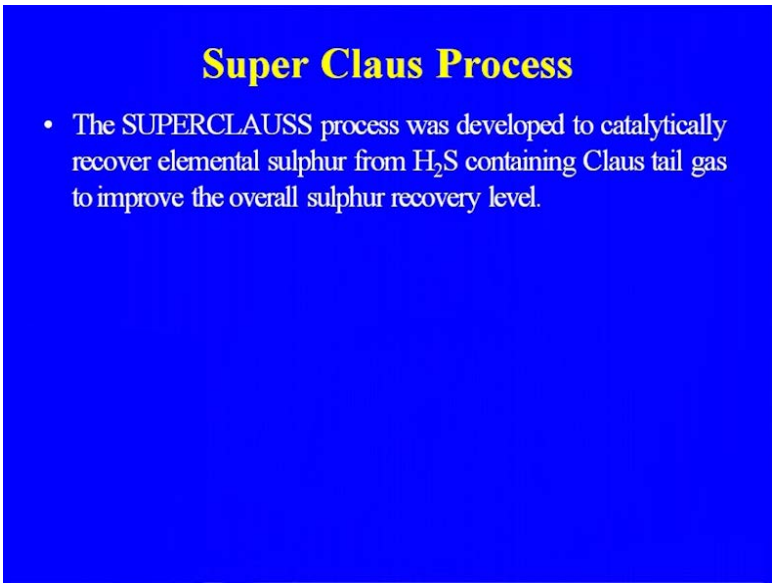

So, the super claus process was developed to catalycally recover elemental sulphur from H2S containing claus tail gas to improve the overall sulphur recovery level in the diefining.

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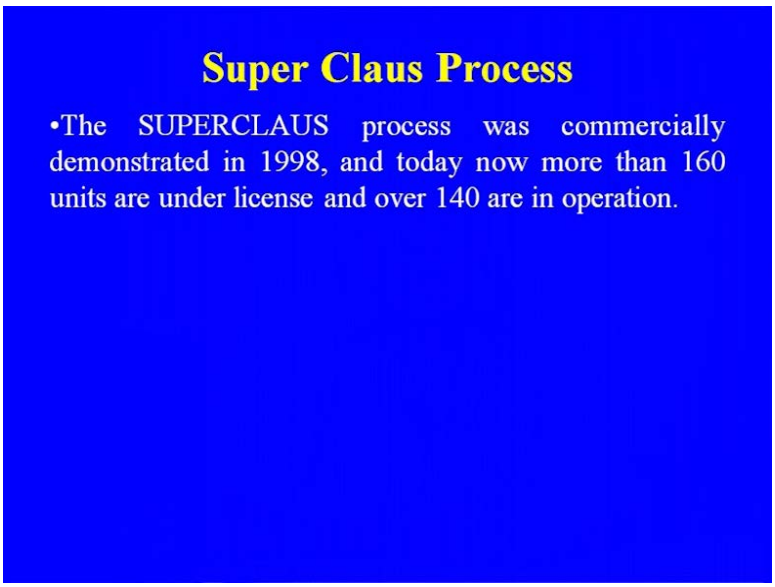

The super claus process was commercially demonstrated in 1998 and today more than one sixty units are under license and over 140 are in operation.

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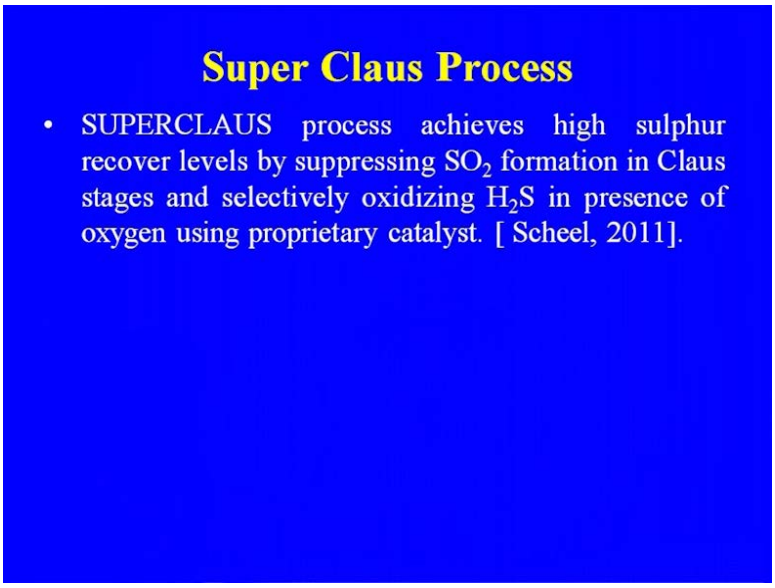

Super claus process achieves high sulphur recover levels by suppressing SO2 formation in claus stages and selectivity oxidizing H2S in presence of oxygen using proprietary catalyst.

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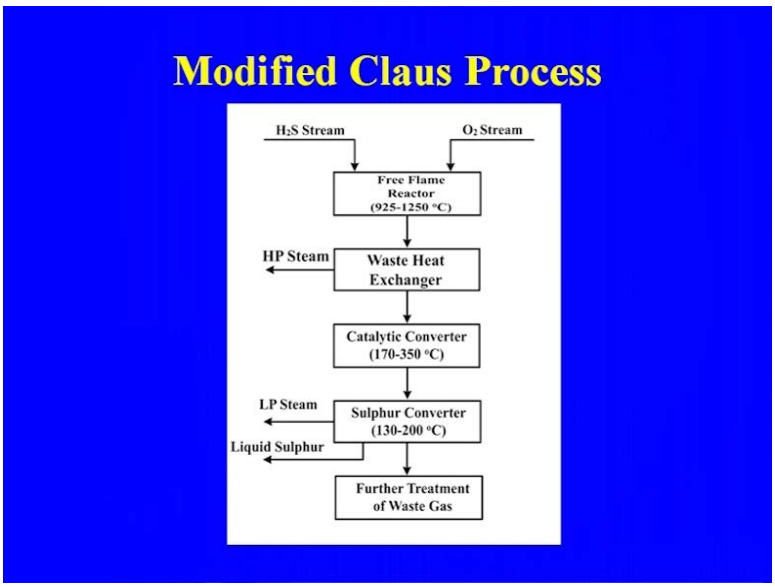

This is the modified claus process here you see the H2S that is the stream term director oxygen is stream. It is going to waste heat boiler, catalytic converter, sulphur condenser. From where we are getting sulphur and further treatment of the waste gas that is so, the modified claus process. So, what are the various typical of the super claus process?

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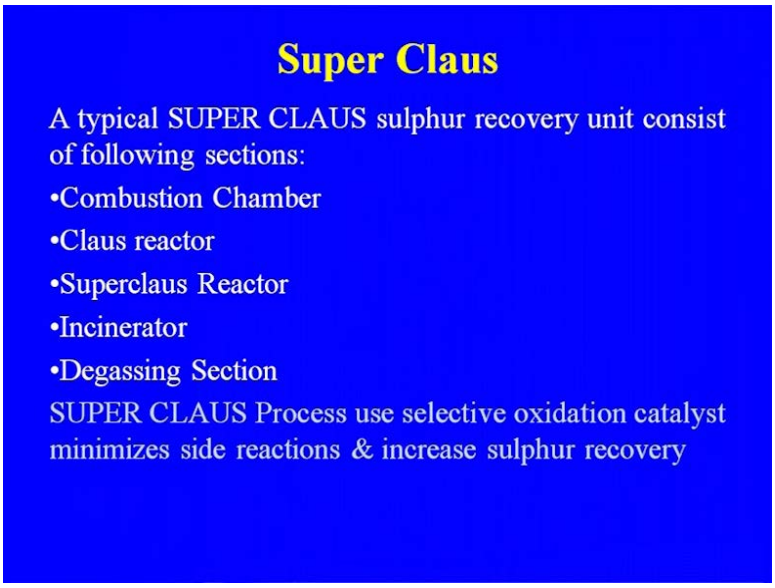

Combustion chamber, claus reactor, super claus reactor, incinerator, degassing section. Super cluas process use selective oxidation catalyst minimizes side reactions and increase sulphur recovery.

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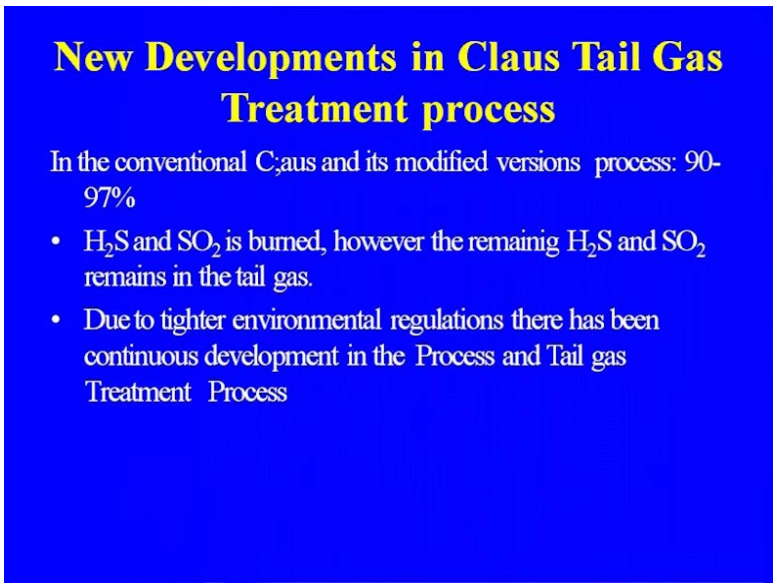

New development in claus tail gas treatment process in the conventional claus and its modified versions process 90 to 97 percent, because 90 to 97 percent that is on the hard side depending upon the efficiency of the claus process. The emission the conversion that may be as low as 90 percent H2S and SO2 is burned, however the remaining H2S

and SO2 remains in the tail gas. That was the problem in case of the conventional claus process. Due to high environmental regulations there has been continuous development in the process and tail gas treatment process.

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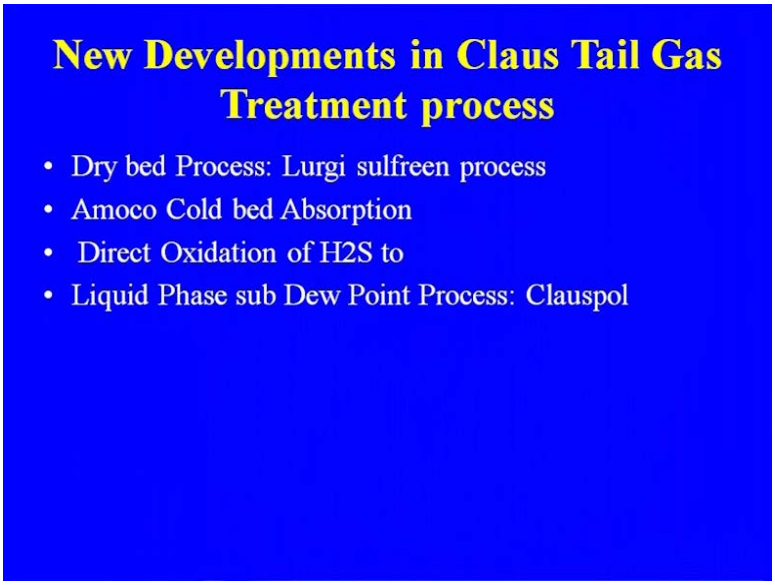

So, these are the some of the process developed for the treatment process is dry bed process, Lurgi sulfreen process, amoco cold absorption, direct oxidation of H2S, liquid phase sub dew point process: that is clauspol process.

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This is another process that we are using which we are liquid redox process: uses solutions of chemically chealted metal ion oxidize H2S to elemental sulphur. So, these are some of commercial process which are available for stretford process, sulfolin process, sulferox process, locat process, castol process. These are the some of the process that is available to meet the required standards the chemical process.

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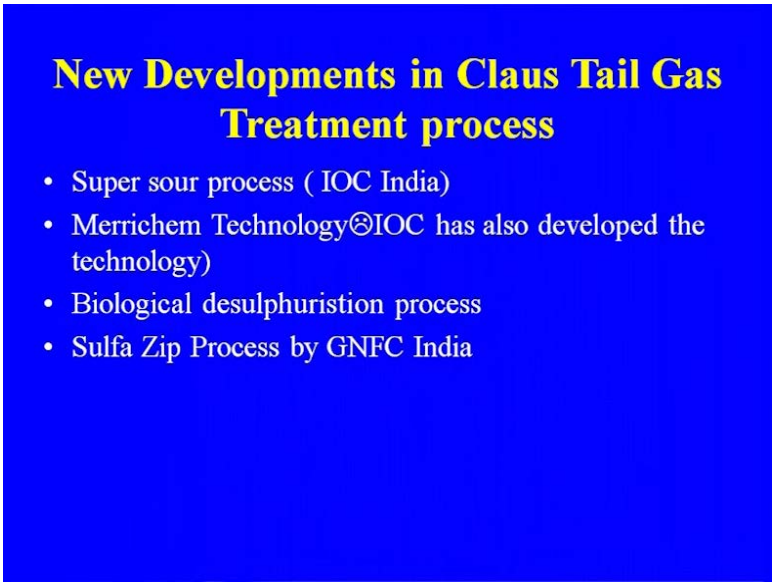

Then the another process, which has been developed by super sour process that was by Indian oil corporation. In India that is sour process, I will be discussing this super process. Merrihem technology has been developed that is by the IOC also. Biological desulphurization process that is biological process. Sulfa process that is by the Gujarat navodaya fertilization corporation India. So, they are using the sulfa process one over the sulphur compound.

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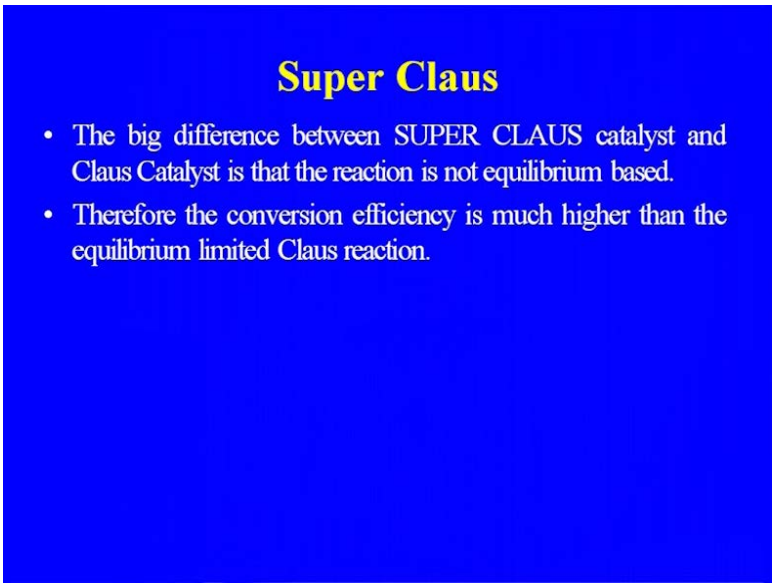

Super claus the big difference between super claus catalyst and claus catalyst is that the reaction is not equilibrium based. Therefore, the conversion efficiency is much higher than the equilibrium limited claus reaction.

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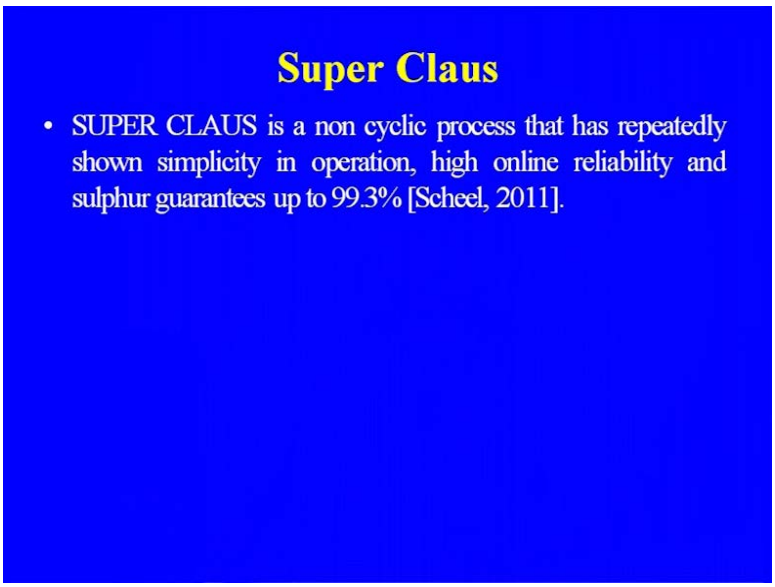

Another feature of super claus it is non cyclic process, that has repeatedly shown simplicity in operation, high online reliability and sulphur guarantees up to 99.3 percent. Now let us discus the super sour process which has been developed by corporation.

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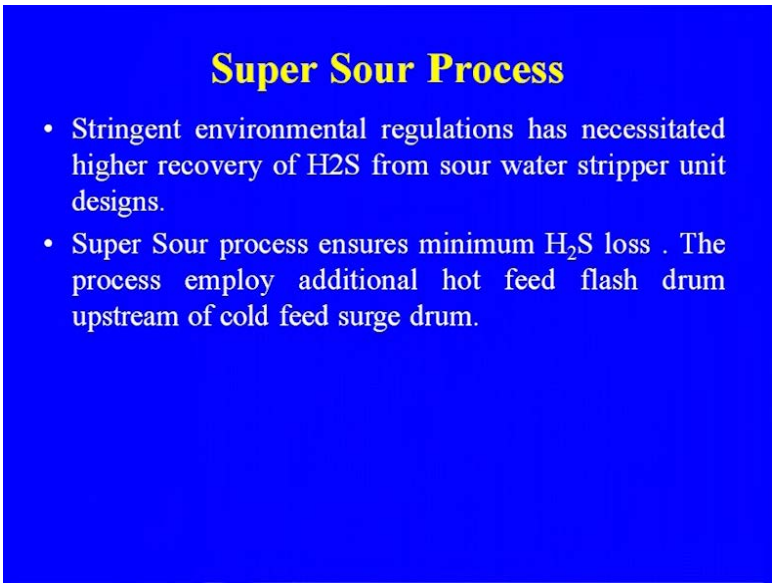

Stringent environmental regulations has necessitated higher recovery of H2S from sour water stripper unit designs. Because you see the sour water that is also one of the major source to find because, we are treating high sulphur crude oil in the process and so, during the removal in various section is the sour water, which is generated and the sour water of the S2P gases that is going for the treatment. Super sour process minimum H2S loss the process employ additional hot feed drum upstream of cold feed surge drum.

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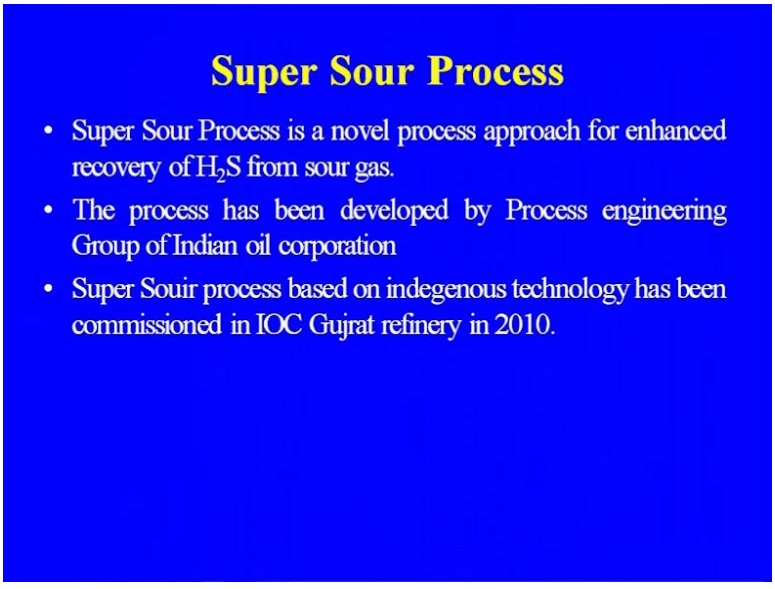

Super sour process is a novel process approach for enhanced recovery of H2S from sour gas. The process has been developed by process engineering group of Indian Oil Corporation. Super sour process based on indigenous technology has been commissioned in IOC Gujrat refinery in 2010. Because there was lot of the problem in refining emission of sour gas emission of sulphur compounds by sour water. So the process was developed by IOC that has been commissioned there.

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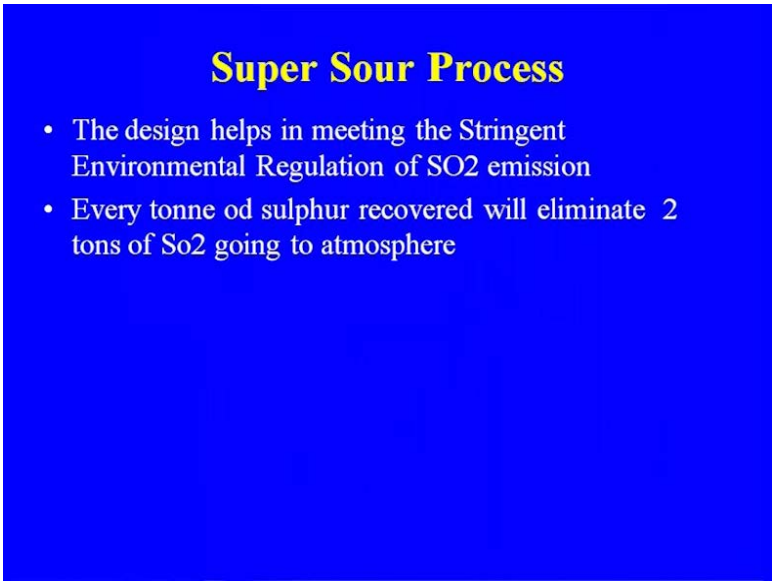

The design helps in meeting the stringent environmental regulation of SO2 emission, every tone of the sulphur will eliminate 2 tons of SO2 going to the atmosphere. So, this is how the recovery part will be important. So, this is actually, the conventional process on the comparison of the super sour process.

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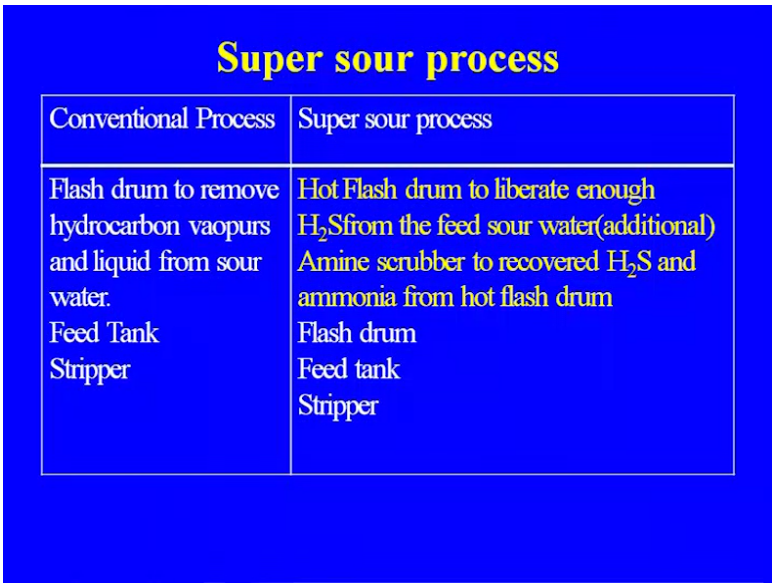

Conventional process flash drum to remove hydrocarbon vapors and liquid from sour water, feed tank and the stripper. Here actually, some modification that are conventional that we are not only having the we are doing the stream thing of the sour water and these are the some of the units they are. But if this is the completely with this your super sour process. So, this is the some of the additional unit hot flash drum to liberate the enough H2S from the sweet sour water.

So, this is the additional amine scrubber is recovered H2S and ammonia from hot flash drum flash drum feed tank and stripper because these are the that is also there in the piece of conventional processes, where we are being what it is over. So, in case of this super we have one half that has been added amine scrubber is recovered. So, that are the emission that is so this is the advantage that is influencing the conventional sulphur soap process.

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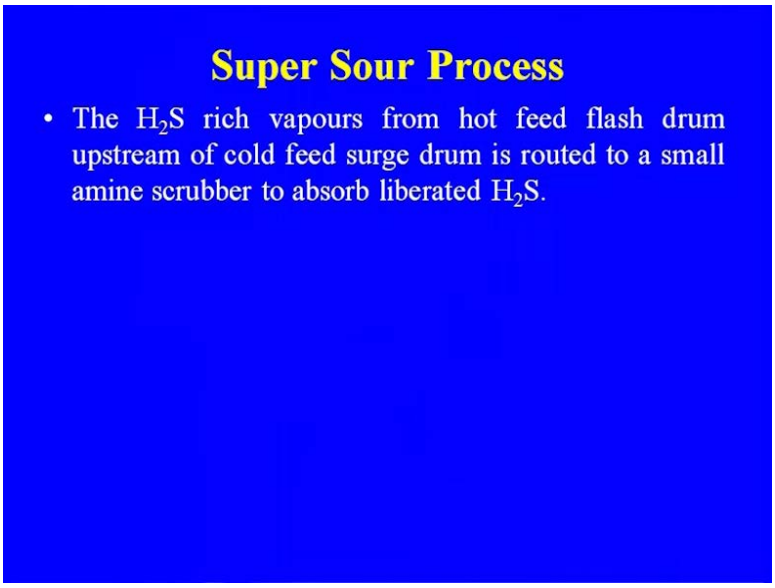

In case of the super sour process the H2S vapors from hot feed flash drum upstream of cold feed surge drum is routed to a small amine scrubber to absorb the liberated H2S. So, that is the telling at the additional, which I feature of the super sour process that is going to the amine from the recovered from this part. So, that is going amine discovered and the weightier involved efficiency there.

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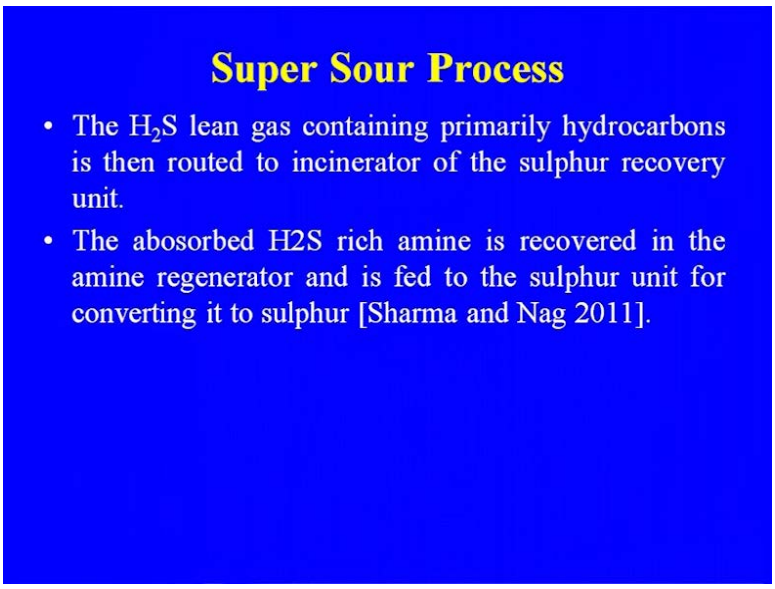

The H2S lean gas containing primarily hydrocarbons is then routed to incinerator of the sulphur recovery unit. The absorbed H2S regenerator amine is recovered and is fed to the

sulphur unit recovering the for converting it to elemental sulphur. So, this approximate that they are using for the sour water, another technology that is been developed merichem process content technology even this technology that has been also developed by Indian oil corporation.

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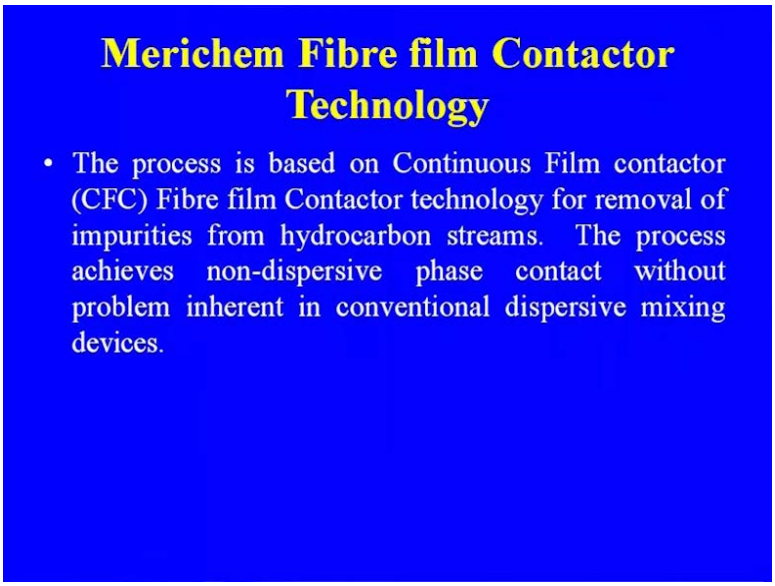

The process is based on continuous film contractor, fiber film contractor technology for removal of impurities from hydro carbon streams. So, this is the new development in sulphur recovery process. The process achieves non-dispersive phase contact without problem inherent in conventional dispersive mixing devices. So, this is one of the contracting that improves because of the continuous film contractor.

So, this was about the sulphur recovery decomposition process and you can see the general have become the more and more stringent. So, definitely the disulphide process and the sulphur recovery section of the refinery that is going to play very important tool. Because definitely, these tenders these whole we are have 50, SO2 we do not know what happens to 0 4, 0 5, 0 6 in the features because and at the same time the amount of the sulphur, which is released which is produced in the refining that will increase with the utilization of more and more crude oil from available from the various resources.

Now, actually there is also the reason why the refining is done here also that the refining that many of the refining of the heavier crude oil also, that is cheaper than these goods that is also. So, they are having the blend whatever they are having oil processes in the

refining is not only from the singular seeds. It is behind because definitely it has to have our requirement about 65 percent of the requirement that has to meet to be imported. So, the whole economy of process that will depend on the process. So, this processes the sulphur recovery and the desulphurization process because in the process, we are moving sulphur so that will play.

In the next lecture it will be on the petro chemical, already we have discussed from the starting from the introduction to the refining and then the to the crude oil evolution distillation of the crude oil. And some of the further conversion process using the refinery it may be for the FCC hydro cracker for the forming. So all the process we have discussed and then next part is the petro chemical that is the in the future you may have the petro chemical refining not only refining because of concept of the defining that these are changing. And so the now we are talking about the gasoline process we are talking about the GTL refinery, we are talking about the wire refining. So, the next lecture on the introduction of the petro chemical industry.