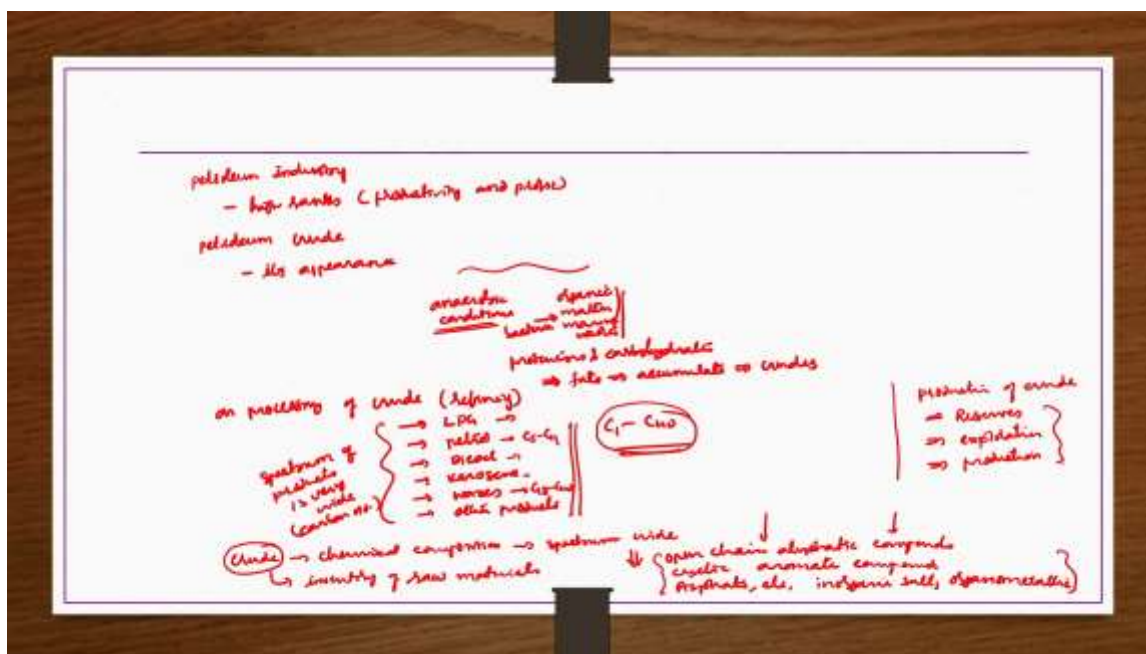


Lec 19: Petroleum Refinery Products, Characteristics and Processes.

Welcome to the MOOCs course organic chemical technology. The title of today's lecture is petroleum refinery products, characteristics and processes. In the previous lecture, we started discussing on petroleum industry and then we had a discussion to make a connection between chemical engineering and then importance of chemical engineering in petroleum refineries, etc. Then we started discussing a few basic concepts of petroleum crudes, production of petroleum crudes, composition of petroleum crudes, etc.

(Refer Slide Time: 1:03)



So before going into the today's lecture, we will have a recapitulation of what we have discussed in previous lecture. We started discussing on petroleum industry, then where we have found that it ranks very high both productivity wise and then profit wise as well, economics point of view also, it ranks very high amongst all chemical industries.

Then we started discussing about petroleum crude, so its appearance, how it appear naturally because petroleum industry or production of petroleum crude whatever is there that comes under natural product industry because whatever the crude petroleum crude is there that forms naturally. This comes because of the anaerobic conditions existing underneath the earth where you have the organic matter, marine waste. So, what will happen? Selective bacteria will attack these matters. These matters what they consist, they consist of proteins and carbohydrates in general.

So, when this bacteria under oxygen or air deficient conditions attacks these proteins and carbohydrates of organic matter or marine deposits, then they produce fats. These fats

would accumulate to form crudes, petroleum crudes that is what we found. Then we started looking at the on processing of crude which refining we may call. So then what kind of products we may get? We may get you know LPG, we may get the petrol spirits, we may get the diesel, we may get kerosene, we may also get you know waxes and then several other products as well. So that means the spectrum of products is very wide especially in terms of carbon number.

So, number of carbons are present in these components if you see, you have C_1 to C_{40} and even higher ones also in the crude. So actually, this LPG you get C_3 , C_4 and then petrol you get C_5 to C_{17} , etc. Diesel also C_5 to C_{17} , etc. Things would be there but in waxes C_{18} into C_{40} , etc. These kind of semi solids, etc. maybe there. Whatever, the crude is having if you see its chemical composition then you can find out that you know this spectrum of chemical composition would also be white from the raw material point of view. Actually, crude whatever is there that you can take it as a kind of inventory of raw materials for several petrochemicals productions, etc. So, these raw materials that spectrum if you see it is having open chain aliphatic components, aliphatic compounds, cyclic or aromatic compounds are also there. Then asphalt, etc. are also there. Some inorganic salts there. Then organometallic components are also there. So much of wide range of organic chemicals are present. So, then we have seen in detail what are they comprise of let us say open chain aliphatic we have in paraffins, isoparaffins under cyclic aromatic compounds.

We have simple cyclics as well as the aromatics then polyaromatic hydrocarbons, etc. Then heteroatom containing aromatic components, etc. Those things there some of the structures etc. also we have seen. Then finally we concluded the lecture with the production of crude.

Production of crude is very important one because the how effectively are you taking out all the crude depending on that one your profit will depend. If you are not able to take all crude efficiently then you may not get much profit out of it because the extraction of the crude or production of the crude itself involves lot of scientific technology to get properly. So here we did not get into the details because it is not part of the course. But some basics we have seen like you know reserves, what do you mean by reserves? Then what are the exploration techniques are available? Then what are the production techniques are there? Those things we have seen and then concluded our lecture. Now today we start with petroleum refinery products.

What do you mean by petroleum refinery products? That means you take a crude petroleum crude depending on its nature whether it is paraffin-based crude or naphthene based crude or intermediate based crude accordingly your products would be forming. So, if it is paraffin-based crude then more of the petrol diesel kind of products you may get. If you have the naphthene based crude then more of the lubricants, waxes, etc. you may get or gas oils, etc. you may get. So that how are you getting? You are getting by doing some kind of refinery process. Refinery process crudely if you wanted to say some kind of chemical

conversion followed by the separation and then finishing. So crudely that way we can see the refinery of a petroleum crude. We are going to discuss in detail about different types of you know refinery products, their production process using the flow chart, engineering problems, etc. in the subsequent chapters of the course anyway.

But for the time being we are enlisting let us say you have a particular petroleum crude and then you are applying refinery process or you are doing the refining of such crude. So then what kind of products you may get? What is the spectrum of products that you can get and then what are the reactions involved in general? What are the physical chemical changes are involved? Those things we are going to discuss in this particular lecture.

(Refer Slide Time: 8:28)

Petroleum refinery products

- Crude petroleum must be separated into numerous products to achieve maximum economic return
- A portion of separation takes place in the oil fields where
 - Natural gas, LPG, and natural petrol are removed before remainder of crude is put into pipelines or tankers for shipment to refineries
- Flowsheet (next slide) shows operations to produce all of products from a typical refinery
- A suitable classification of all products is listed below:
 - 1) Gas fraction
 - 2) Light ends
 - 3) Intermediate distillates
 - 4) Heavy distillates
 - 5) Residues
 - 6) By-products

Handwritten notes: A bracket on the right side of the list groups items 1 through 5, with a note "Light ends, Intermediate distillates, Heavy ends, Residues". Next to item 6, "By-products", is a note "NGLs, Hydrogen, Catalysts".

Crude petroleum must be separated into numerous products to achieve maximum economic return that is very essential because by now already we understood that crude petroleum or petroleum crude is a raw material not only for different types of petrochemicals but also different types of synthetic chemicals as well. Synthetic chemical industries are also depending on that one. So then how effectively are you separating crude into different fractions of products that is going to dictate the economics of your plant.

A portion of separation takes place in the oil fields itself. So when you do the exploration and then production when you find resource by some kind of exploration methods and then you are confirmed that when you apply the production method you can find quantum of crude which is going to be fruitful or you know profitable for you because what you are going to invest lot of money in the exploration as well as the extraction of or in a production of a crude from the underneath of the earth surface. So, lot of money is involved. So then

if enough quantum of crude is there then only you can go forward for the production of the crude otherwise you cannot. So, let us assume that you found enough quantum of the crude and then you start doing the production.

So, during the production process itself some of the gases like natural gas, etcetera are you know collected during the production in the oil fields itself. Some amount of petrols, etcetera also recovered in the oil fields itself. So, what do you mean by petrols? Petrol may be natural petrol as well as the petrol spirit or motor spirit that we use. So that depends on the octane number, etcetera. So low octane or the low-grade petrol you can get during the crude production in the field itself.

So those things we are going to see now. So, a portion of separation takes place in the oil fields where natural gas CH_4 with some impurities if at all maybe there obviously they will be there because you are doing it on field. So, they will be purified anyway later on. LPG you get and then natural petrol you get which is low grade petrol which may be containing impurities like sulphur, etcetera. So, these are removed before remainder of crude is put into the pipelines or tankers for shipment to the refineries.

So, in the oil fields itself you recover them or separated them and then remainder of the crude only you are sending through pipelines or tankers for shipment or refineries. Basically, what does it mean by? In the next slide we are going to see. So, when you do the refinery process of petroleum then you get the gas fractions and then lighter ends, then intermediate ends, then heavy ends and then residues. These kind of fractions you may get by doing the refinery process that with flowchart we are going to discuss in the next slide anyway. So out of these things most of the gas fractions and lighter ends are recovered at the oil fields themselves and then some amount of intermediates are also recovered.

Remaining heavy ends residues with some amount of intermediates only are being transported through pipelines or tankers. Flow sheet is shown next slide where it shows the operations to produce all of the products from a typical refinery. Refinery also depends whether it is primary refinery or intermediate refinery or complex refinery. What does it mean by primary, intermediate and then complex refinery that based on the duty that is taking or how much duty, how much extra work is involved based on that one refineries are being characterized. So that is also we are going to see.

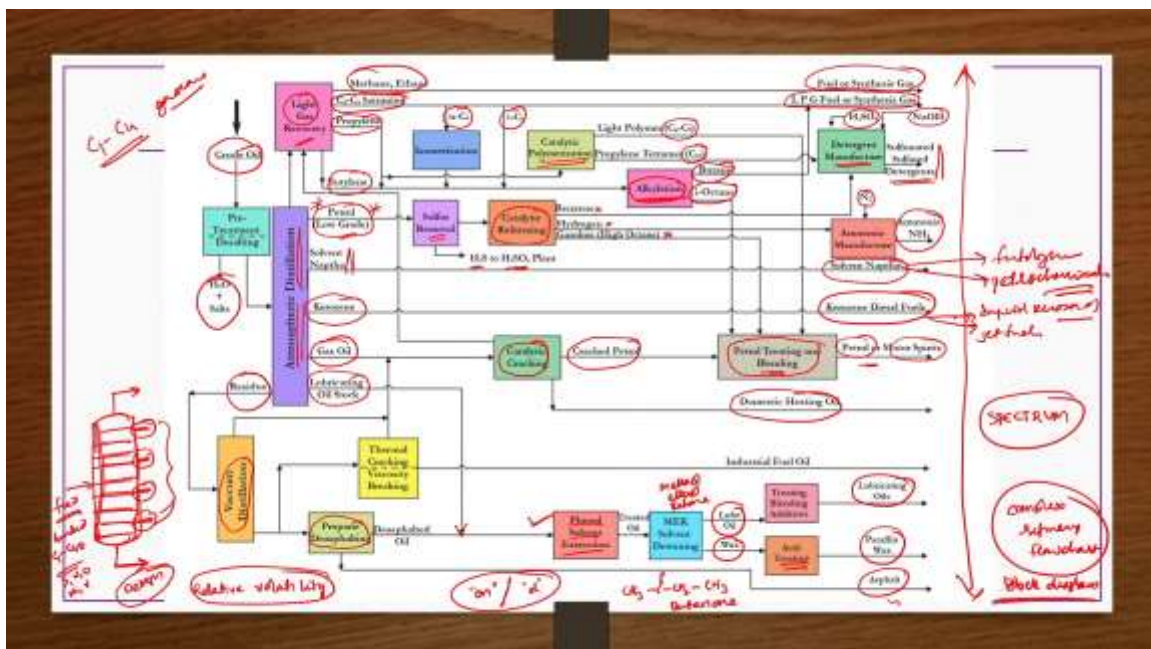
So, the flowchart that we are going to see in the next slide is an example of a complex refinery. So, it will show all the operations that are required to produce all of the products from a typical refinery. A suitable classification of all products is listed below as I already written here gas fractions, light ends, intermediates, heavy distillates and residues. So, there would be some byproducts also. How this classification is done, what do you mean by gas fractions? So then gas fractions are highly volatile and then you can easily get.

Light ends, they are coming from the liquid kind of products, but they are more volatile compared to the other ones. Then intermediates are slightly less volatile compared to the light ends, whereas the heavy distillates are the low volatiles. Volatility is the important factor in refinery process because by distillation operations, we are going to separate these fractions from the crude. Then you take a crude and do the proper distillation, atmospheric distillation, then different fractions you can get. Gas fractions you may get from the top, highly volatile liquids whatever are there, you get from the top as vapors and then they would be condensed to get as light ends.

And then intermediate distillates which are less volatile compared to the light ends, they would also be collected from the intermediate trays. Then heavy distillates would be collected not from the bottom, but few trays above from the bottom they will be collected because these are low volatiles. Residues are the lowest volatility having fractions. So, based on the volatility of the mixture that whatever is there, that fraction that you are getting, so in that order they are presented here. This is the lowest volatile and then this is the highest volatile amongst the liquids.

Residues are also like semi-solid waxy kind of things as we have seen and there are also possibilities of some byproducts like ammonia because hydrogen you are getting, so you react with the nitrogen to get the ammonia. Some fertilizers also because you are getting naphtha, etc. If you do the cracking of the naphtha, then you can get the fertilizers, etc. Then something like detergents also you may get or the source for the detergents you may get so that you can do the required reaction with H_2SO_4 , NaOH , etc. to get the detergents. In one of the previous lectures, we have seen manufacturing of the detergents.

(Refer Slide Time: 14:55)



Now this is the flowchart and this is an example of complex refinery and it is presented in the form of block diagram only because we are not giving any engineering parameters like temperature, pressure, flow rate, etc. those things we are not providing. So, we are presenting the operations also in simple blocks. So, it is a block diagram type flowchart.

So, the crude oil, petroleum crude, whatever you get from the petroleum production fields, then that would be having several types of salts and water, etc. So, you have to do certain kind of pretreatment to remove water and salts. After removing water and salts, you can do atmospheric distillation. Actually, distillation what we have already seen in one of the previous lectures. We have a column, so in that column several trays are there, perforated trays are there.

Number of trays you know that depends on the design calculations of operation that you are going to do. So, in this column number of trays you have to calculate, those are the design calculations that we are not going to see now and then to which tray you have to give the feed. Now feed here is the crude whatever the pretreated crude is the feed. Then whatever the high volatiles, gases, etc. and then high volatile liquid components, etc. you can get from the top. Whereas the lowest volatility having components may be collected as bottoms from the bottom. But depending on the volatility in between also you can have different collections. You can have different intermediate collections as well. So that depends on the volatility because that crude that is you are having it is not having 1 or 2 components or 3, 4 components as you might have studied in the mass transfer. It is having hundreds of components actually.

Because we understand that C_1 to C_{40} range organics are there in this crude. Some inorganics also there. Some metallic components are also there. So different fractions are possible and then how effectively are you taking.

So, let us say light ends whatever is there. Here also you can get intermediate ends you can get from the here high ends and then residues you can get from the bottom something like that. But from which tray you need to collect the light ends, intermediate ends and then heavy ends, etc. These things depends on your calculation design calculations. So, design of you know distillation column for the cracking of the crude is very complex process much more difficult than the distillation column design that you might have learned in your mass transfer course. Because in your mass transfer course you might have learned distillation column designing based on the 2 or 3 components mixture only.

But now here hundreds of components are there and then more than 5, 6 fractions you are collecting as product. Whereas in your UG course mass transfer course you might be having only 1 feed tray and then you may be getting only 2 product streams top and bottom. Now here in different product streams are there. So, from which tray the remaining of the product stream should be collected all that very important design calculation of petroleum

refinery engineering that is not part of this course so that we are not going into the details. So, all this separation here in the distillation column is based on the relative volatility.

This is very much essential not only for the distillation but some other kind of operations also like absorption, etc. So, let us say after doing the pretreatment if you do the atmospheric distillation of crude oil then you can get different fractions. One fraction is the light gas fraction another one is the light ends another one is the intermediates another one is like you know heavy ends and then residues like this. So now these are the fractions you are getting from different trays of your distillation column. After getting them there are wide number of processes are there to get the wide spectrum of products as shown here and then in between within the flow chart as well.

So that we are going to discuss now. Let us say whatever the light gas there you primarily recover the methane and ethane and then use it as a fuel or synthesis gas and in the light gas actually C_1 to C_4 are having the gaseous form that we already understood in previous class. C_3 C_4 saturates we are not calling unsaturated saturates only that means propane and then butane normal butane as well as the isobutane whatever are there you can collect them as a LPG fuel or synthesis gas purpose. Earlier it was used only for the LPG fuel but nowadays it is being used for the synthesis gas production as well. So light gas may also contain some amount of unsaturates as we have discussed unsaturates like ethylene, propylene, etc. are very small quantities they are present in the crude.

So only small fractions of propylene and butylene you may get negligible fraction probably. So, what you can do you can take these things and then mix with these normal butane. This normal butane also you can do the isomerization to get the butane isomers and then this isomers of the butane and then propylene, butylene are taken to catalytic polymerization. When you do the catalytic polymerization of these components you may get light polymers having C_6 to C_9 range as well as the propylene tetramer like C_{12} range something like that. This propylene tetramer may be used as a base to get the detergents after reacting with H_2SO_4 and appropriately using NaOH.

Then what you get? Sulfonated or sulfated detergents or both sulfonated and sulfated detergents you may get. This process we have already discussed in one of the previous lecture. So, whereas the light polymer C_6 to C_9 whatever are there they would be mixed with the normal petrol or the low-grade petrol after removing the sulfur, etc. Then when you mix this one with this light polymers so you can have petrol or motor spirits, etc.

Here you may also be adding some kind of blending, etc. That is a different thing. So that is what. So, this is about the fraction. So, these isomers whatever are there and then propylene, butylene, etc. whatever are there they can also be undergoing alkylation if you want.

That depends on your product. If you do the alkylation, alkylation, hydrodealkylation, polymerization, pyrolysis, etc. these kind of processes are involved in the refinery. Those things we are discussing tomorrow with appropriate flowcharts separately. So, we are not going into the details of individual process. We are going in the discussion of the block diagram of a refinery process.

So, when you do the alkylation then you can get the butane from this propylene, butylene and then butane isomers, etc. So, the normal butane you can mix with the LPG fuel stream and then use it for the LPG purpose or you can do synthesis gas production also. From the alkylation you may also get isooctane that will also be mixed with the gasoline and then petrol, low grade petrol, etc. to get the petrol or motor spirits.

That is about the gases fractions. Now the second fraction is that you know light ends. In the light ends you may have the petrol and then solvent naphtha. So, let us take the petrol stream, so which is having the low-grade petrol because it is having impurities like sulphur, etc. and then any refinery this stream whatever the quantity of this stream is there or yield of this stream is there that people try to maximize especially in India.

So especially wherever the petrol requirements are more. In fact, petrol requirements are much more than the other requirements in general because of the transportation requirements. So, maximizing the yield of this stream is most important duty of a design engineers when they do the designing of this distillation column for the fractionation of the petroleum crude. Let us say this petrol, low grade petrol whatever you get, so you remove this sulphur in the form of H_2SO_4 plant they can be sent. Then after removing this sulphur if you do the catalytic reforming of petrol, low grade petrol then you can get benzene as one product, hydrogen you may get and then high-octane gasoline you can get which is nothing but the petrol that can be blended with some other additives as per the requirement and then you can get the petrol or motor spirit. Whereas the hydrogen you can collect and then react with nitrogen to get ammonia.

Whereas the benzene you can take and then use as a source for the manufacturing of detergents because benzene and then benzene related aromatics are forming basis for the several of the detergents manufacturing that we have already discussed. So that is about the petrol product stream from the cracking of a petroleum crude. So, another stream product stream you get from the cracking of a petroleum crude is solvent naphtha that you can collect and then you can do the reforming to get different types of products including the fertilizers, etc. And then also you can get you can use it as a source for preparation of different types of petrochemicals wide range of petrochemicals you can produce from here. Other product stream coming out from this fractionation of petroleum crude is kerosene that you can use as a superior kerosene oil as diesel fuels, etc. for that purpose it can use or it can also be used for jet fuels nowadays. Gas oil comes under the intermediate to heavy ends because their volatilities are low. So, this fraction when you do the catalytic cracking

3 products you get one is the cracked petrol that you can mix with the gasoline high octane gasoline and then other additives blenders, etc. to get the petrol and motor spirits. And then other product of catalytic cracking of gas oils will give the domestic heating oil and then third product is nothing but you know some kind of gaseous components like you know methane, ethane and then saturates, etc. they will be mixed with light gas fractions and then do the processing as already discussed. So, the heavy ends or residues whatever are there they are collected from the bottom and then these residues what you do you do separately vacuum distillation. So, when you do the vacuum distillation of these residues or the heavy ends then what happens you will form 2 fractions one is the high volatiles out of these residues only not from the crude. So high volatiles of the residues would be collected and then when you collect you find you know you do the catalytic cracking of those high volatiles of the residues along with the gas oil compositions and then you get the cracked petrol domestic heating oils and then some gases. Whereas the low volatiles of the residues that you get after vacuum distillations are primarily propane deasphalting.

So here asphalts you separate and then you collect. So, this one you can do the processing to get the wax, etc. lubricants, etc. After the deasphalted oil whatever is there that you can do the phenol solvent extraction and then treating with some kind of oil and then doing this solvent de-waxing by methyl ethyl ketone MeK is nothing but methyl ethyl ketone that is nothing but $\text{CH}_3\text{COOCH}_2\text{CH}_3$ this is also known as the butanone. Remember, none that ON you write for the ketones OL ol you write for the alcohols. So, this is the part of organic chemistry I assume that you already know it. So, after doing this de-waxing then you can get two fraction one is the lube oils another one is the wax.

Wax fraction you can do the acid treating to get the paraffin wax whereas the lube fraction you can do the treatment with the blending additives, etc. to get the lubricating oils. Another high end is the lubricating oil stocks that you can mix with the low volatiles of residues after vacuum distillation and then mix with this the aspartate oil and then you do this processing. So, this is what you know typical refinery it is only actually you know only some of the details are only presented. If you go for the expanded much more complicated details of refinery then more number of products you can get.

Now you can see the spectrum of product very wide. So that is the reason this crude petroleum crude whatever is there it is not only primary source of energy but also it is a very much important raw material for several of synthetic organic chemicals. Now whatever these gas fractions light ends intermediate ends heavy ends residues, etc. are there. So, all of those things individually we are going to discuss and then what kind of components or products you get that we are presenting in the form of text now here.

(Refer Slide Time: 30:13)

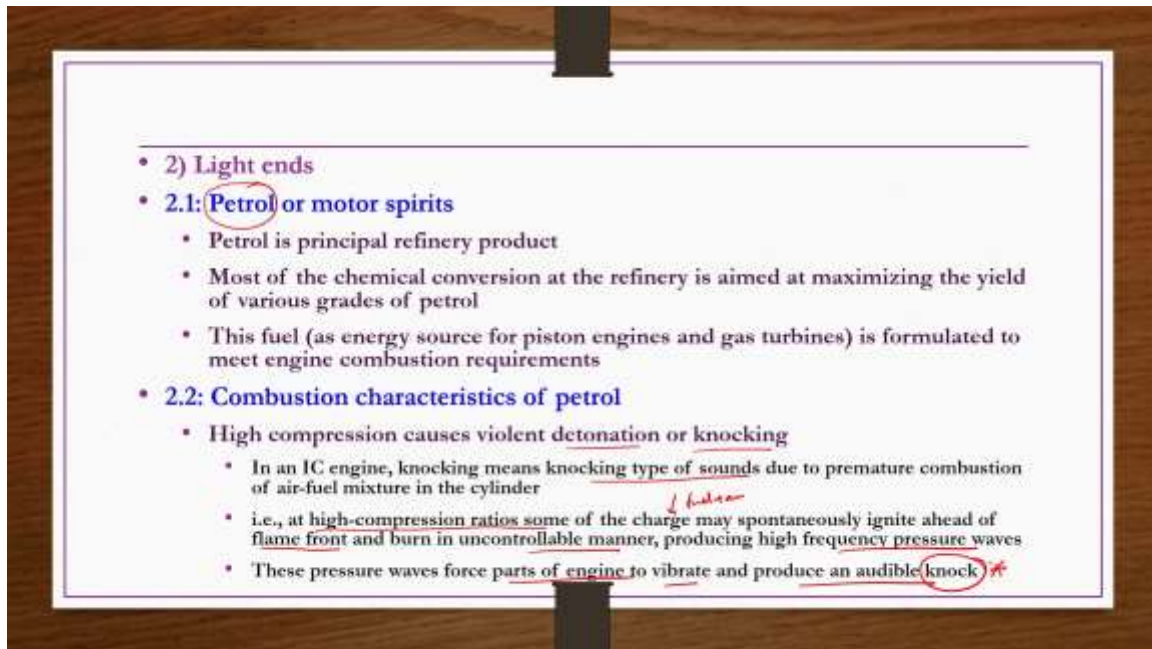
- 1) Gas fraction
- Gaseous fractions were previously used only for fuel
- But now shifting in usage to preparation of synthesis gas
 - Natural gas: largely CH_4 with some C_2 as separated at well
 - Light gas (C_1 and C_2) from distillation of petroleum crudes at the refinery
 - Off-gas from petroleum conversion operations at the refinery such as H_2 , H_2S , SO_2 , C_1 , C_2
 - LPG as propane and butane, liquefied and used for domestic fuel, winterizing gasoline, or for synthesis gas

Let us say gas fraction gaseous fractions were previously used only for fuel but nowadays they are also used for synthesis gas production. Natural gas largely contains CH_4 with some C_2 as well which are separated at the oil fields itself.

Whereas the light gas which consists C_1 and C_2 from distillation of petroleum crudes at the refinery this is collected at the refinery when you do the fractionation or distillation whereas natural gas primarily you get at the wells. Off-gas from petroleum conversion operations at the refinery you can have and these off-gases are nothing but H_2 , H_2S , SO_2 , C_1 , C_2 , etc. all of them are having some kind of one or other kind of applications. LPG which is nothing but propane and butane but these are primarily liquefied and used for domestic fuel because these are in the gases form under the normal conditions. So, they have to be liquefied in order to store in the LPG cylinders and then they can be used for domestic fuel purpose.

They are also used as a winterizing gasoline or synthesis gas purpose as well.

(Refer Slide Time: 31:30)



Now the light ends of a crude petroleum fractionation product. When you do the fractionation or distillation of crude petroleum the light ends you get. So now we are going to discuss about those light ends.

It includes petrol or motor spirits. Petrol is principle refinery product. Most of the chemical conversion at the refinery is aimed at maximizing the yield of various grades of petrol. This fuel as energy source for piston engines and gas turbines is formulated to meet the engine combustion requirements. So, this is very much essential. This petrol is very much essential which is also known as the motor spirit. Now if you see the combustion characteristics of the petrol under high compression condition it causes violent detonation or knocking.

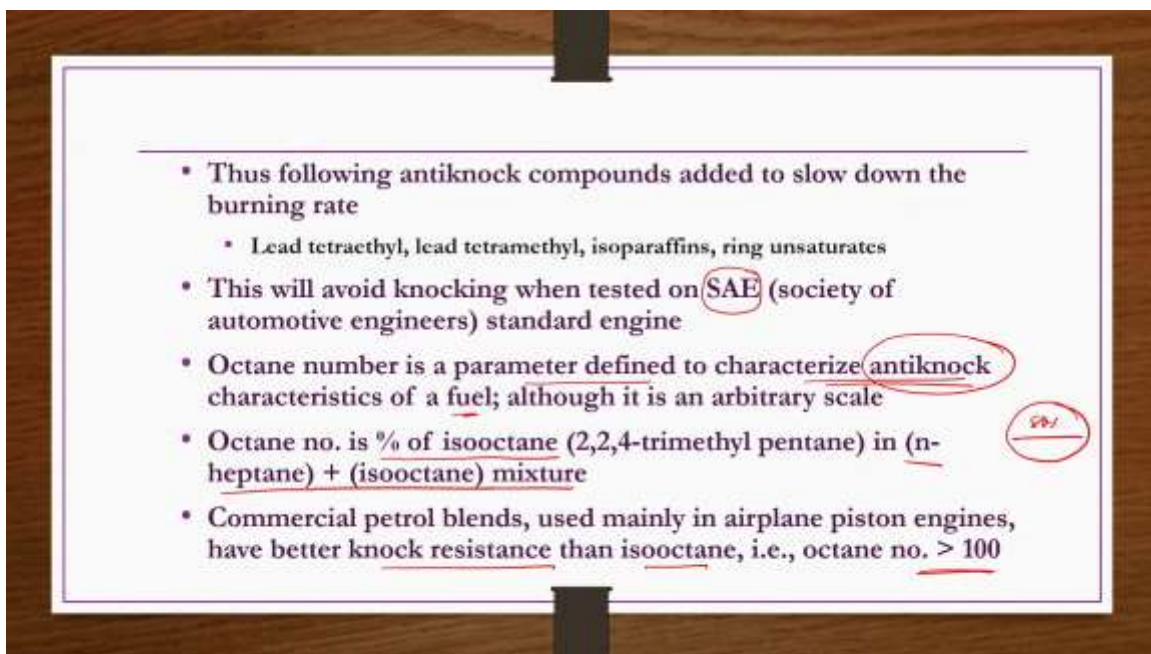
What happen when you release the petrol and then start the ignition then combustion takes place and then that combustion releases the energy that energy would be utilized for the movement of the vehicle. So how does it happens and all that? That is part of the design and then working principles of IC engines we are not going into that one. But if that process does not take properly or premature combustion takes place when you take this air and fuel mixtures and then try to start the ignition before the starting the ignition itself combustion somehow it takes place. Some cases it takes place actually. Then what happens a kind of uncontrolled combustion takes place within the cylinder and then that releases that causes some kind of pressure waves.

These pressure waves causes to move or vibrate some of the parts of the cylinder and then that leads to some kind of knocking kind of sound which is clearly audible. So, this kind of premature combustion of fuel air mixture is very dangerous not only from the

performance point of view also from the safety point of view. So, this has to be avoided for that purpose some kind of anti-knocking agents are there. So, in an IC engine knocking means knocking type sounds due to premature combustion of air fuel mixture in the cylinder that is at high compression ratios some of the charge in the sense here fuel plus air or oxygen may spontaneously ignite ahead of flame front and burn in uncontrollable manner producing high frequency pressure waves. These pressure waves force parts of engine to vibrate and produce an audible knocking knock sound.

So that is the reason this is known as the knocking it has to be avoided it should not be there.

(Refer Slide Time: 34:30)



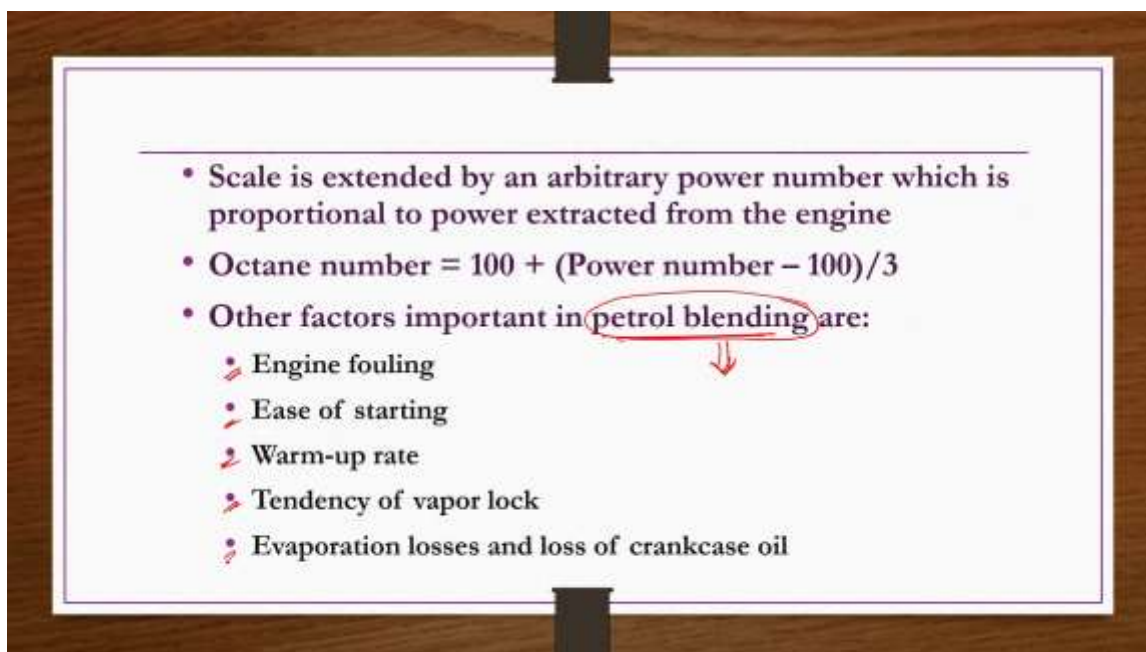
So thus, following anti-knock compounds added to slow down the burning rate these are lead tetraethyl, lead tetra methyl isoparaffin and then ring unsaturates are also used in general for this purpose. This will avoid knocking when tested on a standard SAE engine. SAE is the society of automotive engineers they have the standard test for each and every aspect of the automotive engines. So, then these automotive engines whatever are there they should follow and then pass the recommendations of SAE then only that can come to the market.

So, if you add these anti-knocking agents then that will avoid knocking and then that can be clearly tested on any standard engine. So how do you know knocking is there or not? So, octane number is a parameter defined to characterize anti-knocking. So, octane number is a parameter defined to characterize anti-knock characteristics of a fuel though it is an arbitrary scale. Octane number is percentage of isooctane in n-heptane plus isooctane

mixture. So, in the isooctane n-heptane mixture how much percentage of isooctane is there that is known as the octane number.

Let us say if you have 80 percent of isooctane in n-heptane plus isooctane mixture then you can call octane number as 80. Commercial petrol blends used mainly in airplane piston engines have better knock resistance than isooctane that is octane number even having more than 100 is also possible. So, this is if you have only 2 components but how do you calculate the octane number for a fuel which is having you know C_5 to C_{17} chemicals especially saturates one.

(Refer Slide Time: 36:35)

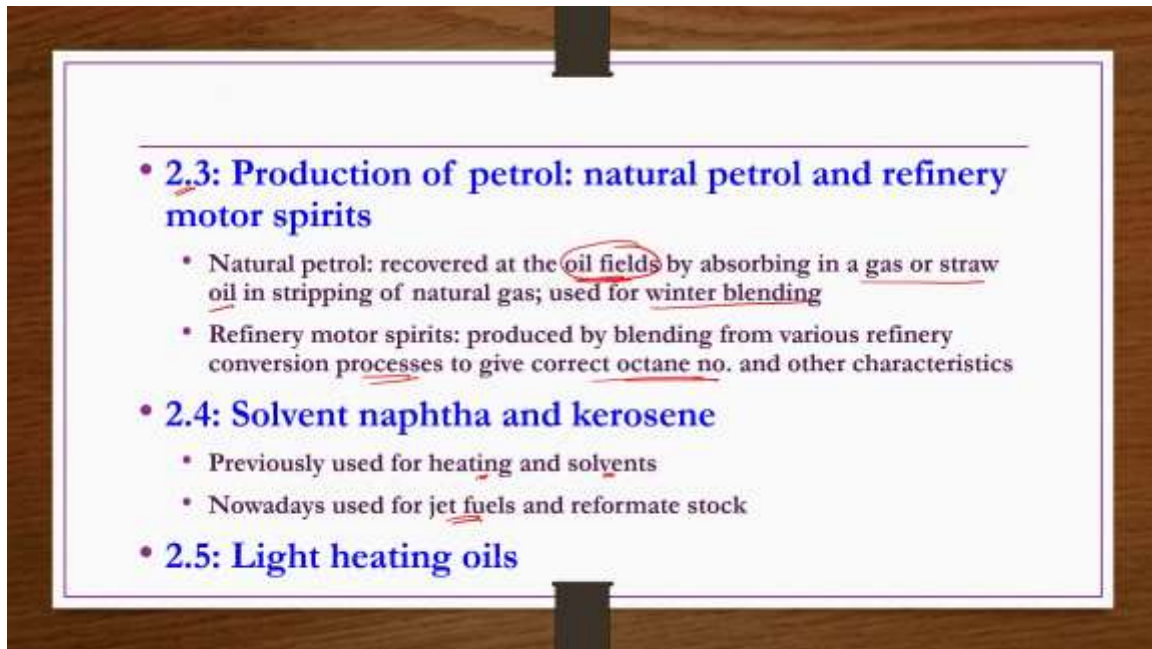


- Scale is extended by an arbitrary power number which is proportional to power extracted from the engine
- Octane number = $100 + (\text{Power number} - 100)/3$
- Other factors important in petrol blending are:
 - Engine fouling
 - Ease of starting
 - Warm-up rate
 - Tendency of vapor lock
 - Evaporation losses and loss of crankcase oil

Then there is an equation octane number is 100 plus power number minus 100 by 3. So, power number is nothing but the power extracted from the engine it is some proportional number or constant to power extracted from the engine that power number minus 100 by 3 you do plus add 100 then you get the octane number for a given fuel.

Other factors that are important in petrol blending are engine fouling, ease of starting, warm up rate, tendency of vapor lock, evaporation losses and loss of crankcase, oil, etc. All these things are also important to check before having final petrol blending. So, it is not that arbitrarily any percentage of blenders or additives you can add to the high-octane gasoline and then you consider that is your the final petrol no. You have to see all these things are also being properly managed by the final petrol blending or petrol or motor spirit whatever is there.

(Refer Slide Time: 37:45)



Now production of petrol this is again within the light ends only. These numbers are given accordingly one for the gas fractions two for the light ends. So, production of petrol so two types are there natural petrol and refinery motor spirits. Natural petrol recovered at the oil fields by absorbing in gas or straw oil in stripping of natural gas and it is used for winter blending. So, these are obtained on field. On field also, we are recovering some gas fractions and light ends like you know low grade petrol, etc.

So those are known as the natural petrol other than the gas fraction whatever the liquids that you collect on field during the oil production in the oil fields. So that is known as the natural petrol. Refinery motor spirits produced by blending from various refinery conversion process to give correct octane number and other characteristics as per the requirement of the petrol as per the government norms.

So, what are these processes, etc. we are not going into the detail. We have seen in the flow chart when you take the low-grade petrol remove the sulphur and then you do the cracking then you can get the different products including the high-octane gasoline. High octane gasoline is also may not be suitable as per the government norms. So, then you have to add appropriately blenders additives, etc. and then make sure that you get correct octane number and then other characteristics required as per the government norms to use it as a motor spirit in vehicles.

Solvent naphtha and kerosene are other fractions that are possible in light ends. So previously these are used for the heating and solvents purpose but nowadays they are also

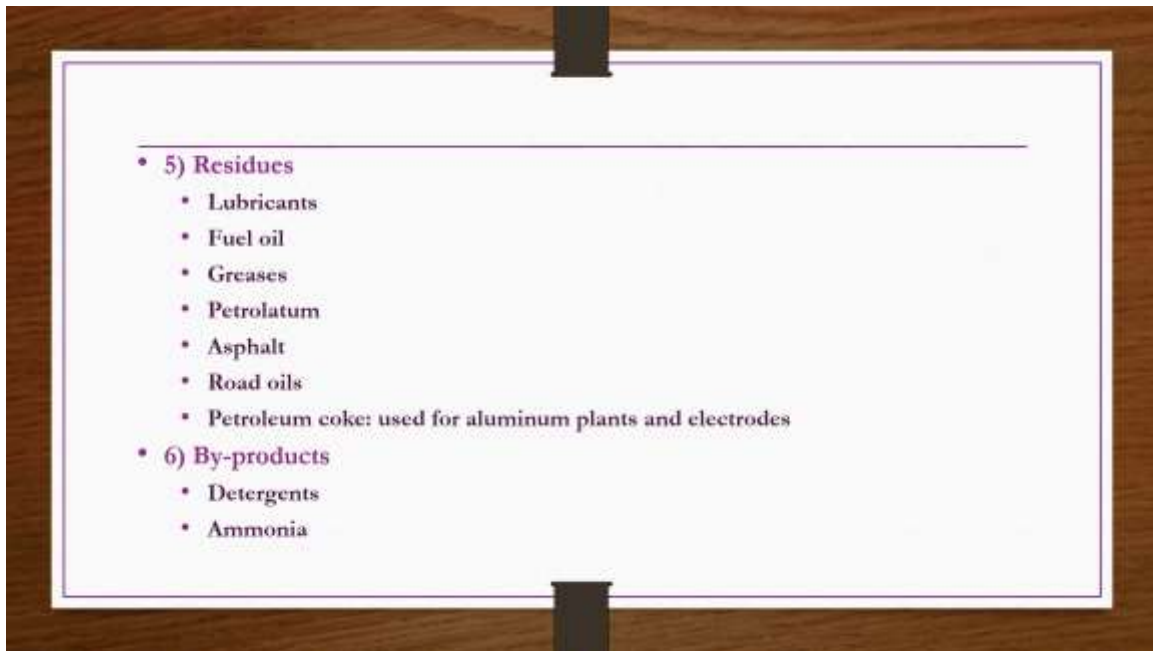
used for the jet fuels reformat stock, etc. Other fraction that is possible in the light ends is the light heating oils as well.

(Refer Slide Time: 39:51)



Third one is the intermediate distillates under the intermediate distillates we may have the heavy fuel oils, diesel oils, gas oil and then fourth one is the heavy distillates where we can have the mineral oils, flotation and frothing oils, waxes, lubricating oils, etc.

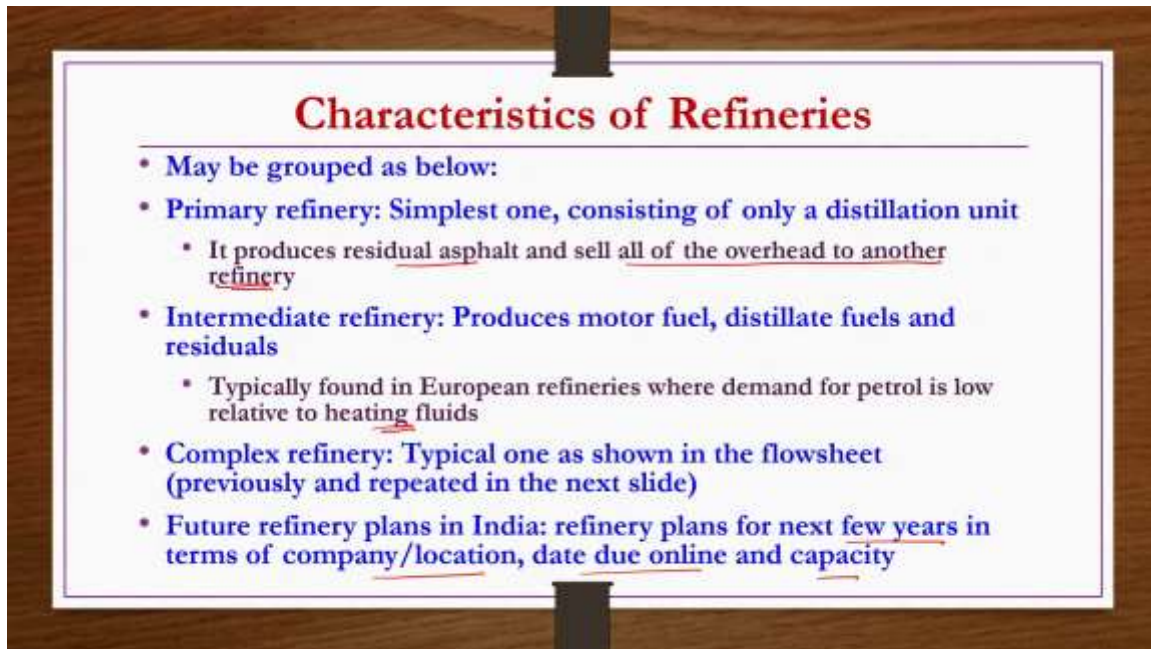
(Refer Slide Time: 40:11)



And then under the residues we may get the products like lubricants under the residues in the sense when you do the fractionation or distillation of the petroleum crude whatever the residues that you get those residues you can take and do some kind of processing as shown in the flow chart then you can get the lubricants, you can get the fuel oil, greases, petrolactam, asphalt, road oils, petroleum coke, etc.

In addition, as a byproducts you can get detergents, ammonia, etc. when you do the fractionation or distillation of the petroleum crude you can also get the byproducts as detergents and ammonia. Some sulphur and derivatives may also get as a you know byproducts. That is about the petroleum crude refinery products.

(Refer Slide Time: 41:04)



Characteristics of Refineries

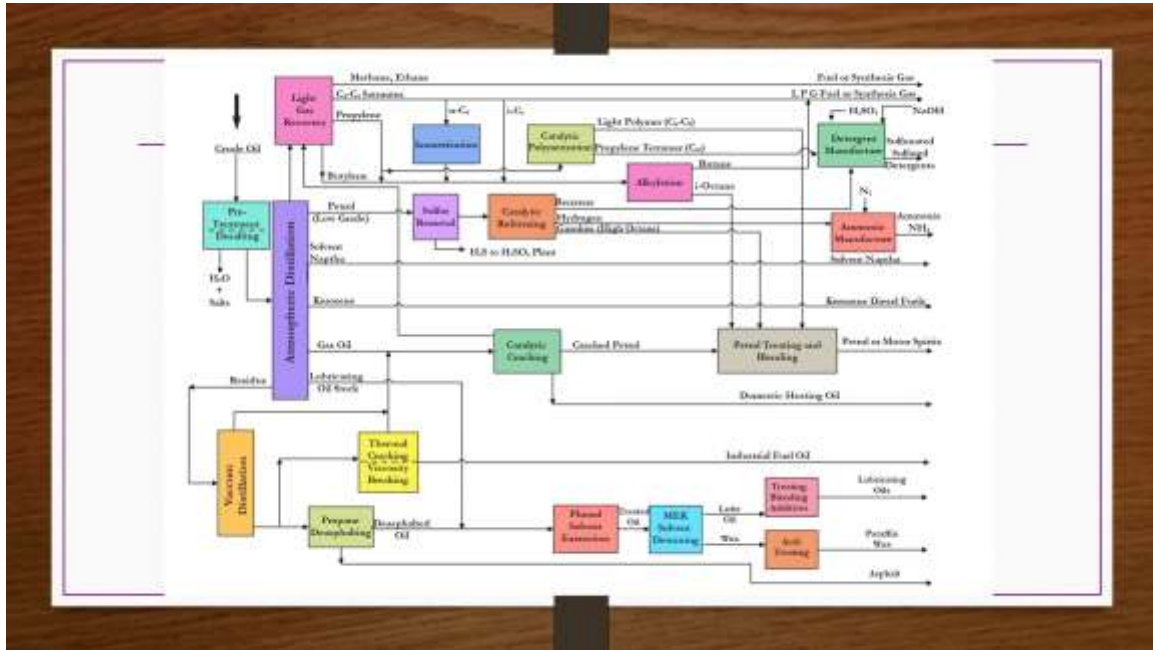
- May be grouped as below:
- **Primary refinery: Simplest one, consisting of only a distillation unit**
 - It produces residual asphalt and sell all of the overhead to another refinery
- **Intermediate refinery: Produces motor fuel, distillate fuels and residuals**
 - Typically found in European refineries where demand for petrol is low relative to heating fluids
- **Complex refinery: Typical one as shown in the flowsheet (previously and repeated in the next slide)**
- **Future refinery plans in India: refinery plans for next few years in terms of company/location, date due online and capacity**

Now we are going to discuss about the characteristics of the refineries. What do you mean by characteristics of the refineries means the amount of duty that refinery is doing based on that one these refineries are you know characterized as a primary intermediate and complex refinery.

In the primary refineries you primarily you have only one particular distillation column and then you try to collect the you know lubricants and residues, etc. that you take one portion and then remaining ones you may be sell to the other refineries for the further processing which is simplest one. There is not much involvement technological involvement. So those characteristics of a refineries we are going to see now. May be grouped as below primary refinery simplest one consisting of only one distillation unit it produces residual asphalt and sell all of the other overhead to another refinery.

If you wanted to collect only residues so that you produce lubricants, greases, waxes, etc. then you collect those from the bottom of the distillation column whereas the other overheads whatever are there you can sell to the other refinery so that they can do the remaining of the extraction for the other products. So, such kind of refineries where you know only one distillation unit is there so that is known as the primary refinery. Intermediate refinery produces motor fuel, distillate fuels and residuals. It is typically found in European refineries where demand for petrol is low relative to the heating fluids. Whereas the complex refinery is the one that we just seen a few slides before and then we are showing it in the next slide as well.

(Refer Slide Time: 43:18)



So, this is an example of a complex refinery which we have already discussed in detail a few slides before.

(Refer Slide Time: 43:26)



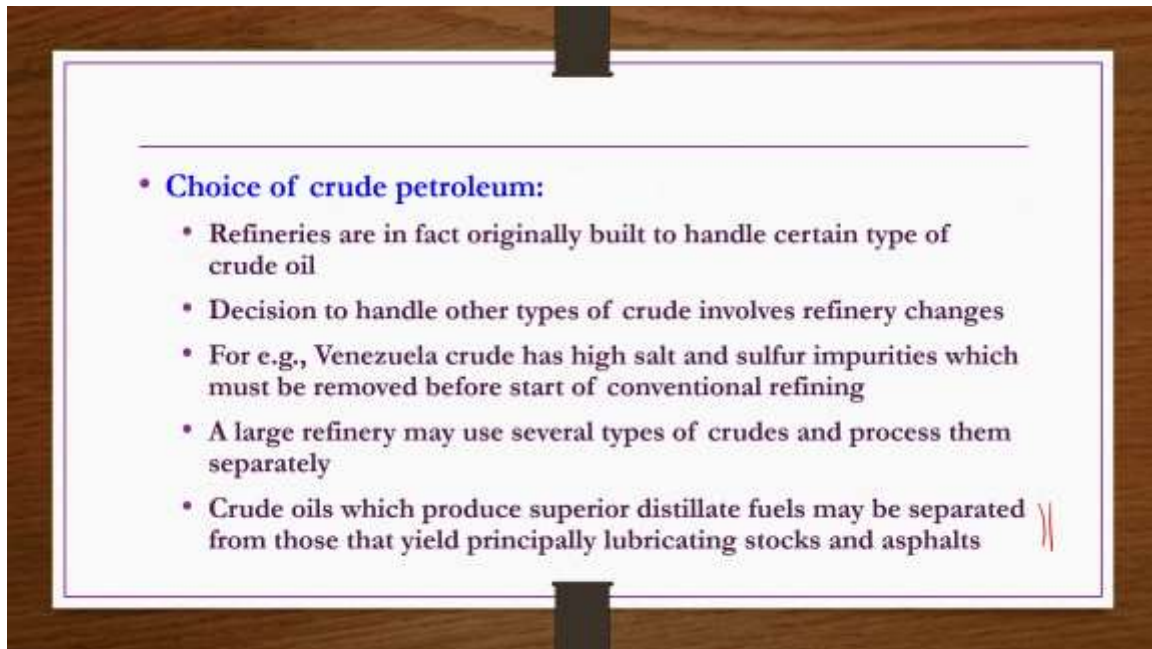
So, this is all about the characteristics of the refineries. Now we are going to discuss about the types of refinery design. It is not the design of refinery, types of refinery design. So here we have independent and integrated. So like characteristics you have primary, intermediate and complex like that.

Design also different types of designs are there independent and integrated. Independent in the sense you know hold up one unit to the other units. So, you know hold up is such a high that you know when you stop operating one particular unit rest of the plant will not be affected. Such kind of things are there. So those are known as the independent ones. Independent operations build with holding capacities between units so that any unit could be operated, shut down and reconditioned independently without affecting the operations being conducted in other units.

Other units are any of the refinery units. May be distillation, may be separation, may be finishing, etc. whatever it may be. So, holding capacities are made such a way that in these independent operations or independent refinery designs.

So, these are nowadays not used much. They were very famous until early 1950s. Integrated operations integrated refinery can be built with 20 to 30 percent investment savings here. It is designed with little hold up capacity between units since refinery maintenance requirements can be reliably scheduled accordingly.

(Refer Slide Time: 45:08)



Now choice of crude petroleum also. Crude petroleum classification yesterday we have already discussed. Yesterday we have already discussed classification of the petroleum crude where we have paraffin-based crudes and then naphthene based crudes, intermediate based crudes.

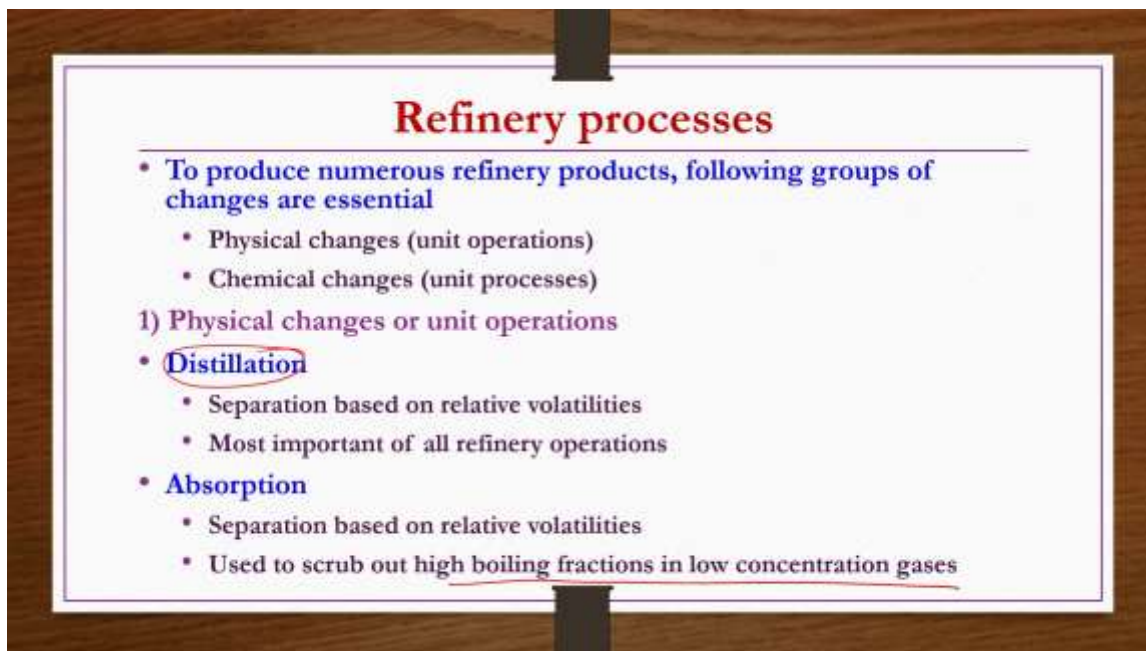
If that depends like you know selection depends on what kind of products are you planning to have in your plant. Let us say we are planning to have more lubricants, greases and waxes, etc. then you should select the naphthene based crudes in general. If you are planning to produce more light ends, kerosene, solvent naphtha, etc. then you should go for you know paraffin-based intermediates. But if you wanted to have both of all the wide spectrum of the products then better you go for a intermediate based crude which will be having not only paraffin based as well as the naphthene based components.

Both of them would be there in large quantities. So, refineries are in fact originally built to handle certain type of crude oil. The decision to handle other types of crude involves refinery changes. Obviously when you do the designing of your refinery then itself you have to decide what kind of products are you planning to have. Because in future after 5 or 10 years if you wanted to produce some other products then you may need to do several changes in the design in the refinery.

So, for example, Venezuela crude has high salt and sulphur impurities. So, they must be removed before start of conventional refining. Likewise, Indian crude if you take they are mostly naphthene based crude. So, they are suitable for primarily producing the lubricants, greases, waxes, etc. A large refinery may use several types of crudes and process them

separately. Crude oils which produce superior distillate fuels may be separated from those that yield principally lubricating stocks and asphalt in general.

(Refer Slide Time: 47:19)



Refinery processes

- To produce numerous refinery products, following groups of changes are essential
 - Physical changes (unit operations)
 - Chemical changes (unit processes)
- 1) Physical changes or unit operations
 - **Distillation**
 - Separation based on relative volatilities
 - Most important of all refinery operations
 - **Absorption**
 - Separation based on relative volatilities
 - Used to scrub out high boiling fractions in low concentration gases

Now we talk about the refinery processes. What do you mean by refinery process? It is a grouping of refinery process that we are going to discuss. Actually, any plant whether it is petroleum production plant, petrochemical plant, polymerization plant or you know rubber industry, detergent industry any plant you take what are the processes are involved. Basically, unit operations and then unit processes. Some details of unit operations and unit processes we have already discussed at the beginning of the course. But here now we are discussing such unit operations and then unit processes specific to the petroleum production industries and then petrochemicals industries.

So physical changes or unit operations and then chemical changes or unit processes are unavoidable in the refinery process which are very essential without them you cannot get the wide spectrum of products as we have discussed in complex refinery flow chart. Typical physical changes or unit operations which are common in refinery process are listed here. So, these things we have already discussed in the first chapter of the course where we have discussed some details. Now here we are going to see only what is the driving force and then for what purpose such kind of unit operations are used in the refinery processes.

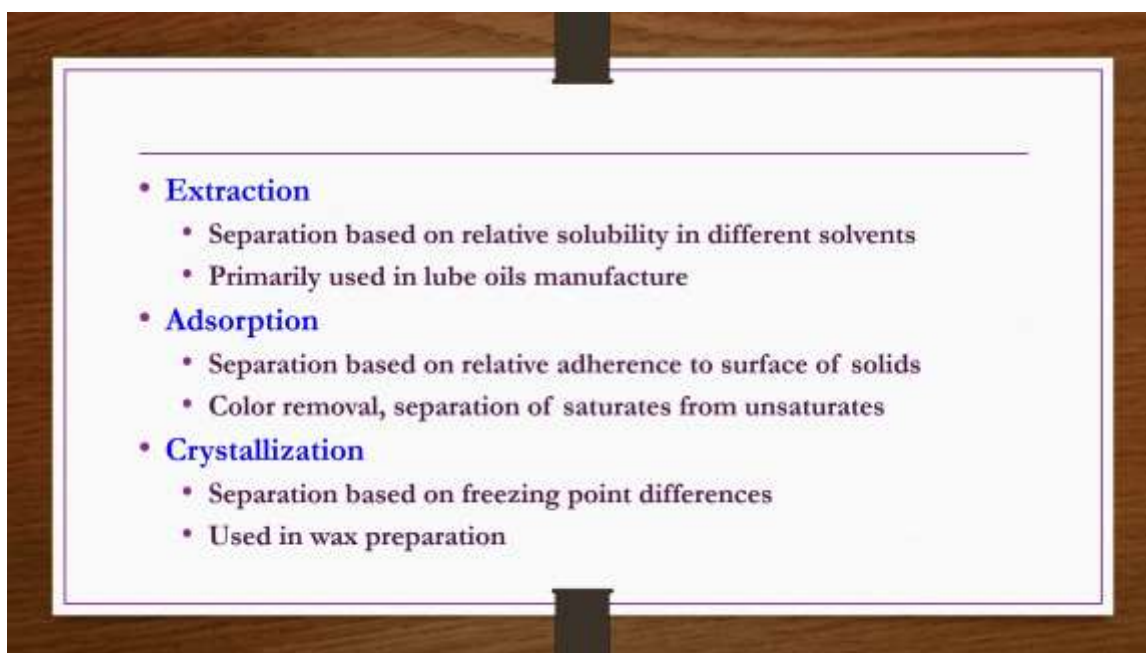
Only these two points we are going to discuss now here. Because much details are already discussed in the first chapter of the course. Even more details are required then you have to go for the specific course on mechanical unit operations, mass transfer, heat transfer, etc. Distillation is the most important unit operation of any of the petroleum refinery plant.

In distillation, separation takes place based on the relative volatilities. It is most important of all refinery operations. Absorption is also based on relative volatilities and then it is used to scrub out high boiling fractions in low concentration gases. Actually, in the complex refinery flow chart, the first atmospheric distillation is there.

From there only all other coming. After that only the rest of the things are coming. Like H_2S , etc. are there. Your sulphur if you want to remove in the form of H_2S then scrubbing you do in general. So, these are coming after the distillation. So, distillation is very much important or the most important rather very much important.

It is the most important unit operation of refinery plants.

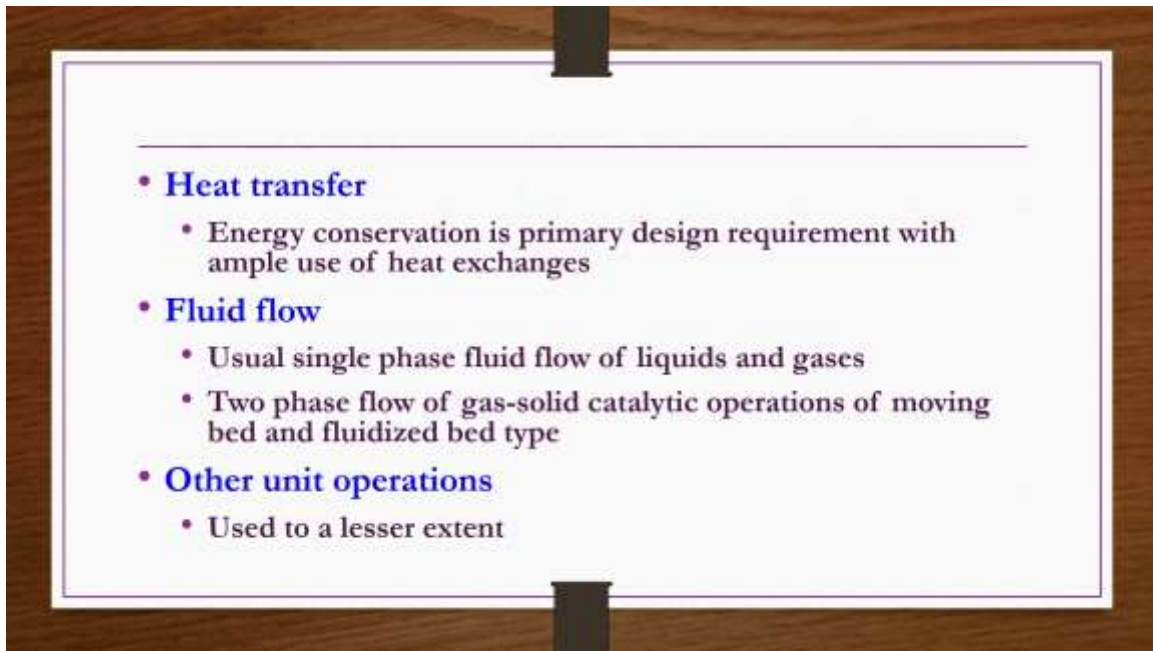
(Refer Slide Time: 50:03)



Next unit operation is extraction. It is based on relative solubility of a component in different solvents primarily used in lube oils manufacture. Adsorption, the separation based on relative adherence to a surface of solids. It is primarily used for the colour removal, separation of saturates from unsaturates in the refinery plants.

Crystallization, it is based on the freezing point differences. So, it is used in wax preparation in refinery plants.

(Refer Slide Time: 50:39)



Heat transfer, energy conservation is primary design requirement with ample use of heat exchangers in general. So different types of heat exchangers, reboilers, condensers, etc. are there. So, their design one can go through if required. Fluid flow, different types of pumps, etc. are required not only for the single-phase fluid flow of liquids and gases in the refinery but also two-phase flow of gas liquid catalytic operations of moving bed and fluidized bed type, etc. So those things are also we have discussed. So other unit operations may be there but they are used to very less extent.

(Refer Slide Time: 51:20)

2) Chemical changes or unit processes

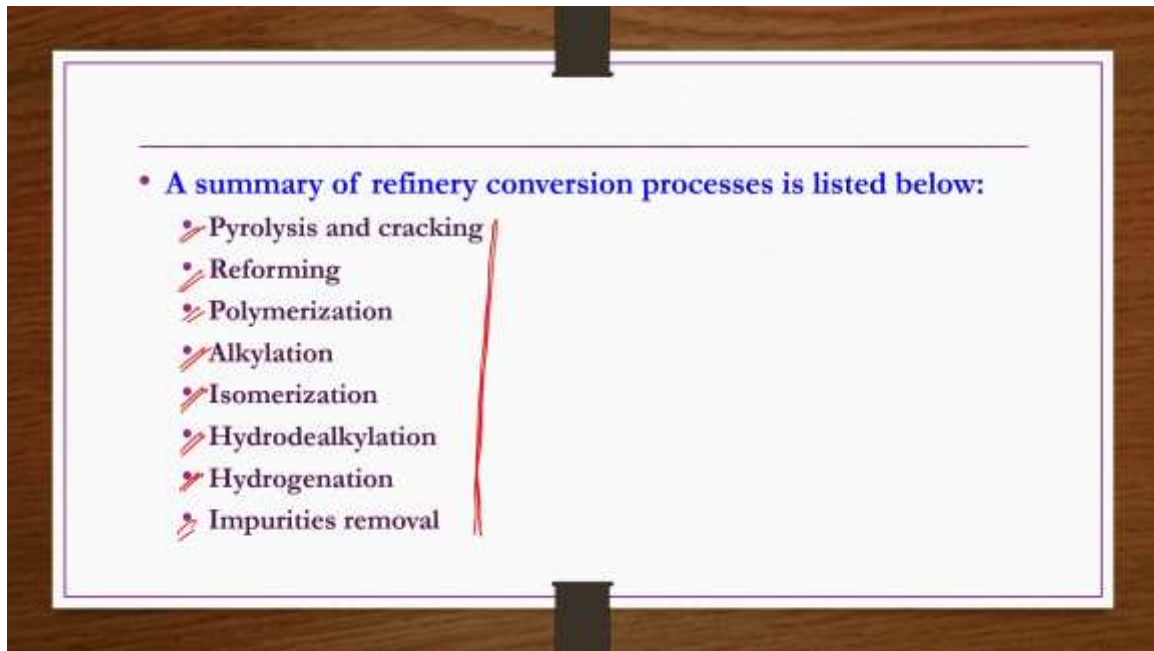
- Already discussed several unit processes of refineries in the first chapter of the course
- For e.g., depending on grade of crude, fraction of crude petroleum existing in petrol molecular range ($C_5 - C_6$) is only 25-40%
- Even the arrangement of these molecules is unsatisfactory for current petrol requirements
- Since current refinery output of high quality petrol may be as high as 50% in US, numerous conversion processes are used to accomplish this upgrading
- In India, process conditions are set up to maximize kerosene-diesel oil product yield and reduce petrol yields
- In addition, excess naphtha which accumulates is being converted by steam cracking to fertilizer and petrochemical starting chemicals
- Reforming and hydrodealkylation operations are used to produce primary aromatic chemicals such as benzene

Now the chemical changes or unit processes. Many of the unit processes associated with the refinery plants, not only associated with the refinery plants but also in general to organic chemical technology we have seen in the first chapter of the course.

But however, a summary of requirement of unit processes and other details are being discussed here with respect to the petroleum refinery plants only. For example, depending on grade of crude, fraction of crude petroleum existing in petrol molecular range is only 25 to 40% in general when you do the refinery process. So even the arrangement of these molecules is unsatisfactory for current petrol requirements. Since current refinery output of high-quality petrol may be as high as 50% in US, numerous conversion processes are used to accomplish this upgrading. In India process conditions are set up to maximize kerosene diesel oil product yield and then reduce petrol yields because these diesel requirements are more compared to the petrol requirements.

However, nowadays scenario is slightly changing, it is tending more towards the more petrol consumption than the diesel consumption. In addition, excess naphtha which accumulates is being converted by steam cracking to get the fertilizers and petrochemical starting chemicals. Use the naphtha as raw material to get different types of petrochemicals also or you can do steam cracking to get different types of fertilizers. Reforming and hydrodealkylation operations are used to produce primary aromatic chemicals such as benzene from this naphtha, etc. that we have already seen.

(Refer Slide Time: 53:18)



Now we have a summary of refinery conversion processes. Until now what we have discussed? We have discussed the products of refinery processes. When you do the refinery process on to a petroleum crude, what kind of products you get, those details we have seen with flowchart and then characteristics of different types of refineries we have seen. Then we have seen the processes that are involved in the refinery like unit operation and unit process, etc. Now we see specific to refinery plant, a summary of refinery conversion processes we are going to see like pyrolysis, cracking, polymerization, alkylation, hydrodealkylation, etc. those things. Here we are giving only list like pyrolysis and cracking, reforming, polymerization, alkylation, isomerization, hydrodealkylation, hydrogenation and then impurities removal. In the previous lecture and then today's lecture several of these terminology we have used to get some kind of products or to explain some kind of topic. So, it is very essential to understand how does these processes occur in general and then what are the reactions involved, what are the engineering problems, what are the appropriate flowcharts, etc. for these processes are need to be discussed. Those things we are going to discuss in the next lecture.

(Refer Slide Time: 54:48)

References

- C.L. Dryden, Outlines of Chemical Technology, Edited and Revised by M. Gopala Rao and S. Marshall, 3rd Edition, Affiliated East West, New Delhi, 1997.
- T.G. Austin and S. Shreve, Chemical Process Industries, 5th Edition, McGraw Hill, New Delhi, 1984.
- R.E. Kirk and D.F. Othmer, Encyclopaedia of Chemical Technology, 4th Edition, Interscience, New York, 1991.
- P.H. Groggins, Unit Processes in Organic Synthesis, 5th Edition, McGraw Hill, 1984.

References for today's lecture are presented here. Outlines of Chemical Technology by Dryden, edited and revised by Gopal Rao and Marshall 3rd edition. Chemical Process Industries by Austin and Shreve 5th edition. Encyclopedia of Chemical Technology by Kirk and Othmer 4th edition. Unit Processes in Organic Synthesis by Groggins 5th edition. Thank you.