

**Technologies for Clean and Renewable  
Energy Production  
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**Lecture-16  
Impurities Removal from Liquid Fuels**

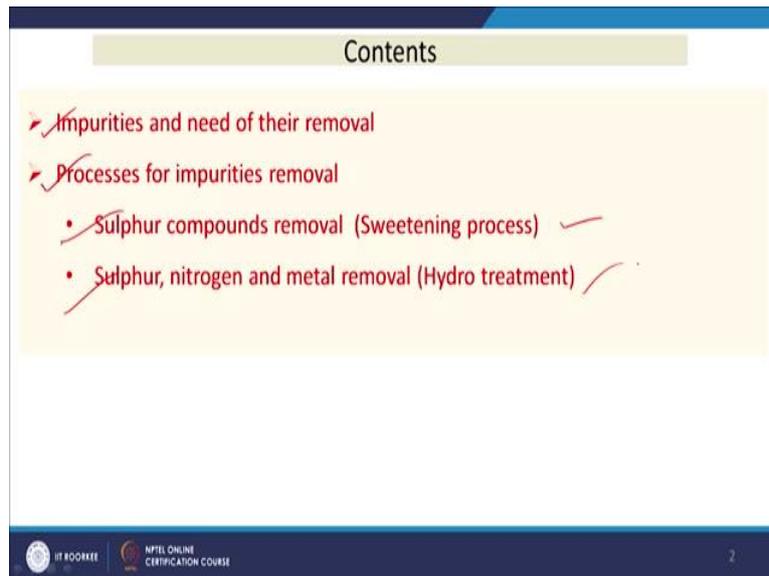
Hi friends, now we will discuss on the topic cleaner liquid fuel production from petroleum crude. In the previous class we have discussed how to produce liquid fuel from petroleum crude and now we will see how the liquid fuels can be produced more cleaner. Actually, we have come to know that the petroleum crude contains different types of impurities, let us say salt content sulphur, nitrogen, oxygen etcetera.

These impurities can create some problem and during the refining process, these can also be transferred to the liquid fuels and when the liquid fuel will be used as a transport fuel at that time pollutions will come. So, we need some cleaning options, the some methods to remove those pollutants from the liquid fuels. Secondly, we have come to know that the residual part particularly the one vacuum residue contains high asphaltene, high sulphur, high metals etc.

And this part is of less interest to the refiners and poorly managed and creates lot of environmental problems. So, up gradation of this vacuum residue is required and that can give us a cleaner route or cleaner option to the overall refining process. And it will also help to increase the economy of the refining process. Thirdly, we have come to know that gradually the petroleum crude quality is decreasing its sulphur content is increasing, viscosity increasing and degree API is reducing.

So, the processing of this heavy crude through the conventional technology is not that effective may not be that effective. So, we need some alternative technology to use these feedstock heavy feedstocks for its refining. So, these are the topics or sub topics we can say we are going to discuss in this module.

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And in this class we will discuss basically on the impurities removal. And the contents are impurities and need of their removal. Then process for impurities removal, like sulphur compound removal and then sulphur nitrogen and metal removal. So, sulphur can be removed by sweetening process. And all Sulphur, nitrogen and metal can be removed by hydro treatment and we will make some more discussion on this topic. So, as you have discussed that crude oil contains different types of impurities, salt and Sulphur, nitrogen oxygen etc.

And desalting processes used to remove the salt from the crude oil, but that salt which is dissolved in emulsified water or in the crystalline form. And basically we have seen their sodium, calcium, magnesium, chloride are removed mostly apart from these. We also have some other, other metals. So, we will discuss how to remove those and sulphur can also be present in this case, as inorganic sulphur and organic sulphur. So, we will discuss how the sulphurs can be removed.

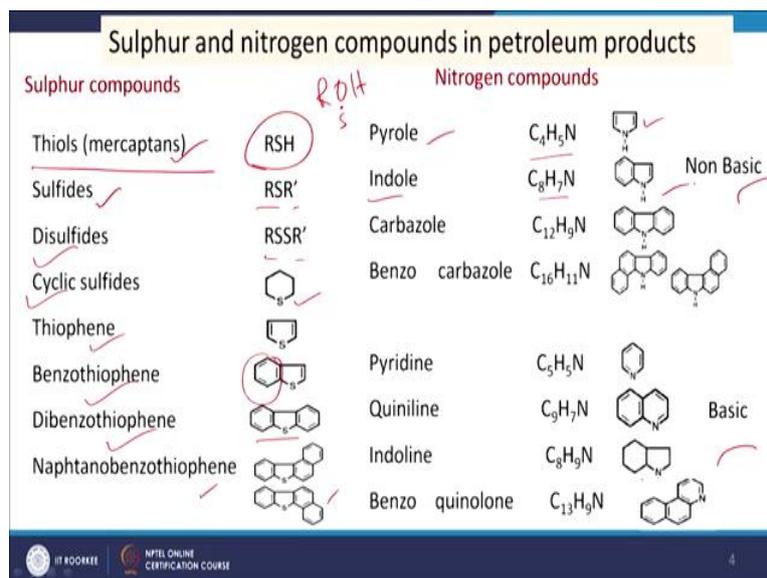
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## Impurities and need of their removal

- Fractions or streams produced by crude distillation, cracking, and other refinery processes often contain small amounts of impurities such as organic compounds containing sulfur, nitrogen and oxygen; dissolved metals and inorganic salts; and soluble salts dissolved in emulsified water.
- Impurities removal needed to achieve the quality of finish products (colour, orour, oxygen stability etc.) as well as to prepare feedstocks for other processes such as *polymerization and reforming* in which catalysts would be harmed by impurities.
- Impurities may be removed by chemical reagents, by catalysts, and by adsorption on clays or similar materials.
- Removal of **Sulphur compounds** (sweetening) is most important for refiners and is carried out by **alkali extraction (caustic sweetening) and hydrotreatment**
- A variety of intermediate and finished products, including middle distillates, gasoline, kerosene, jet fuel, and sour gases are dried and sweetened

So, this sulphur removal process is called the sweetening process, sweetening of the liquid fuel and it is most important for the refiners to improve the quality of the liquid products. And this is done by alkali extractions and hydro treatment.

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The impurities removal are very important because it helps to improve the quality of the, of the product. Now, we will see in which form sulphur is present in crude oil. So, it can be an inorganic form or maybe an organic form. So, organic form basic compound is thiols RSH, so, alcohols ROH so, this O is replaced by sulphur, then it is called thiols and mercaptans. So, this is the major compounds present in petroleum crude, and then sulfides will be RSR.

So this two alkyl groups with sulphur that can also be available or disulfides, RSSR and may be cyclic sulphides as shown here and thiophene, Benzothiophene, from benzene ring can also be

available with the thiophene and then Dibenzothiophene this is the structure and naphthanobenzothiophene. So, these are the molecular structure of these compounds, which are present normally in petroleum crude.

And if we think about the nitrogen as compound, so, those are some non basic type and some basic type. So, non-basic type are pyrole, this is  $C_4H_5N$  and this is the structure and Indole  $C_8H_7N$  in this is the structure Carbazole then Benzo carbazole it may have basic type that is Pyridine, Quiniline, and then Indoline and Benzo quinolone. So, Benzo quinolone.

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The slide is titled "Processes for impurities removal" and "Sweetening processes". It lists four processes:

- Caustic wash
- Doctor treatment
- Copper sweetening
- Merox process

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So, these are some compounds. Now we will see how these compounds can be removed, we will discuss first how the sulphur can be removed and for the removal of sulphur compounds, number of methods have been reported and used. So, those are caustic wash, then Doctor treatment, then copper sweetening and Merox process that was the advanced one. So, we will discuss about all the processes. So, if we want to remove the sulphur, and if it is present is sulphide, sulphide is acidic in nature.

So, if we use alkaline solution, so that sulphides or  $H_2S$  will be dissolved in this  $NaOH$  solution. And if we use this alkali solution that is caustic lye, so, that caustic lye and crude oil or any other liquid oil will be mixing well. And then there will be two layer one aqueous layer and another is your organic layer that is oil layer so, that all the impurities like sulphur mercaptans and sulfides will come to the lye solution.

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**Caustic wash**

The process consists of mixing a water solution of lye (sodium hydroxide or caustic soda) with a petroleum fraction.

The treatment is carried out as soon as possible after the petroleum fraction is distilled, since contact with air forms free sulfur, which is very corrosive and difficult to remove.

The lye reacts with any hydrogen sulfide present to form sodium sulfide, which is soluble in water. Mercaptans are converted as follows.

$RSH + NaOH \rightarrow NaSR + H_2O$

Caustic solutions ranging from 5 to 20% w/w are used at 20 to 45°C and 5 to 40 psi. High temperatures and strong caustic are usually avoided because of the risk of color body formation and stability loss. Caustic-product treatment ratios vary from 1:1 to 1:10.

*Spent lye* is the term given to a lye solution in which about 65% of the sodium hydroxide content has been used by reaction with hydrogen sulfide, light mercaptans, organic acids, or mineral acids.

A lye solution that is spent, as far as hydrogen sulfide is concerned, may still be used to remove mineral or organic acids from petroleum products

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And reactions is represented here  $RSH + NaOH$  that will give us  $NaSR + H_2O$ . So, this is the conversion which takes place during this process and the Mercaptans are made free from the sulphur. So, sulphur removal will take place like this way, and then it will come to liquid phase and that sulphur recovery and lye recovery can take place.

Now, this process we use the lye solution of lower concentration not high sodium hydroxide concentration, which is 5 to 20% weight by weight are used at 20 to 45 degrees centigrade and 5 to 40 psi pressure. If we use the high concentration of NaOH and high temperature, then it will have some drawback that it may produce some colour body as well as the product may lose the stability.

That is why this condition is maintained and when the lye solution we are using that it is not possible that all the lye or NaOH solution is consumed by sulfides. So, if it is around 65% sodium hydroxide is consumed by the sulfides then we call it as a Spent lye solution. This Spent lye solution can be used further for the removal of hydrogen sulphide, light mercaptans, organic acids or mineral acids.

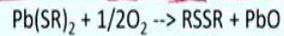
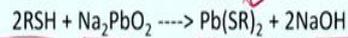
Lye solution that is Spent, as far as hydrogen sulphide is concerned, may still be used to remove mineral or organic acids from petroleum products. Now we will see what is the doctor treatment. So, Doctor treatment in this process Mercaptans is removed by the use of sodium plumbite and elemental sulphur.

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## Doctor treatment

### Doctor Sweetening

It is the treatment with sodium plumbite solution ( $\text{Na}_2\text{PbO}_2$ ) and elemental sulfur to convert mercaptan to disulfide.



### Disadvantages

- Too much elemental sulfur added cause excess formation of polysulfides which leads product to fail copper strip corrosion test.
- If sulfur added is less, lead mercaptide remains in oil and its oxidation to lead oxide causes failure to pass water tolerance test.

So, the mechanism is like this, this Mercaptans will react with sodium plumbite and this  $\text{PbSR}_2$  will form and then sodium hydroxide will be formed. And this  $\text{PbSR}_2$  which is produced here that will react with sulphur it will react to sulphur and then it will give us  $\text{RSSR} + \text{RS}_x\text{R}$ , x is a number say 2345 like this, + 2 PbS, so, + 2PbS and then  $\text{PbSR}_2$  also can be oxidized to some extent to produce  $\text{RSSR} + \text{PbO}$ .

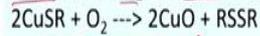
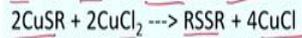
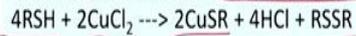
These are the chemical reactions which take place for the conversion of Mercaptans to these products. Now, these processes have some disadvantages like say we are using excess sulphur. So, if we can make some mistake and more sulphur is added then that sulphur will produce more polysulphides, which is not desirable in terms of corrosive nature of the fuel. So, it may fail the copper strip corrosion test.

And when more Sulphur is used then that  $\text{PbSR}_2$  will be more and that can also be converted to PbO. So that PbO conversion can be more and more PbO it will create some other problem that will be called water tolerance test. So, that water tolerance will be reduced. So, these are the two major disadvantage of Doctor Process, and then you will see copper sweetening process.

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## Copper sweetening

It is the treatment with copper chloride to convert mercaptan to disulfide



### Disadvantage

- Some oil soluble cuprous mercaptide remains in treated oil
- Copper chloride reacts with naphthenic acids, phenols and other polar compounds to form oil-soluble copper compounds
- Oil soluble cuprous mercaptide oxidation to copper oxide causing failure to pass water tolerance test.



Another process which was used to remove the mercaptans was the use of copper chloride. So, if we use copper chloride, so, mercaptans will react with this copper chloride so, Cupric chloride, so,  $2\text{CuSR} + 4\text{HCl} + \text{RSSR}$ . This is the reaction and then if we have Cuprous chloride, then the reaction will be this. So,  $\text{CuSR}$  which is produced here, it can again the react with  $\text{CuCl}_2$  and give us  $\text{RSSR} + 4\text{CuCl}$  and then  $\text{CuSR}$  can also be oxidized to  $2\text{CuO}$  and  $\text{RSSR}$ .

So, these processes also have some drawback. So, what will happen in this case, this cuprous mercaptide that is oil soluble cuprous marcaptide captide remains in treated oil. And then copper chloride reacts with naphthenic acids, phenols and other polar compounds to form oil soluble copper compounds. The oil soluble cuprous mercaptide oxidation to copper this reaction will make this product to fail the water tolerance test. It will prevent the product to pass the water tolerance test.

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### Merox process

- Merox is one of the most successful treating processes licensed by UOP introduced in 1958.
- Completely replaced the older processes
- Success attributed due to simplicity, diversity and economy.

Mercaptan Reduction can be accomplished in Two Ways

- Extraction of low molecular weight mercaptans from LPG or light straight run naphtha (LSRN) with alkali and subsequent catalytic oxidation to disulfides.
- Conversion of high molecular weight mercaptans present in heavy naphtha, FCC gasoline, ATF and kerosene into disulfides.

LPG / S.R. Naphtha  
 ↓ NaOH  
 Alkali  
 ↓ Catalytic Oxidation



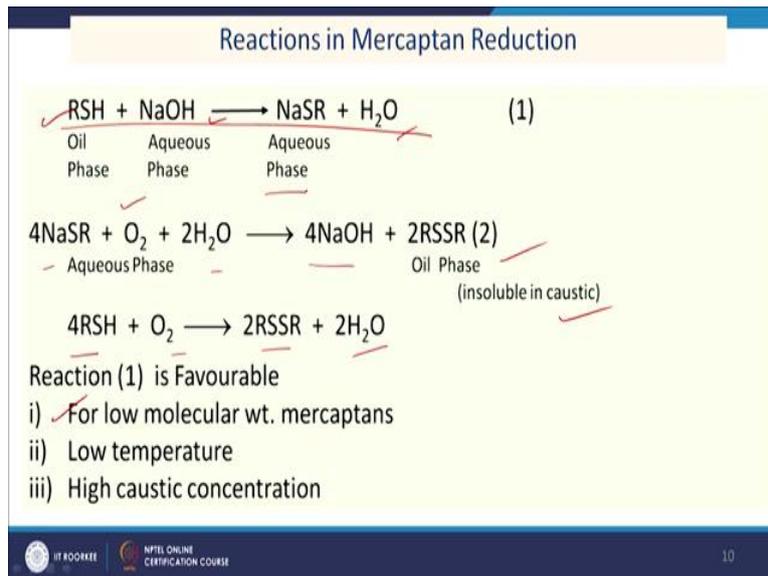
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9

Then we are coming to Merox process. So Merox process is the advanced one. So it replaces the previous processes. And in this case, we use some catalyst and this process is developed by UOP in the year 1958 and it completely replaced the older processes and it is very simple with respect to others. And it can be performed by two ways. One is light molecular weight mercaptans from the LPG and light straight run naphtha, those can be separated by using some alkali solution, then that can be catalytically oxidized.

So, we have say LPG or straight run naphtha. So, this will be reacting with some alkali solution and it will give us the mercaptans will come here in the solution alkali solution and then the solution will go for catalytic oxidation. So, this is a mechanism through which we can do or directly we can also handle high molecular weight mercaptans present in heavy naphtha, FCC gasoline ATF and kerosene into disulfides. So, this is the two ways of processes for two different type of feedstock.

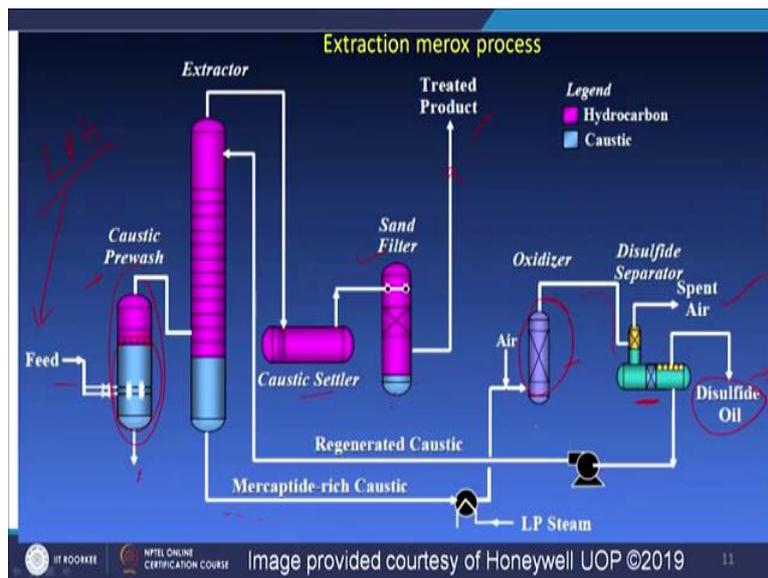
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And the basic reactions are RSH + NaOH Oil phase with Aqueous phase it is giving us NaSR + H<sub>2</sub>O and then NaSR produced here that will be oxidized and then 2H<sub>2</sub>O gives NaOH + 2RSSR again oil phase we are getting insoluble in caustics. So, this is insoluble in caustics and will be getting it and separate it. So, 4RSH + O<sub>2</sub> is 2RSSR + 2H<sub>2</sub>O. So these are the reactions which take place in this Merox process for mercaptans removal.

Now, this reaction one this is very mostly applicable for low molecular weight mercaptans and at low temperature and high caustic concentration. Now we will see how the merox process work.

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So, this say we are putting our feed then we need one caustic prewash, so then, after watching some mercaptans is going out so rest is coming here and here extractor were giving suction

time, this place basically inorganic sulfides are removed and then it is coming the mercaptans removal here in this extractor and then the mercaptans rich alkali solution is coming in here. And it is going to second stage for air addition.

And this is our oxidizer, catalyst are used then disulfides forms here. So disulfide is coming and here it is separated so disulfide separation spent air is going out and then disulphide. We are having a two phase disulfide phase oil phase and here Aqueous phase. Aqueous phase your alkali phase and Oil phase. So this is insoluble in water so or alkali solution. So we are getting the disulphide oil and Aqueous layer containing alkali.

It is recycled back to this column extractor for further extraction and which goes here that is coming to caustic settler and then sand filter and then treated product. Basically, if it is a LPG stream if feed is the LPG stream than that will be gas will come here and we will pass it through the sand filter. So, other impurities if something from here, so, that will be removed and gas will go here.

So, this is a flowsheet for the mercox process which represents to LPG, then in this process, we see one is your caustic prewash, another your oxidizer these two very important steps apart from these extractor.

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**Caustic prewash**

- The petroleum fraction is subjected to pretreatment for removing hydrogen sulfide and catalyst toxins. This treatment increases the process efficiency and reduces catalyst consumption.

$$\text{H}_2\text{S} + \text{NaOH} \longrightarrow \text{Na}_2\text{S} + 2\text{H}_2\text{O}$$
$$\text{Na}_2\text{S} + \text{H}_2\text{S} \longrightarrow 2\text{NaHS}$$

The following reactions could occur in oxidizer

$$2\text{Na}_2\text{S} + 2\text{O}_2 + \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaOH}$$
$$2\text{NaHS} + 2\text{O}_2 \longrightarrow \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$$
$$\text{Na}_2\text{S} + 2\text{O}_2 \longrightarrow \text{Na}_2\text{SO}_4$$

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So, what we do in prewash our objective is to remove the inorganic sulfides just I have mentioned. So,  $\text{H}_2\text{S} + \text{NaOH}$ , it will form  $\text{Na}_2\text{S} + 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{S} + \text{H}_2\text{S} \rightarrow 2\text{NaHS}$ . So, this type of reaction takes place in the caustic prewash and in the oxidizer which is happening  $\text{Na}_2\text{S}$

which is available in the caustic solution, then it will come in an oxidizer it will react with oxygen and then  $\text{Na}_2\text{S}_2\text{O}_3$  will form.

And these will be NaOH so these are regenerated our alkali solution we are getting so that is recycle. NaSH will react with  $2\text{O}_2$  gives  $\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$  and again  $\text{Na}_2\text{S} + 2\text{O}_2$  that gives us  $\text{Na}_2\text{SO}_4$ . So, these are the reactions which take place in oxidizer.

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Air Injection :

It supplies oxygen for oxidation reaction in the oxidizer. Stoichiometric requirement is  $0.84 \text{ Nm}^3/\text{kg}$  of RSH-sulfur. Necessary to have excess air in the range of 110-200%. Increasing air rate causes rapid and complete caustic regeneration. With very high air rate :

- Dissolved oxygen could cause sweetening in extractor.
- Spent air will have higher oxygen leading to increased corrosion and hazard.
- Settling of catalyst.

$$\text{Air} = 1.5 \times 0.84 (F) (SG) (RSH)/1000$$

where Air = Air injection rate  $\text{Nm}^3/\text{hr}$

F = LPG flow rate,  $\text{m}^3/\text{hr}$

SG = Specific gravity of LPG at  $15.5^\circ\text{C}$

RSH = Mercaptan sulfur, ppmw

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Now, in this oxidizer we supply air so what will be the air requirement? Obviously, we have to provide excess air than stoichiometric requirement and typical values given here  $0.84$  normal meter cube per kg of RSH-sulphur. This is a stoichiometric requirement and excess air is 100 to 200% is provided. If we increase the air, then it causes rapid and complete caustic regeneration. But if the air supply is very high then some disadvantage we may get.

That is dissolved oxygen will be more and that can cause sweetening in extractor, because we are, we are we are recycling this in this. And spent air will have higher oxygen leading to increased corrosion and hazards. So, that is a one important drawback if we use very high oxygen air or air here and setting of catalyst may also take place. Now, how can you quantify the air requirement?

There are some formula it is provided here in case of LPG the air requirement is  $1.5$  into  $0.84$  into F into SG into RSH by  $1000$ . So, AR injection rate is normal meter cube per hour. F is the LPG flow rate meter cube per hour and is the specific gravity of LPG at  $15.5$  degrees centigrade and RSH is the mercaptans sulphur in ppmw weight basis.

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**Catalyst for merox reaction**

- ✓ Merox WS is a totally water-soluble and specialy formulated catalyst for use in extractive or liquid-liquid sweetening
- Form Liquid Solution
- Sp. gravity at 15°C 1.16 ± 0.01
- Freezing pt. °C 0
- Active ingredient 1 Kg / gallon (3.8 ltr)
- ✓ Merox FB catalyst is developed for in-situ impregnation of the fixed-bed sweetening version of the UOP Merox process. Merox FB catalyst is as water slurry ready for use in the fixed bed Merox reactor impregnation step.
- Form Liquid Dispersion
- Sp. gravity at 15°C 1.15 ± 0.01
- Freezing pt. °C 0 ; Active ingredient 2.5 Kg / 2.5 gallon (9.5 ltr)

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So, now, this oxidizer or oxidation unit of Merox process is a catalytic process and UOP have developed two catalyst. One is Merox WS and another is merox FB. So Merox WS, WS is it totally water soluble and specialy formulated catalyst for using extractive or liquid-liquid sweetening. So it is the liquid process, liquid solution in this form, the catalyst is available and specific gravity 1.16 +- 0.01 and freezing point 0 degree centigrade and active ingredient is 1 kg per gallon.

Now Merox FB catalyst, this is developed for in-situ impregnation of the fixed bed sweetening, version of the UOP Merox process. So some fixed bed is used in this case, and Merox catalyst is impregnated on it as water slurry ready for use in the fixed bed Merox reactor impregnation step. So, this is two type of catalyst they have developed on application point of view and here it is also liquid dispersion.

Specific gravity 1.15 +- 0.01 and Freezing point 0 degree centigrade and Active ingredient 2.5 Kg for 2.5 gallon. Now, examples of applications of the Merox process so, different type of feedstock we can use, different types of feedstock can be cleaned through this process.

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Stream	Applicable Treatment
LPG	Extraction for Mercaptan Removal
Light Straight run naphtha	Extraction / Liquid-Liquid Sweetening
Visbreaker Gasoline	Fixed Bed Sweetening
FCC Gasoline	Fixed Bed Sweetening or Liquid-Liquid Sweetening
Full Boiling Range straight run naphtha	Fixed Bed Sweetening
Kerosene, Aviation Turbine Fuel	Fixed Bed Sweetening

And these are the applicable treatment. So, how, what the people have done for different type of feedstock what type options of the Merox process have been implemented is provided here. See it if it is a LPG mostly extraction based process and the light straight run naphtha- extraction or liquid-liquid sweetening; Visbreaking gasoline- fixed bed sweetening and FCC gasoline -fixed bed sweetening.

And then, Full boiling range straight run naphtha, liquid-liquid sweetening, fixed bed sweetening and both can be used and then kerosene, aviation turbine fuel we are getting fixed bed sweetening. So, these are the preferred configurations of Merox process for different type of feedstock. Now, we will discuss the hydro treatment. Now, how the hydrogen is used to remove the impurities?

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**Hydro treating/Hydro processing**

**Hydroprocessing** : Thermal conversion process in which hydrogen is used to accomplish the objectives of the refiner

**Hydrotreating**: A process in which H<sub>2</sub> is used to convert heteroatom constituents into their heteroatom hydrogen analogues and hydrocarbons

$$R-S-R_1 + H_2 \longrightarrow RH \ R_1H + H_2S$$

**Hydrocracking**: Thermal decomposition is extensive and H<sub>2</sub> assists in the removal of the heteroatoms (S & N) as well as mitigating the coke formation which normally accompanies thermal cracking of high molecular weight polar constituent.

**Major differences between hydrotreating and hydrocracking are the time at which the feedstock remains at reaction temperature and the extent of decomposition of non heteroatom constituent and products**

So, in terms of hydro treatment, we can term it as hydro processing. So this hydro processing is thermal conversion process in which hydrogen is used to accomplish the objectives of the refiner. So these hydro processing can we have two types: one is hydrotreating and another hydrocracking. So hydro hydrotreating means we provide hydrogen under such conditions for a certain duration that only sulphur and nitrogen those compounds will be separated from this.

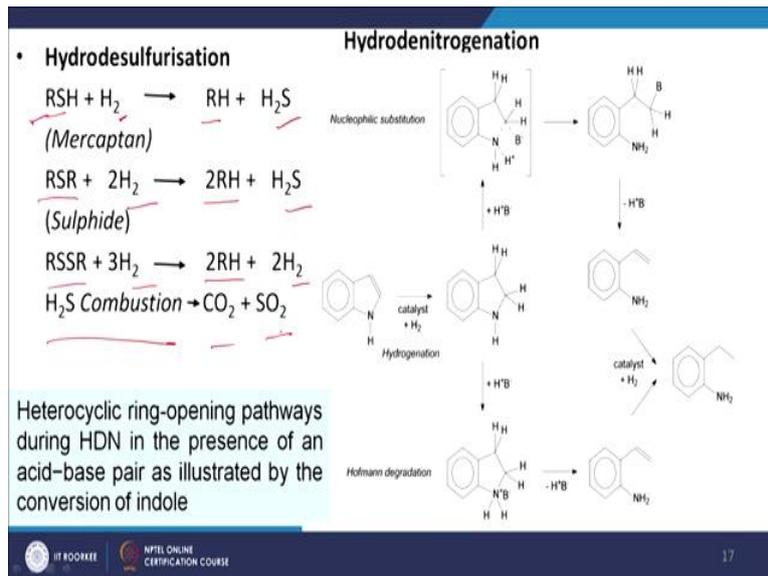
So, if this is the process in which hydrogen is used to convert heteroatom constituents into their heteroatom hydrogen analogues and hydrocarbons, so, this is  $RSR_1 + H_2$ . So,  $RHR_2H + H_2S$  so that this HS is removed by hydrogen to produce  $S_2S$  so that sulphur is removed. There is no cracking or molecular chain in this compound and hydro cracking is a thermal decomposition.

Its extensive and hydrogen assist in the removal of the heteroatoms as well as mitigating the coke formation which normally accompanies thermal cracking of high molecular weight polar constituents. So, if we go for thermal cracking, then what happens there is a coke formations on the catalyst. But if we use hydro hydrocracking, so, that coke formation will be reduced, because those will be converted by this addition of hydrogen. So, coke will not be deposited. So, that is called as hydrocracking.

So, hydrocracking will reduce it will break the bigger molecules and it will convert it into lower hydrocarbons rather than deposition of coke unlike thermal cracking process. So, major differences between hydro treating and hydro cracking are the time at which the feedstock remains at reaction temperature and the extent of the decompositions of non hetero constituent and products.

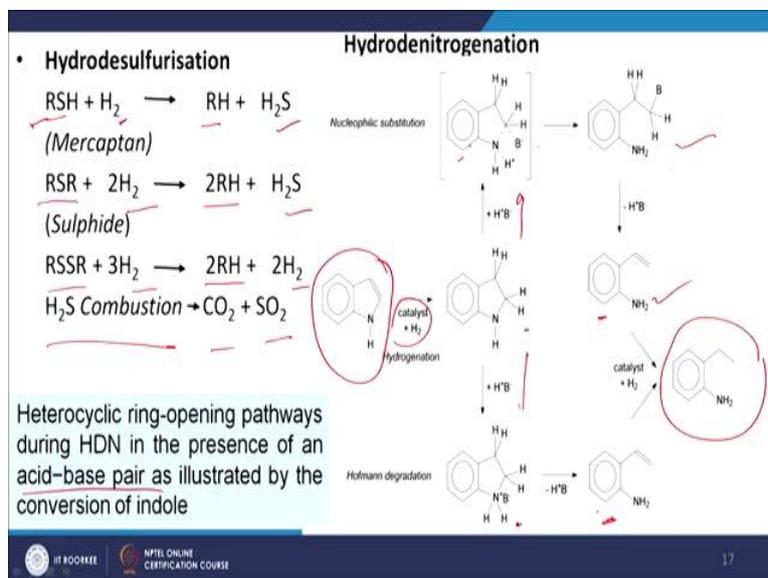
How long we are providing this feedstock in contact with hydrogen and what is the condition of the reactor, so those will differentiate this low less, ok. So now we will see the comparison of these the processes.

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And before that, we will see the reactions mechanism which take place during hydro treatment or hydro processing. So, sulphur compound when hydrogen is added RSH is converted to RH + H<sub>2</sub>S. And then RSR + 2H<sub>2</sub> ->2RH + H<sub>2</sub>S. RSSR + 3H<sub>2</sub> ->2RH + 2H<sub>2</sub> and H<sub>2</sub>S is combusted to CO<sub>2</sub> + SO<sub>2</sub>, so these are the reactions which take place during the hydro processing or hydro treatment of the feedstock. And then for nitrogen removal, when we add hydrogen, the nitrogen is also removed and this is mechanism.

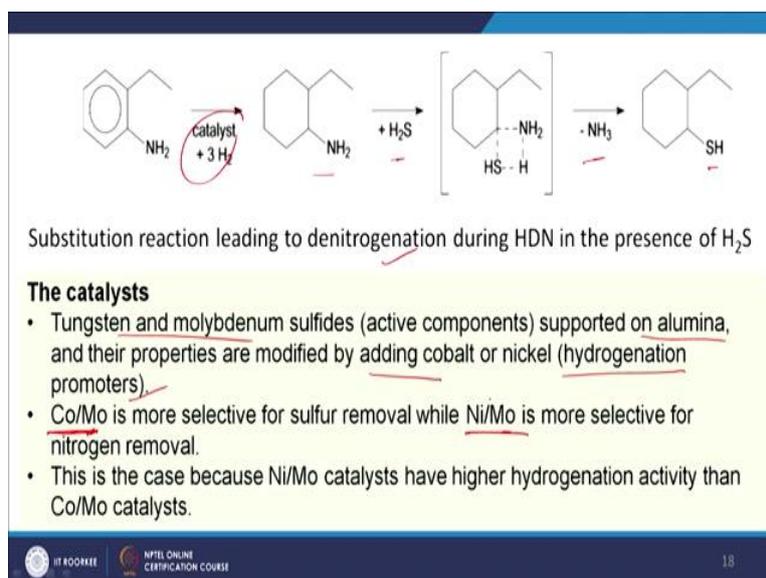
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We have one hydrogen containing compound. So, that is we are using some catalyst and H<sub>2</sub> this catalyst is basically acid base pair + H<sub>2</sub> that converts this one to this and there are to two reaction states. Two routes that is one and another is 2. So, this intermediate products forms in this route and that is converted to this one and again finally converted to this product and we get ultimately this one typical presentation of this phenomena.

And other route we get this intermediate product. So, here it is coming to this one almost similar. So substitution one and two reactions, and then it is converting to this one. Ultimately, this one nitrogen is removed from the compound. Now substitution reactions leading to Denitrogenation, these were the compound.

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So H<sub>2</sub>S is present. So, this N will be replaced by S. That can also be possible by the ammonia release. So, these are different type of reactions which may take place during the denitrification process denitrogenation process. And here the catalyst which are used those catalyst are basically tungsten and molybdenum sulphides on alumina, supported on alumina and their properties are modified by adding some cobalt and nickel.

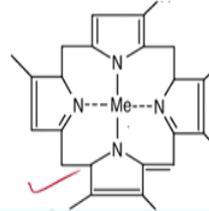
So, those are because of hydrogenation promoters, so, cobalt and nickel. So, cobalt molybdenum and nickel molybdenum, two active ingredients we are getting for the nitrogen removal sulphur and nitrogen removal. So out of these two, these ones Ni/Molybdenum is less active than nickel molybdenum for nitrogen removal, because the nickel molybdenum catalyst have higher hydrogenation activity than cobalt molybdenum catalysts.

Now we will see the metal removal, how the metal can be removed from the product or the feedstock.

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## Metal removal

- The metals found are sodium, potassium, lithium, calcium, strontium, copper, silver, **vanadium**, manganese, tin, lead, cobalt, titanium, gold, chromium and **nickel**.
- The concentration of the vanadium varies from as low as 0.1 ppm to as high as 1200 ppm, while that of nickel commonly varies from trace to 150 ppm.
- Vanadium and nickel are thought to occur in petroleum in two forms; porphyrinic and nonporphyrinic. Little is known about the nature of nonporphyrins. However, the porphyrins have been extensively studied
- The heavy metals (Me) in crude oil residue are agglomerated in asphaltenes in the form of porphyrin compounds. The molecular weight of this type of compound varies between 420 and 520 i.e., from  $C_{27}N_4 - C_{33}N_4$



So, as you have seen that in in crude oil different types of metals are available, some metals are available in water, in emulsified water, the calcium, magnesium, sodium etcetera and some metals are also their that is vanadium, manganese, tin, lead, cobalt, titanium, gold etcetera. Those are in less amount and typically vanadium and nickel, those are mostly available in crude and the concentrations are vanadium varies from 0.1 to as high as 1200 ppm.

And nickel commonly varies from trace to 150 ppm. So nickel and vanadium these are the two measure metals are present in petroleum crude and which needs removal from it to get high quality liquid product. In which form these vanadium and nickel exist? There are two thoughts. One is told that that is your porphyrinic and another is your nonporphyrinic.

So, for porphyrinic state or nonporphyrinic state in which form they are existing. So, most of the literature prefers the porphyrinic state and more information is available on this. Other one is not widely reported and this may be the molecular weight of this type of compounds 420 to 520 and molecular formula  $C_{27}N_4$  to  $C_{33}N_4$ . For this is the representation of these porphyrinic metallic compounds. So, we have to remove these metal.

So, for the removal of these metals, different types of methods are applied, physical and chemical methods.

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- The physical method is essentially deasphalting. The chemical method includes thermal processes such as visbreaking and coking; and chemical treatment.
- In the deasphalting process, the lighter oils are physically separated from heavier asphaltenes by mixing the heavy oil/residue with a very low boiling solvent such as propane, butane or isobutene. The thermal processes are basically the reshuffling of the hydrogen distribution in the residue to produce lighter products containing more hydrogen while the asphaltenes and metals are removed in the form of coke or visbreaking residue.
- The basic chemical concept of demetallization is to selectively remove the metal from the organic moiety with minimal conversion of the remaining petroleum. The demetallization of metalloporphyrins by acid is a reversible reaction and can be represented by the following equation:
 
$$\text{PM} + \text{HX} \longrightarrow \text{PH} + \text{MX}$$
- Catalytic hydroprocessing is a hydrogenation process used to remove compounds containing nitrogen, sulfur, oxygen and/or metals from liquid petroleum fractions.



20

So, physical methods basically solvent extraction, so, we add some solvent. So, lighter parts from the vacuum residue it comes to the solvent and heavy asphaltenes etcetera where the porphyrinic compounds those go at the bottom. So it is separated from the, from the oil. So, that way it can be done or thermal process also used, there is the visbreaking etcetera.

And the chemical concept of the demetallization is to selectively remove the metal from the organic moiety with minimal conversion of the remaining petroleum. The demetallization of metalloporphyrins by acid is a reversible reaction. So, this is the reactions it is shown that  $\text{PM} + \text{HX}$  porphyrinic metal and acid  $\text{HX}$ . So, that H may react with metal chloride we can get and that will be the compound porphyrinic compound without metals.

So, that way the addition of acid can convert the metal into their salt, respective salt. So, then catalytic hydro processing, these are the chemical and physical methods. Apart from this, we can go for hydro processing steps using some catalyst. In that way also, these metals can be removed along with nitrogen, sulphur and oxygen.

So, these are the different routes through which the metals sulphur and nitrogen are removed from the liquid oil to make it more cleaner, transport fuel. Thank you very much for your patience.