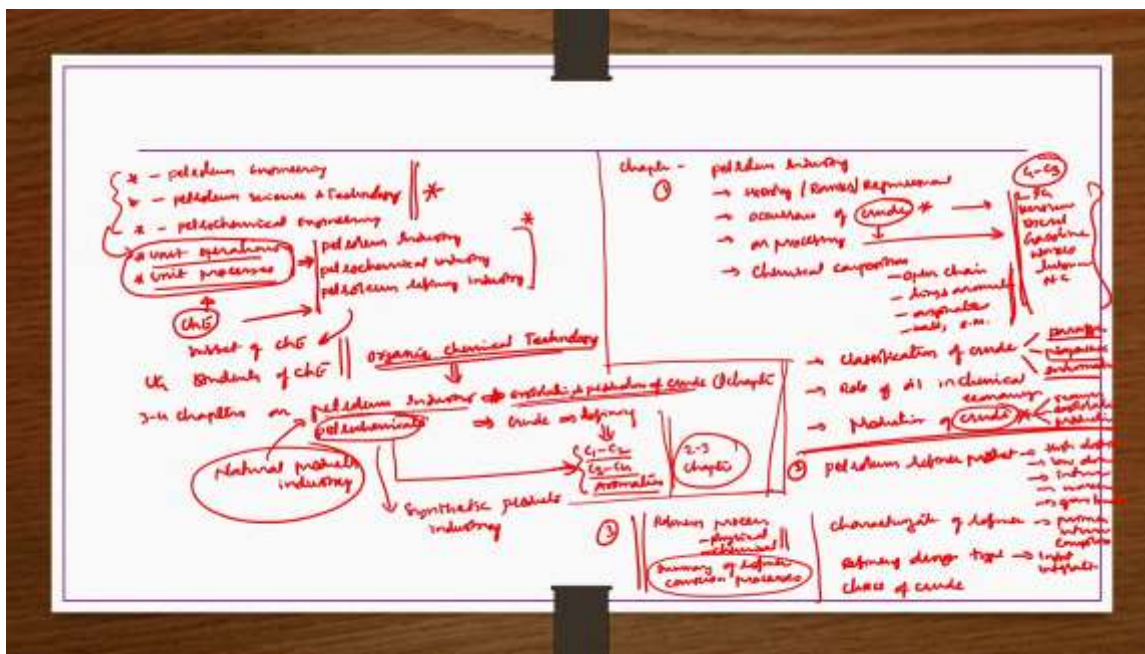


Lec 18: Petroleum Industry.

Welcome to the MOOCs course organic chemical technology, the title of today's lecture is petroleum industry.

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In many of the universities nowadays what we have? We have petroleum engineering as a separate discipline or course, undergraduate course or PG courses are also there like you know petroleum science and technology, etc. Different names are there, the contents you know how much they are covering that depends. Actually, petroleum industry, petroleum crude production itself is one particular industry kind of thing and then after getting the crude, processing it, refining it and getting different types of petrochemicals is a different kind of industry, right? So that way you know depending on what is the purpose, the titles may be slightly changing like you know petrochemical engineering also some universities they are having. But whether they call it petroleum engineering or petroleum science and technology or petrochemical engineering whatever, in these industries you know in their courses obviously they must be having you know courses on something like you know unit operations and then unit processes. What I mean to say that whether it is petroleum industry or petrochemical industry or petroleum refinery industry whatever it is, in these industries you have several of physical changes and then chemical changes, physical or mechanical and chemical changes would be there.

The physical and mechanical changes we call them unit operation and then whatever chemical changes we call them unit processes. All these unit operations and then unit processes that are required to handle these industries, petroleum related industry, all these

things are coming from the chemical engineering background or you know the basic unit operations and unit processes that are involved in petroleum related industry. All those basic unit operation and unit processes are core courses of a chemical engineering or derived from the chemical engineering curriculum. So, that is the reason though there are separate courses on petroleum technology, petroleum industry, etc., you know they are subset of chemical engineering only. All these industries are subsets of chemical engineering only and then because of such reasons as UG students of chemical engineering, it is essential for us to understand a few basics, if not entire details because obviously you can understand if there are separate courses with these engineering degrees. So that means the course maybe it is for 4 years, so then so many contents may be there, all of them we cannot cover in one single course. But from the organic chemical technology point of view, we have to see or extract the required information from these industries and then we try to learn them. What are the things from the organic chemical technology point of view are important to learn with respect to the petroleum industry or in connection to the petroleum industry that we have to list out and then we have to learn as a chemical engineer because this petroleum industry also subset of chemical engineering or subset of chemical industry and it cannot survive without the knowledge of chemical engineering, right? So that way if you see, we try to have 3 to 4 chapters on petroleum industries and petrochemicals, right? What do you mean by petroleum industry and petrochemical separately? So, petroleum industry here something like exploration and production methods of a crude petroleum or petroleum crude.

So, all those things which are natural part are available naturally in the nature. So those aspects related to those aspects that is exploration and production of crude, they are counted under the petroleum industries and then using this petroleum crude whatever is there that you do some kind of refining, refining in the sense some kind of operations like conversion, separation and finishing, etc. may be required. That you do then you can get large amount of wide variety of organic chemicals, something like C_1 to C_2 chemicals, C_3 to C_4 chemicals, aromatics, etc. These things you can produce from these crude.

So, production of these chemicals whatever are there from the crude by doing some kind of refining process, all they are counted as petrochemicals and they come under petrochemical industries. This petroleum industry whatever is there that is counted under natural products industry as per the classification that we have done in this particular course. So, this petroleum industry part comes under the natural product industry because petroleum crude that is occurring or forming underneath the earth, that is happening because of some natural processes. We are going to see all of them, whereas the production of these petrochemicals, etc. from the crude whatever are there.

So, there are several synthetic processes are there. They come under synthetic products industry. So, we cannot cover all aspects of petroleum engineering or petrochemical engineering, etc. but what we can see at least we can try to understand or try to have some

information on this petroleum industry in one chapter and another 2 to 3 chapters we dedicate on production of different types of synthetic organic chemicals from the petroleum crude. For that we have another 2 to 3 chapters, whereas we try to have one chapter on petroleum industry.

So, what are we going to discuss in these 3 to 4 chapters that we have a kind of enlisting at the beginning so that we can have a clear picture about the limitations as well as the boundaries of what are we going to discuss on the petroleum related aspects in this particular course on organic chemical technology. So, the first one is the petroleum industry that chapter if you take. What we have here? We have you know some kind of history, ranks, etc., requirement, why it is required? We know that the energy petroleum is the most important energy resources and then from this petrochemicals enlisting whatever I have given from here we can understand it is a raw material for production of a huge number of organic chemicals. So, it is a basic raw material whatever the crude petroleum is there that is a basic raw material for the existence of several synthetic chemical industries.

So those things we discuss. Then how it is occurring, occurrence of crude petroleum, what is happening underneath the years that we are getting and then we are trying to find out and then explore and then try to do the production. After doing the production of crude, we are doing several kind of refining process to get the petrochemicals, etc. So how the basic thing is that this is the crude, so how it is occurring that is we are going to understand. Then obviously this crude you know having several products if you do the production So then you can get the LPG, you can get the kerosene, you can get the diesel, you can get gasoline which is also known as the petrol, waxes you can get, lubricants you can get, natural gases also you can get in general.

So, these many products you are getting. So, it is important to know on processing what kind of chemicals are you going to get. So those things we try to understand. So, since these many chemicals we are producing LPG let us say C_1 to C_3 range alkanes only there. kerosene and then diesel, C_5 to C_{17} , you know alkanes in general would be predominating.

If you take the waxes like you know then you have more than C_{18} kind of organic hydrocarbons would be there. So now up to C_{40} also there in some kind of components. So, then that means you know wide variety of chemicals you are producing so it becomes very much essential to know what is the chemical composition. So that is what we are going to see chemical composition of the crude. So then here we have the open chain aliphatic, etc. then ring and aromatics, etc. then asphalts, etc. these kind of you know different chemicals in organic salts, organometallic components, etc. would be there. So, all these things we are going to realize.

Then crude is not same like coal that we get in Assam, that coal that we get in Telangana and then that coal we get in Chhattisgarh they are all different in their characteristics. The

crude also very different you know from one location to the other location. Some of them are rich in paraffins, some are rich in naphthenes, some are intermediate both of them would be there. So, depending on domination if the paraffins are dominating in the petroleum crude then we call paraffin base petroleum crude like that. If the naphthenes are dominating in the crude then we call naphthenes base you know petroleum crude like that you know some classification is required.

Then role of oil in economy and then chemical industry, etc. Those things we are going to see then production of crude. All these things are important up to this point we have seen only production of petroleum see under the production you have to find out the reserves where are they available. Then you have to find out the exploration methods when you explore you will realize whether it is explorable or producible or not otherwise you may be investing lot amount of money than what the profit you may be getting. So, exploration methods are important then production methods like drilling, etc.

Those things we are going to see, but we are going to see only a few basics not all the aspects but we see only a few basics. Then let us say if we covered all these in lecture 1. So, in the lecture 2 of this particular chapter we will be discussing about petroleum refinery products when you do the refinery. So now in the first lecture we do up to the production of crude. So once this crude is there then you can do the refinery.

You can take them to the refinery and then do some refinery processes. So, where some chemical conversions, separations, finishing, etc. would be there. So then here you can get high distillates, low distillates and then intermediates, waxes, etc. So many kind of fractions may be there even gas fractions would also be there.

So, all those things we discuss. Then characterization of refinery like primary refinery, intermediate refinery, complex refinery, future plan refinery, etc. these kind of things are there. So those things we discuss. Then we discuss refinery design types.

So, we are not going to see the design of refineries that is very complicated that required entire semester course separately then only we can understand. So, but we see what are the types like in independent refinery and then integrated refineries, etc. are there. Then choice of crude. As I already mentioned crude may be paraffin base, naphthene base or intermediate base.

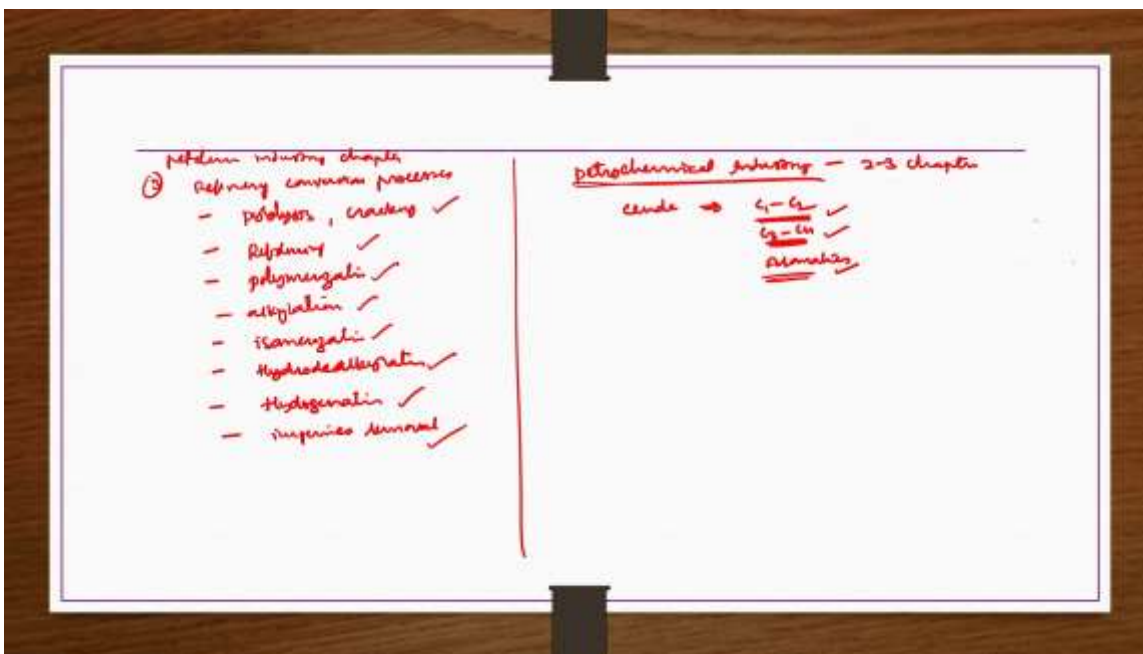
So as per your requirement you have to select the base. Let us say if you wanted to produce more waxes and lubricants, etc. then you have to go for the paraffin base crude. If you wanted to produce more diesel and then petrol, kerosene, etc. then you have to go for the naphthene base crude.

So, such kind of details we discuss. Then we discuss about the refinery process. Refinery process that are nothing but physical and chemical changes which we have already

discussed in this first chapter of the course where we discussed basics of unit operations and then unit processes. But here we discuss only those which are relevant to the petrochemicals industry. Then finally summary of refinery conversion processes.

After this we conclude the second lecture and then in the third lecture of the chapter on petroleum industry we will be discussing a detail of these refinery conversion processes like polymerization, alkylation, hydrodealkylation, etc. these kind of methods are there. Those things would be discussed in the third lecture.

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In the third lecture of petroleum industry chapter we will be discussing about the refinery conversion processes. That include pyrolysis, cracking, reforming, polymerization, alkylation, isomerization then we will be discussing about hydrodealkylation, then hydrogenation, then removal of impurities, impurities removal like sulphur, etc. are present in general crude. So, they have to be you know removed. So, when you understand these processes then you would be able to understand each and every aspect of petrochemical industries. After completing this chapter we will be discussing petrochemical industries where 2 to 3 chapters would be there. So here what we do basically you utilize the crude and do some kind of refinery process to get some chemicals like C₁ to C₂ chemicals, let us say ethylene, etc., propylene, etc. if you wanted to get how to get C₃ to C₄, aromatics like this you know with flowchart particular raw materials, raw materials also based on which type of crude all those things we discuss and then engineering problems, economics of the process all those things we are going to discuss in subsequent 2 to 3 chapters which are primarily on petrochemicals industry. So, with this background we have a clear idea of what are we going to discuss or what aspects of petroleum industry or petrochemicals are

we going to discuss in organic chemical technology course that you understand. This understanding is very essential to have our boundaries on to up to what are we going to study about the foreign subject in this organic chemical technology, the so-called petroleum industry related aspects we are discussing in organic chemical technology.

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Petroleum industry

- Amongst all chemical industries, petroleum industry ranks top both in productivity and profit
- It is treated under natural products industry, whereas petrochemicals industries are grouped under synthetic products industry

crude petroleum

↓ *raw material*

C_1-C_2
 C_3-C_4
Aromatics
- It is most important of natural products available because
 - It is a major source of energy
 - Basic raw material for much of synthetic organic chemical industry

↙ ??
- Because of excessive use of petroleum crude, their reserves depleting faster and conservation has become concern for the world

Petroleum industry amongst all chemical industries petroleum industry ranks top both in productivity and profit because it is major source of energy and not only that it is also a basic raw material for production much of synthetic chemicals. So many other synthetic chemical industries are also based on the success of this petroleum industry because this crude is going to be utilized as raw material for several of the synthetic chemical industries.

So from that point of view productivity and then profit from that point of view as well petroleum industry ranks very high amongst the chemical industries and then it is treated under natural product industries as I mentioned the crude production whatever is there or petroleum crude whatever is there that production part you know that is coming under natural products industry because whatever the petroleum crude is there that is forming naturally under the anaerobic conditions that we are going to discuss anyway. So, whereas the petrochemicals that is this petroleum crude whatever is there that you use as raw material and then produce different chemicals C_1 to C_2 chemicals C_3 to C_4 chemicals or more than C_5 chemicals aromatics actually n number of chemicals you can produce but we are going to discuss a few of them. So, since these processes are having several synthetic processes so these production of different types of chemicals from the crude petroleum whatever are there so such industries are known as the synthetic product industry. So, petroleum industry or petroleum production industry is a natural product industry whereas

the petrochemicals industries are synthetic products industry as per our definition of natural versus synthetic products industry that we had in the first chapter of this course. It is most important of natural products available because it is the major source of energy not only that one it is a basic raw material for much of the synthetic organic chemical industry.

If it is not available so this the success of such synthetic organic chemistry industry would also be questionable or you know their future would be under question mark. Because of excessive use of petroleum crude their reserves are depleting faster and conservation has become concern for the world because these petroleum crudes are forming naturally and then for that formation it takes you know hundreds and even sometimes thousands of years. So, compared to that one we are utilizing them at a much faster rate. So, because of that one conservation has become primary concern nowadays. So, we have to use the petroleum resources with responsibility keeping future in mind.

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• Occurrence of petroleum crude

- Formed several million years ago from organic matter of marine deposits
- It formed in oxygen deficiency atmosphere, i.e., under anaerobic conditions
- Selective bacterial attack destroyed proteins and carbohydrates of deposits
- Because of this attack, fats formed and accumulated as oil reserves, hence these are known as fossil fuel
- Rate of formation is very low (almost nil) compared to rate of present consumption

Handwritten diagram illustrating the process of petroleum formation:

```
graph TD
    A[carbohydrates] --> B[protein]
    A --> C[organic matter]
    B --> D[decomposition]
    C --> D
    D --> E[into]
    E --> F[acids]
    E --> G[alkanes]
    E --> H[alkenes]
    E --> I[alkynes]
    E --> J[alkenes]
    E --> K[alkynes]
    E --> L[alkenes]
    E --> M[alkynes]
```

So then how this petroleum crude would occur? So, what happens you know they are formed several million years ago from organic matter of marine deposits you know underneath the earth. And this organic matters these are all organic matters maybe like you know plants, etc. or maybe animals, etc. or maybe any kind of organic matter it can be. So, such organic matter of marine deposits whatever are there they would be attacked by bacteria in the absence of air or oxygen.

Anaerobic process is taking place here. So, when these bacteria attacks these deposits so these deposits usually have you know carbohydrates, proteins, etc. So, when they are attacked by the bacteria then what will happen fats would be formed. These fats would be

accumulated over the years and they form reserves of crude petroleum. So, this is happening and this is happening in a deep underneath the earth right. So, whatever the organic matter of marine deposits are there they would be attacked by certain kind of specific bacteria and these bacteria what they do under the anaerobic conditions are in the absence of air they convert the carbohydrates and proteins of these deposits into fats and those fats are being accumulated as a crude resources.

It formed in oxygen deficiency atmosphere. Selective bacterial attack destroys the proteins and carbohydrates of deposits because of the this attack fats formed and accumulated as oil reserves. Hence these are also known as fossil fuels but however rate of formation is very low almost nil compared to the rate of present consumption. We are consuming a lot amount whereas the formation takes over you know millions of years right. So, compared to the production rate the consumption rate is very very high. So that we can say that you know production is almost nil compared to the consumption rate so we have to consume it carefully responsibly.

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Processing or refining (conversion, separation, finishing, etc.) of crude oils shall produce:

- 45 – 50%: Gasoline
- 20 – 25%: Diesel and heating oils
- 18 – 20%: Other products
- 08 – 10%: Jet fuel
- 04 – 05%: Liquefied petroleum
- 03 – 04%: Asphalt

Handwritten notes and diagram:

- Diagram showing the separation of hydrocarbons into three fractions:
 - Gas:** C_1, C_2, C_3, C_4
 - Liquid:** $C_5 - C_{17}$
 - Solid:** $> C_{18} - C_{40}$
- Other products: C_6, H_2, N_2, O_2

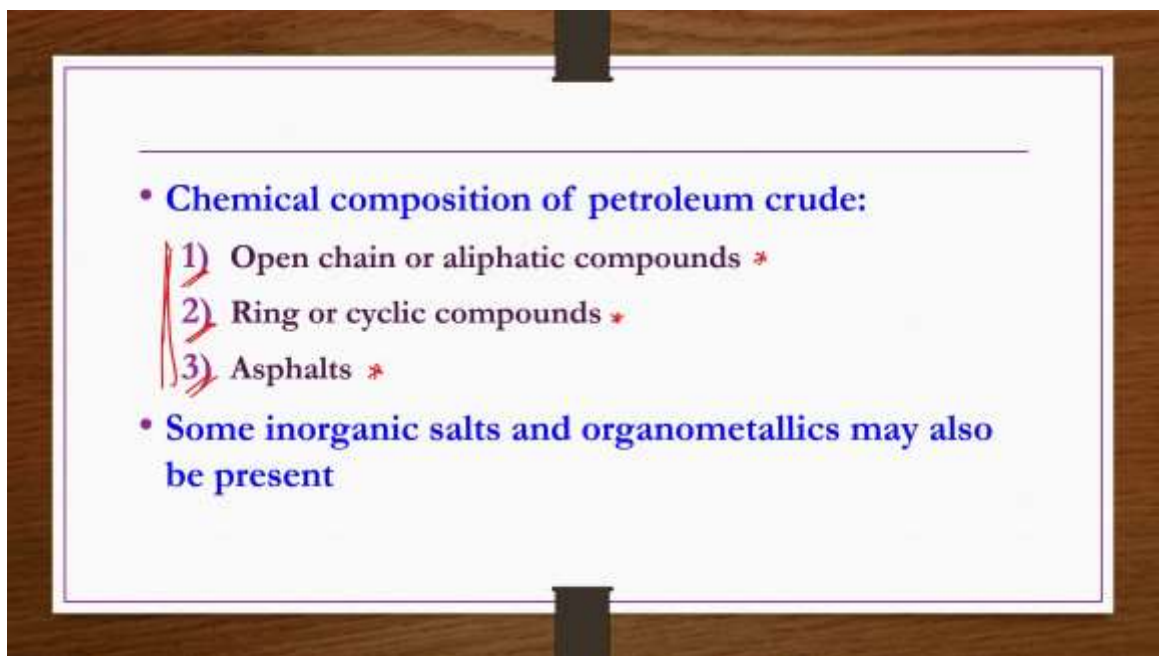
Now processing or refining, refining in the sense some kind of conversion chemical conversion some kind of separation some kind of finishing of crude oils may take place. When you do this one you get gasoline that is 45 to 50% roughly and then diesel and heating oils you get 20 to 25%. Other products 18 to 20 products like benzene, xylene, toluene, etc. such kind of products waxes lubricants, etc. Jet fuels 8 to 10% you get and then liquefied petroleum 4 to 5% you get asphalts 3 to 4% you get.

So, these variations based on the you know what is the base of the crude which base crude are you having? Are you having naphtha base crude? Are you having paraffin base crude or intermediate crude? Based on that one these variations may be there. Let us say if you have a paraffin base crude so then more of these gasoline diesel kind of products you get. Now when you see the chemical composition of these components then what you can have you may be having from C_5 or even gases also less than C_1 , C_2 , C_3 gases also there C_4 gases also there and then liquid C_5 to C_{17} and then solids or you know semi solids or waxes these kind of thing up to C_{40} these things are there. What do you mean by C_1 , C_2 , C_3 , etc. because all these are you know organics organic chemicals.

These organic chemicals primarily they have C, H, O and then some foreign inorganic atoms like N, S, O, N, S, etc. these kind of things would be there some kind of metals would also be there primarily C, H, O are there. So, they are characterized based on the carbon number so that carbon number C_1 , C_2 , C_3 like that we write depending on how many carbon atoms are there in the given formula. So, these are gases these are the liquids and these are the solids.

Solids are you know waxy material kind of thing. You can see wide variety of you know or you can see wide spectrum of products being formed by doing some kind of processing. So, from where are they coming all of them are coming from the crude. So that means one way or other way all these are present in the crude may not be in the direct form that you are only doing physical change to separate out there may be some chemical changes are also there to get these products.

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- **Chemical composition of petroleum crude:**
 - 1) Open chain or aliphatic compounds *
 - 2) Ring or cyclic compounds *
 - 3) Asphalts *
 - **Some inorganic salts and organometallics may also be present**

So, it becomes very essential to understand what is the chemical composition of the crude in general that if you see you have open chain or aliphatic compounds, then ring or cyclic compounds, asphalt and then some inorganic salts and organometallics may also be present. So now see almost all category of you know organic chemicals are present here.

So that means you need to have a very good sound knowledge of organic chemistry if you wanted to become a very good engineer or very good petroleum engineer. Now we see a few basics of all these things few basics only otherwise if you wanted to see all details then you have to go for organic chemistry courses.

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1) Open chain or aliphatic compounds: n-paraffins and isoparaffins

- n-paraffin series (C_nH_{2n+2}): normal paraffins or normal alkanes
 - These are open straight chain saturated hydrocarbons $CH_3 - CH_2 - CH_2 - CH_3$
- Isoparaffin series (C_nH_{2n+2}): branched type hydrocarbons starting with isobutane
 - Branched chains are desirable, but not naturally occurring to any extent $CH_3 - CH - CH_3$
 - These must be produced by alkylation, hydroforming and isomerization
- Compounds with different structures but same formula are called isomers
- Though their formula are same, they possess different properties due to molecular interactions and dispersion forces
- Isoparaffins have high octane number than n-paraffins
- For e.g., n-butane and iso-butane have same chemical formula (C_4H_{10}) but boiling point of n-butane is higher than that of iso-butane

Handwritten notes on the slide:
 - Top right: A skeletal structure of n-butane.
 - Middle right: A skeletal structure of isobutane.
 - Bottom right: A box containing a skeletal structure of isobutane and the text 'C4 -> 125mbars'.

Open chain or aliphatic compounds they can be grouped as n-paraffins and then isoparaffins. n stands for the normal so they are also known as the normal paraffins or normal alkanes also. Let us say these are open chain what does it mean by you know they will be having some kind of chain structures like C-C-C-C let us say CH_3 , CH_2 , CH_2 , CH_3 .

So sometimes these are also shown like this representation kind of thing 1C, 2C, 3C and then 4C like this also they show. Different representations are there. These are you know if you have only single bonds then they are known as the alkanes and they are having linear chain like this. So then we call them normal alkanes and then their chemical formula would be C_nH_{2n+2} . Let us say n is 1 then you have the methane, if n is 2 then you have the ethane like this, n is 3 you know propane, n is 4 butane like that pentane, hexane and all those components are there.

Their chemical composition is this one and these open chain or aliphatic components are present predominantly in the so-called paraffin-based groups or the petrochemicals or the chemicals that we get from them like LPG or liquid products like gasoline, diesel, etcetera if you take. So, in those products primarily this paraffin should be present. These are open straight chain saturated hydrocarbon saturated in the sense there will only be single bond, there will not be any double bond, triple bond, etcetera. Other category is that isoparaffin series. Paraffins they can be normal paraffins, they can be isoparaffins. Their formula is C_nH_{2n+2} , but they are branch type hydrocarbons starting with isobutane. So here also C_nH_{2n+2} , here also C_nH_{2n+2} . What does it mean? Let us say you have butane $CH_3-CH_2-CH_2-CH_3$, this is n-butane. So, the same thing maybe you can have $CH_3-C(CH_3)_2-H$ and then CH_3 . So that is $CH_3-CH(CH_3)-CH_3$ and then this kind of structure, isomers whatever this kind of structure is there.

So that we call isomer of the linear normal alkane. So, they are branched, they are not linear like n-butane. This is known as the isobutane, it is having branched structure, but the formula is same. Here also it is C_4H_{10} , here also C_4H_{10} that is generalized if you write C_nH_{2n+2} . Branched chains are desirable but not naturally occurring to any extent. These must be produced by alkylation, hydroforming and isomerization.

These processes we are going to see in the third lecture of the present chapter. Compounds with different structures but same formula are called isomers. Though their formula are same, they possess different properties due to molecular interactions and dispersions. Let us say this $CH_3-CH_2-CH_2-CH_3$ actually they are as I mentioned in reality, they are present like this. So, if they are present like this and then if they are present like this $CH_3-CH(CH_3)-CH_3$, here it is $CH_3-CH_2-CH_2-CH_3$.

Now the location, how these are being connected with that you can understand their molecular structure and molecular interactions. Based on the molecular structure, molecular interactions would change. If the molecular interactions are changing, then definitely the corresponding properties will also be changed. So, though here it is C_4H_{10} , here also C_4H_{10} , their molecular structure is different. Since the molecular structure is different, their molecular interactions would be different and then their dispersion forces would be different because of that one, their properties would be different though their total overall formula is same like C_4H_{10} in this case.

Isoparaffins have high octane number than n paraffins that is one example because since though they are having the same formula C_nH_{2n+2} and then C_nH_{2n+2} , same formula but they have different octane number. Isoparaffins are having high octane numbers. For example, n-butane and isobutane have same chemical formula C_4H_{10} , but boiling point of n-butane is higher than that of isobutane. Actually isomers, whatever are they, they start from the isobutane or from C_4 onwards only. C_3 , C_2 , they do not have any isomers, okay? You cannot have branched C_2 or C_3 components.

You can have only normal linear chain C_2 , C_3 components only. Branched components will start from C_4 . So, the same examples I have given here. This is n-butane and this is isobutane. Their molecular structures are different, so their properties are also different.

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$CH_3 - CH_2 - CH_2 - CH_3$

$CH_3 - CH - CH_3$
|
 CH_3

- With increasing carbon atom numbers, no. of possible isomers increases
- For e.g., n-butane can have only one iso-butane, but n-pentane can have three isomers, n-alkane with 8 and 18 carbons atoms can have 18 and 60,523 isomers respectively !!
- Paraffins (n-paraffins, especially) comprises largest fraction of petroleum crudes
- Paraffins ($C_1 - C_{40}$) are often present in petroleum crude oil, constituting up to 20 vol.% of crude
- Here crude oils mean heavier alkanes in liquid solution but not as solid particles
- At normal conditions:
 - C_1 (methane), C_2 (ethane), C_3 (propane) and C_4 (butane) exist in gaseous form
 - C_5 (pentane) onwards and up to C_{27} (heptadecane) exist in liquid form
 - Constitute large fractions in liquid fuels such as gasoline, diesel, jet fuel, etc.
 - C_{28} (octadecane) and heavier compounds exist in waxy state
 - Soluble in lighter paraffins and may present in gasoline, diesel, etc.

Handwritten notes: n-pentane $\rightarrow$ 3, $CH_3-CH_2-CH_2-CH_2-CH_3$, n-pentane, C_5H_{12} , C_5H_{12}

With increasing carbon atom numbers, number of possible isomers increases. Let us say n-butane we have seen only 2 isomers, n-butane and then isobutane. If you have n-pentane, then 3 are possible. Let us say that is CH_3 , CH_2 , CH_2 , CH_2 , CH_3 . So, this you can have CH_3 , CH , CH_3 , CH_2 , CH_3 .

This is isopentane, this is n-pentane. Other one is possible, let us say CH_3 , C , CH_3 , CH_3 and then CH_3 . This is neopentane. What does it mean? Now here carbon atoms, how many are there? 5 are there, right? So, formula is same formula like you know C_5H_{12} that is C_nH_{2n+2} form for all of them, C_5H_{12} . That means as the carbon number or number of carbon atoms increasing, so the possible isomers will increase, right? For example, n-butane can have only 1 isobutane, so only 2 isomers are possible that is n-butane and isobutane, but n-pentane can have 3 isomers like shown n-pentane, isopentane and neopentane.

Likewise, if you have octane, so then 18 isomers are possible. If you have 18 carbon alkanes, then that is nothing but octadecane. If you have octadecane that is 18 carbon atoms alkane, then 60,523 isomers are possible. So, with the increasing the number of carbon atoms, number of isomers not only increasing, it increasing exponentially that is what you can understand from these numbers. This is n-butane, this is isobutane. Paraffins, n-paraffins especially comprise largest fraction of petroleum crudes, whatever the petroleum crudes are there primarily these paraffins are present.

Within the paraffins are n-paraffins are dominating, not the isoparaffins. That is C_1 to C_{40} , paraffins are often present in petroleum crude oil constituting up to 20 volume percent of crude, that is huge one. Here crude oils mean heavier alkanes in liquid solution but not as solid particles. At normal conditions C_1 , methane, C_2 , ethane, C_3 , propane, C_4 , butane exist in gaseous form. Whereas C_5 pentane onwards up to C_{17} that is heptadecane up to that point, they exist in liquid form whereas octadecane C_{18} onwards and then heavier components they exist in waxy solid-state kind of thing. The C_5 to C_{17} alkanes whatever are there, they constitute large fractions in liquid fuel such as gasoline, diesel, jet fuel, etc.

Let us say if you wanted to produce this diesel petrol alternatively by using biomass, etc. as a renewable source, then you have to make sure that the oil whatever you are getting that is primarily having C_5 to C_{17} saturated alkanes, not the unsaturated ones. In fact, unsaturated alkanes like ethylene, propylene, etc. almost negligible in petroleum crude. This C_{18} onwards whatever the heavier components are there, they are soluble in lighter paraffins and may present in gasoline, diesel, etc. as well since they are soluble in paraffins.

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2) Ring or cyclic compounds: naphthene and aromatic series

- Naphthene or cycloalkane series (C_nH_{2n}):
 - Same formula as olefins (or alkenes), but completely saturated (methyl cyclohexane, cyclohexane), i.e., without double bonds
 - Second most abundantly occurring series in crudes
 - For same no. of carbon atoms, physical properties (such as density & boiling point) of cycloalkanes greater than those of n-alkanes
 - Unsaturated olefins (such as ethylene, propylene, etc.) are almost negligible in crude oils

Handwritten notes and diagrams include:

- Chemical structures of cyclopentane and cyclohexane.
- Chemical reaction: $CH_2=CH_2 + H_2 \rightarrow CH_3-CH_3$ (Ethylene + Hydrogen → Ethane).
- Labels: "Cyclopentane", "Cyclohexane", "n-alkane", "olefins", "hydrogenation".

Second category of chemical components that are present in the crude are ring or cyclic compounds. They are 2 types, naphthene and aromatic rings or aromatic series. It is not naphthalene, it is naphthene. So, naphtha-based crude whatever we are saying. In the crude if you have more naphthene components or aromatic components that we call naphtha-based crude.

Naphthalene or cycloalkane series they have C_nH_{2n} formula. Actually, olefins whatever are there or alkenes whatever are there that is like CH_2 double bond CH_2 ethylene, propylene,

etc. whatever are there CH_3 CH double bond CH_2 this is propylene. So, these double bonds whatever are there these are you know unsaturated one because of the double bonds unsaturated ones would be there. Their common formula if you see it is C_nH_{2n} . Whereas this naphthene and cycloalkanes would also have the C_nH_{2n} form, but they are saturated how it is because they are in the cyclic form.

Let us say if you take a cyclohexane. So, this is one C, this is another C, this is another 6 carbon atoms are you know connected cyclic form like this. All of them are having 2, 2 hydrogen atoms like. So, C_nH_{2n} and they are saturated because there are no double bonds, but the same formula if you take the benzene what you have it is having alternative double bonds benzene. So, this carbon 6 carbon atoms are there, but they are having alternative double bonds. So then for that reason each one would be connected with only one H in the benzene because carbon can accommodate maximum 4 bonds.

So, this is cyclohexane, this is benzene. So, all these organic chemistry point of fundamentals you might be having already from your first-year organic chemistry courses, but however some important recapitulation is required here. So, in the cycloalkanes though the chemical formula is C_nH_{2n} like in alkenes they are saturated, they are not unsaturated like alkenes. Why they are not unsaturated like alkenes despite having C_nH_{2n} formula because of this region shown structure like here. Same formula as olefins or alkenes, but completely saturated like cyclohexane without double bonds. Since there are no double bonds then these are saturated one, benzene is not saturated one because there are double bonds.

This category of chemicals are the second most abundantly occurring series in petroleum crudes. For same number of carbon atoms physical properties such as density and boiling point of cycloalkanes are greater than those of n-alkanes. Let us say you have this cyclohexane, n-hexane if you take linear component so that is C, C, C, C, C and then H_3 then in between H, H that is CH_2 , CH_2 , CH_2 , CH_2 . So here breaking of these bonds may be easy because they are linear at any point they may not require much energy.

Whereas here they are joined together and then formed a compact structure like a ring. So then here you need to give more energy for breaking these bonds that is the reason here it is expected to have the higher density and then higher boiling points here compared to the linear n-alkanes. Unsaturated olefin such as ethylene, propylene are almost negligible in crude oils. They are not at all present in crude oils. Even if they are present they are almost negligible.

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■ **Aromatic or benzene series (C_nH_{2n-6}):**

- Present only in small amounts
- Common aromatics of crude oils are benzene derivatives (such as any alkyl benzene)
- Aromatic series with only one benzene ring is mono-aromatics or mononuclear aromatics
- Heavy petroleum fractions may contain unsaturated multirings with many benzene and naphthene rings attached to each other
- These are known as polyaromatic hydrocarbons (PAHs) or polynuclear aromatics (PNAs)
- For e.g., naphthalene, anthracene, pyrene, etc.
- Heavy crude oils generally contain more aromatics than lighter crude oils

Second one under the aromatic series is aromatic or benzene series which is having common formula like C_nH_{2n-6} .

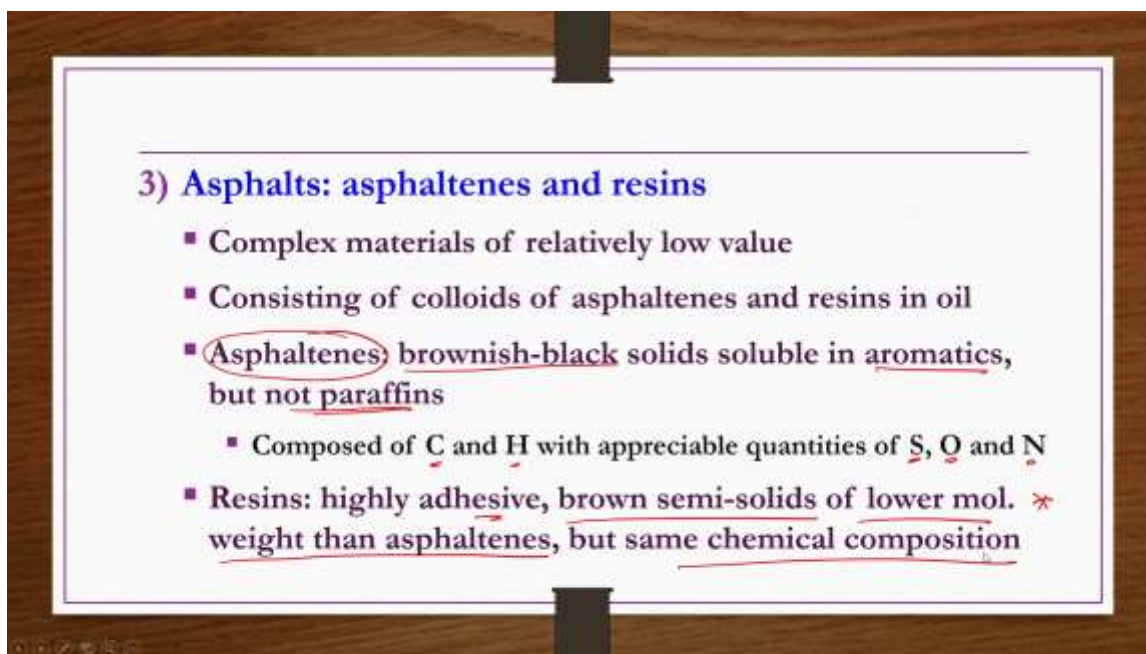
Let us say n is 6 then it is benzene C_6H_{12-6} that is H_6 , C_6H_6 benzene you get. It present only in small amounts in the crude in general. Common aromatics of crude oils are benzene derivatives such as any alkyl benzene. Alkyl in the sense let us say alkane, any of the alkane is there that is C_nH_{2n+2} is there. One H if you remove whatever C_nH_{2n+1} radical is there, radical is indicated with the star something or dot.

So, this is known as the alkyl functional. Let us say if you have methane if you remove 1 H then you have CH_3 star or CH_3 dot which is known as methyl. From the C_2H_6 if you remove 1 then whatever C_2H_5 star or dot is there that is known as the ethyl. So, this alkyl benzene components, so such kind of derivatives may also be present. Aromatic series with only 1 benzene ring is monoaromatics or mononuclear aromatics. Heavy petroleum fractions may contain unsaturated multi rings with many benzene and naphthene rings attached to each other.

These are known as polyaromatic hydrocarbons or poly nuclear aromatics PAH or PNA. Some example naphthalene, naphthalene is nothing but 2 benzene rings if you join like this whatever the structure is there that is nothing but naphthalene. Anthracene is nothing but if you have 3 benzene rings like this so then that is anthracene. If you have 4 benzene rings then pyrene like this. This circle at the inside the benzene rings indicate that the double bonds are alternatively present.

This is naphthalene, this is anthracene, this is pyrene. These are all known as polyaromatic hydrocarbons PAH. Heavy crude oils generally contain more aromatics than lighter crude oils. So, this structure also we have already seen in the first chapter of the course where we were discussing about the common unit processes of organic chemical technology.

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3) Asphalts: asphaltenes and resins

- Complex materials of relatively low value
- Consisting of colloids of asphaltenes and resins in oil
- Asphaltenes: brownish-black solids soluble in aromatics, but not paraffins
 - Composed of C and H with appreciable quantities of S, O and N
- Resins: highly adhesive, brown semi-solids of lower mol. weight than asphaltenes, but same chemical composition

Third category is asphalts which is having 2 subcategories like asphaltenes and resins. These are complex materials of relatively low value consisting of colloids of asphaltenes and resins in oil.

Asphaltenes which are brownish black solids soluble in aromatics but not in paraffins. So, these would not be present in the so-called petrol, diesel, etc. these kind of things. Compost of C and H with appreciable quantities of inorganics like sulphur, oxygen and nitrogen atoms. Resins are highly adhesive but brown semisolids not solids like asphaltenes.

They are semisolids of lower molecular weight than asphaltenes. They are also higher molecular weights compared to the paraffins, isoparaffins, etc. if you compare. But if you compare with asphaltenes then these resins are lower molecular weight but they have same chemical composition.

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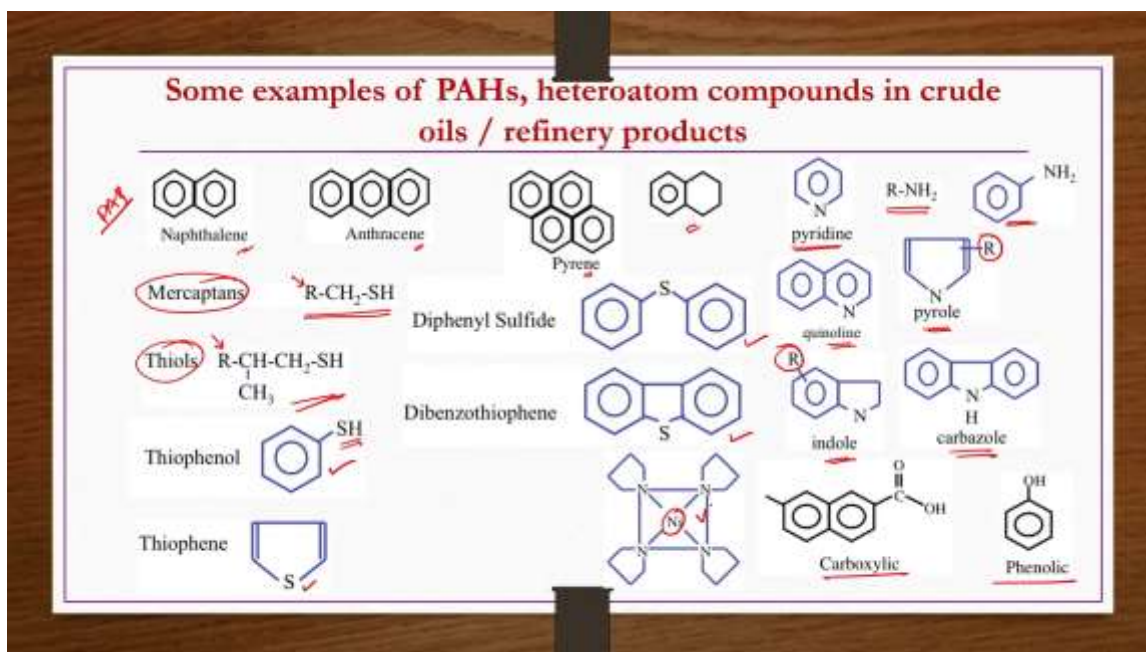
- PAHs of high mol. wt. often contains heteroatoms (S, N, O)
 - Regarded as aromatics because of their electronic configurations
- In petroleum crudes (and even in refinery products), S is important heteroatom and can be found in
 - Cyclic (thiophenes, etc.) and non-cyclic (mercaptans, sulfides, R-S-R', etc.) compounds
- In natural gas, S may be present as hydrogen sulfide

These polyaromatic hydrocarbons of high molecular weight often contain heterogeneous atoms or heteroatoms like sulphur, nitrogen and oxygen.

Some of them may be impurities in the crude. So, regarded as aromatics because of their electronic configurations. Because of these inorganic atoms present some people do not consider them as aromatics. However, based on their electronic configuration some scientists consider them as aromatics. There is a conflict in general. In petroleum crude and even in refinery products S is important heteroatom and can be found in cyclic and non-cyclic components.

Cyclic thiophenes, etc., mercaptans if it is non-cyclic compounds they are present. So, some examples of thiophenes, mercaptans we have seen in the first chapter of the course. We are going to see in the next slide anyway. In natural gas sulphur may be present as hydrogen sulphide impurity. It is present in different forms.

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Some of the forms we are going to see. Some examples of polyaromatic hydrocarbons and heteroatom compounds that are present in oils or refinery products. Naphthalene, 2 benzene rings connected like this anthracene, 3 benzene rings connected like this, pyrenes connected like this and then some structures like this. One side you have benzene ring, another side you have the cyclic compound without the double bond kind of thing.

Such kind of components are also possible. All of them are known as the PAH. These are in general you know may be having heteroatom. So, if you have sulphur and then that structure is linear non-cyclic then we get mercaptans. This mercaptans is not one component, it is a group, a particular kind of homolog, right? Depending on the R different types of mercaptans you can get. Same is thiols also as shown here depending on R different types of thiols you may get; the common structures are shown here for the mercaptans and thiols.

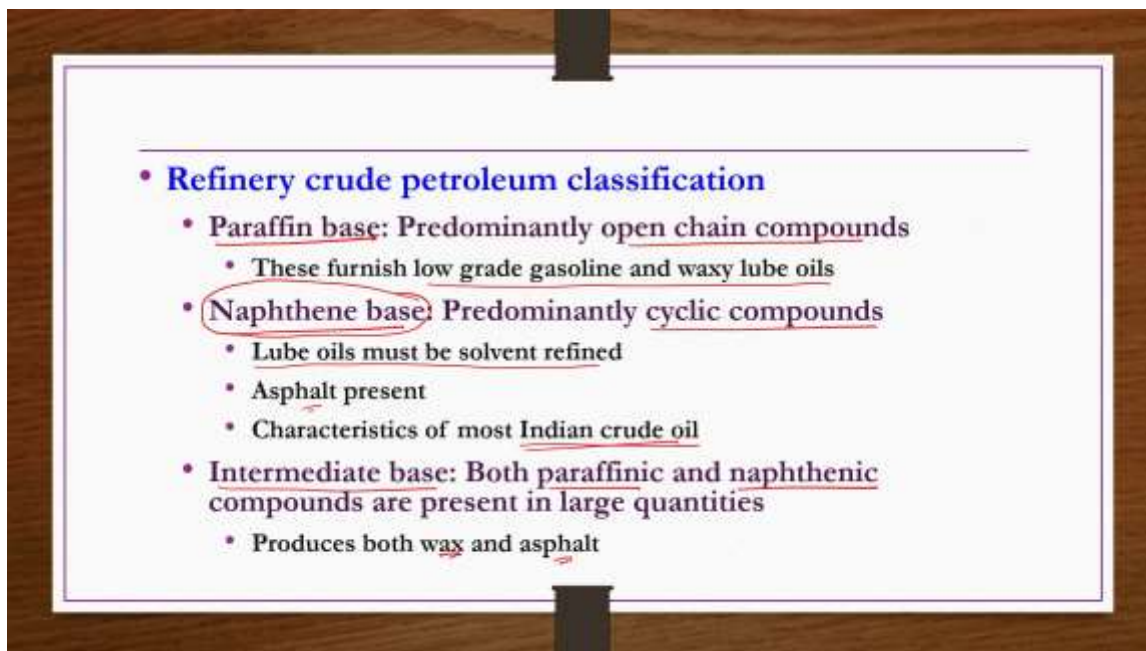
One example of sulphur heteroatom PAH is thiophenol shown it here like phenol C_6H_5OH you have. In the thiophenol you have C_6H_5SH you are having, okay? Thiophene is one of the heteroatom PAH. Another example is diphenyl sulphide, another example is dibenzothiophene, etc. Then if nitrogen is present as heteroatom or nitrogen containing poly aromatic hydrocarbons if you see, one of them is pyridine, common amine or if R is benzene ring or C_6H_5 then this is nothing but aminobenzene.

The same thing is shown here. Quinoline, pyrrole, indole, carboxyl. So now indoles are you know different types of indoles are possible. Pyrroles also different types of pyrroles are possible depending on the R structure. They are a particular group, they are not like

you know one particular component. If you have oxygen then carboxylics, phenolics like this they may be possible.

There may be possible to have you know organometallics in the crude, they may have some kind of structure like this. In between in place of nickel you may be having the vanadium also that is also possible. So that is about some examples of poly aromatic hydrocarbons and then crudes containing heteroatoms.

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Now we see refinery crude petroleum classification. Classification now until now whatever we have seen, we have seen the composition of the crude. So, it is having all different types of chemicals, open chain, branched chain, cyclic components, aromatics, asphaltenes everything is there.

So, based on that information of chemical composition of petroleum crude, we try to classify the petroleum crude. So, this is the classification of petroleum crude. So, one is the paraffin base which predominantly consists of open chain compounds. Another one is the naphthene base which predominantly consists of cyclic compounds and then third one is the intermediate base which contain paraffinic and naphthenic compounds in large quantities. These names paraffin base, naphthene base they are coming based on how much paraffins are present in the crude, how much naphthene present in the crude.

If the paraffins are dominating more quantities there more than 30, 40% then we can call in paraffin base. Otherwise 30, 40% or even higher naphthenes are there then we can call them naphthenes base. Some crudes both paraffin and naphthenes may be present in 30,

40% and remaining may be in the little quantities only. So, they are known as the intermediate base. Most of the Indian crude that is available Indian conditions, they are naphthenes base.

Paraffin base crude usually furnish low grade gasoline and waxy lubricant oils, etc. Naphthenes base crudes are suitable for producing lube oils and they must be solvent refined asphalt also present and then characteristics of most Indian crude oil is naphthenes base crude. So most of the Indian crude whatever available for us they are naphthenes base crudes. Intermediate base crude may also be utilized for production of both wax and asphalt.

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• Role of oil in economy

- Consumption of energy and petroleum products is a good indicator of level of a country's economic development
- India has one of the lowest per capita energy consumption in the world (only 217 kg of oil equivalent) 2400
- This value is only 15% of global average of 1478 kg of oil equivalent
- Similarly, India's per capita consumption of oil is also very low and it is only 11% of world average
- Development is an energy-intensive process, with rising incomes and improving literacy levels leading to high consumption of petroleum products
- Consumption pattern in India is tilted in favor
 - Light and middle distillates: LPG and kerosene (SKO – superior kerosene oil) for households
 - Diesel (HSD – high speed diesel) and gasoline for transportation

Now quickly we see role of oil in economy. So how much energy is available and then how much energy is consumed per capita or per head that will give you a kind of true picture of the status of a country how good it is economically.

And then that depends strongly on energy. So, energy obviously the oil is the major part of the energy. Energy different forms may be there, energy from the coal, energy from the electricity, energy from the nuclear resources, energy from the oil crude sources, etc. So that way one has to see how much energy is being produced and then consumed that gives an indication of the country how well it is established or how good it is economically. Consumption of energy and petroleum products is a good indicator of a level of country's economic development. India has one of the lowest per capita energy consumption in the world only 217 kg of oil equivalent. Oil equivalent in the sense actually different sources

of energies are there as I mentioned already electrical energy, coal energy, nuclear energy, hydro energy, wind energy, etc.

So, when you can count all of them with respect to oil if you project that value, so that is known as the kg of oil equivalent. This value is only 15% of the global average of 1470 kg of oil equivalent. Actually, these numbers are up to 2000 or 2010 or something like that. Now these numbers may be slightly better. You can see the recent statistics for that purpose.

Similarly, India's per capita consumption of oil is also very low and it is only 11% of world average. Development is an energy intensive process with rising income and improving literacy levels leading to high consumption of petroleum products and then consumption pattern in India is tilted more towards what petrol, diesel, kerosene, LPG only primarily. This side only our consumption is more. So, we consume more of the LPG and kerosene which are nothing but light and middle distillates of the petroleum refinery products. We also consume diesel which are nothing but high-speed diesels and then gasoline for the transportation.

So, in those directions only we are consuming petroleum crude more but not much. In other terms like you know this petroleum crude may be utilized for production of several types of different organic chemicals. There our utilization is less that is what it means by. Our utilization is more on the LPG, diesel, petrol, kerosene in this context.

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- **Further, oil is one of the most important source of energy because of its**
 - Excellent combustion properties
 - Convenience of handling, storage and transportation
- **India's consumption of petroleum is increasing**
 - Transportation sector is the largest consumer
 - Household sector is next largest consumer (LPG and SKO)
- **India is a petroleum-deficient country and import petroleum products as well crude to meet demands**
 - Import of crude is much greater than import of petroleum products
 - More than 50% of crude processed by Indian refineries has to be imported
 - However, imports of petroleum products will gradually fall with advent of new refineries

Further oil is one of the most important source of energy because of its excellent combustion characteristics that is most important. And then convenience of handling, storage and transportation because it is present in the liquid form so then handling, storage and transportation may not become very difficult.

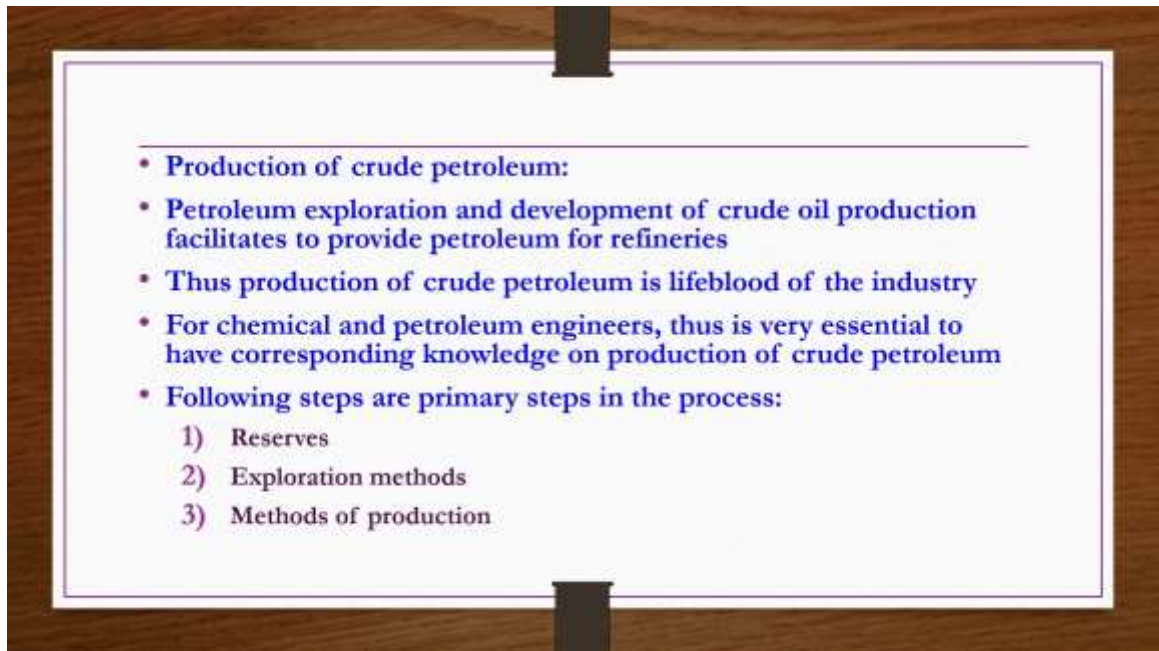
You can take in you know by vehicles also, you can pass through the pipes also you know different possibilities are there, okay? So that should not be an any issue because it is in a liquid form. India's consumption of petroleum is increasing. Transportation sector is the largest consumer from the India's consumption point of view. Household sector is the next largest already mentioned like you know LPG and then superior kerosene oils, etc.

India is a petroleum deficient country and import petroleum products as well crude to meet the demands. Import of crude is much greater than import of petroleum products. We have so many refineries in India. So, what we do? We primarily import crudes rather directly importing the chemicals because if you import the chemicals, individual chemicals you have to import. Whereas if you import the crude from the crude, you do the refining process and then you produce wide spectrum of the products, right? You know not only BTX, ethylene, propylene, etc., huge number of products you can produce from the crude depending on the nature of the crude whether it is naphtha-based crude or paraffin based crude or intermediate based crude.

Based on your intention to produce the products, you have to import such kind of appropriate crudes, right? If you are intending to produce more lubrication kind of product, lubricants kind of product, then you have to import naphthene based crudes. If you are looking to produce more you know diesel, petrol, kerosene, BTX, etc., then you try to import more paraffin-based crude. More than 50% of crude processed by Indian refineries has to be imported.

However, imports of petroleum products will gradually fall with the advent of new refineries.

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- **Production of crude petroleum:**
 - **Petroleum exploration and development of crude oil production facilitates to provide petroleum for refineries**
 - **Thus production of crude petroleum is lifeblood of the industry**
 - **For chemical and petroleum engineers, thus is very essential to have corresponding knowledge on production of crude petroleum**
 - **Following steps are primary steps in the process:**
 - 1) Reserves
 - 2) Exploration methods
 - 3) Methods of production

Finally, we conclude the lecture with the production of crude petroleum. So, production of crude petroleum. Petroleum exploration and development of crude oil production facilitates to provide petroleum for the refineries. Thus, production of crude petroleum is lifeblood of the industry because this crude is not only basic raw material for the refineries to produce diesel, petrol, etc., but also basic raw material for production of a huge number of synthetic organic chemicals. So, it is very essential to do exploration and then production as much carefully as possible. However, you have to pay attention to the economics also. Let us say you find a reserve of crude, but your exploration and then production cost is so much high than whatever the profit you get by selling the crude or processing or refining the crude, then there is no point. So, you have to find reserve such that after exploration and production, you should be able to do refining and then get enough profit.

So, all those points are very essential to consider in the production of crude petroleum, but our course is not completely on petroleum. So, we cannot go into the details of all those exploration and then production methods, but we see a few important points of each of these reserves exploration methods and production methods which are essential for the production of crude petroleum. Following steps are primary steps in the process. One is the reserves, second one is the exploration methods, third one is the methods of production.

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1) Reserves

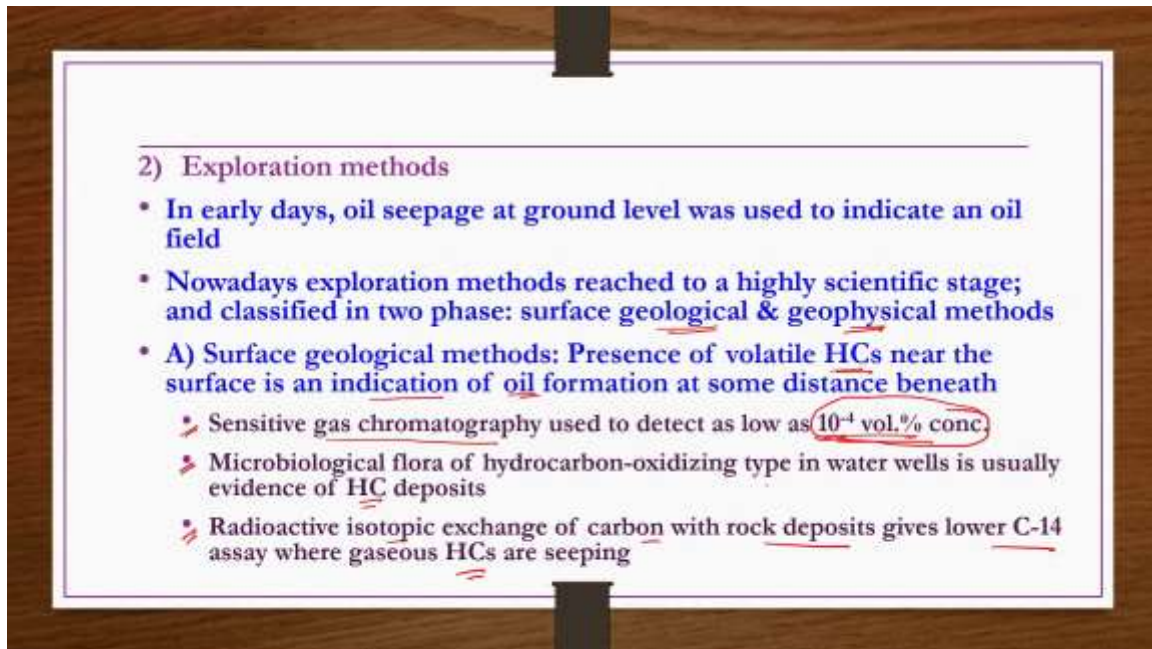
- Reserves are known quantity of crude petroleum
- Expressed in barrels and are available for further processing
- This is similar to inventory of raw materials in other industries
- A constant exploration is carried out on to find new oil fields
- India has prognosticated HC reserves of order of 15-20 billion tons
- About half of which are contained in basins of upper Assam, Cambay and Bombay high
- Only 25% of HCs have been converted into geologically proven reserves
- India's share in total world reserves is negligible (about 0.5% only)

Reserves, reserves are known quantity of crude petroleum expressed in barrels and are available for further processing.

This is something like you know inventory of raw materials for any chemical industry you take. Whatever the reserves that we are calling about petroleum industry, they may be regarded as raw material inventory of any of the chemical industry. A constant exploration is carried out on to find new oil fields in general. India has a prognosticated hydrocarbon reserves of order of 15 to 20 billion tons that is expected one, it may be more than that one or even less than that one also. About half of which are contained in basins of upper Assam and Bombay high. Whatever these reserves that are there, they may not be completely there, but you know your exploration methods has to be advanced so that you can explore and then produce with less cost.

But with the existing technology, we are able to take only 25% of it. Only 25% of hydrocarbons have been converted into geologically proven reserves. So then reserves are important. India share in total world reserves is negligible only 0.5%, very less.

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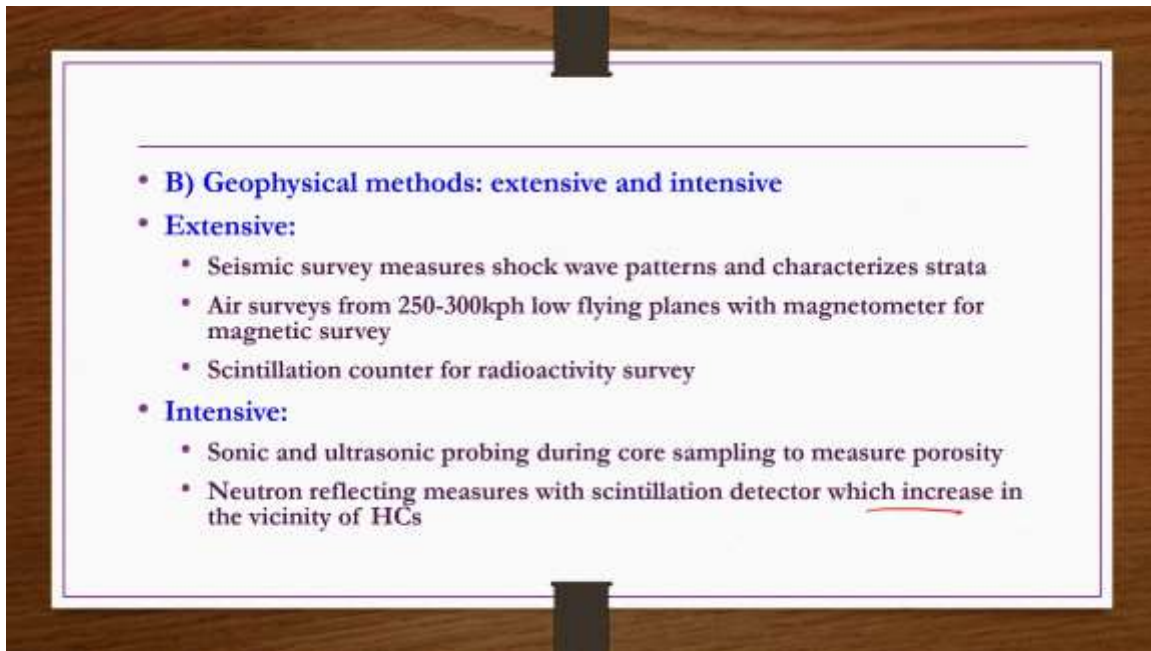


Now next is exploration methods. Once you know there is a reserve or how do you know reserve is there, what quantum of reserves are available that if you wanted to find out then you have to apply these exploration methods.

In early days, oil seepage at ground level was used to indicate an oil field in general. Nowadays exploration methods reach to a highly scientific stage where you can use geological and geophysical methods to explore the reserves. Under surface geological methods, presence of volatile hydrocarbons near the surface is an indication of oil formation at some distance beneath. Sensitive gas chromatography may be used to detect as low as 10^{-4} volume percent concentration of crude is present. That much low concentration crude may also be found by these kind of methods.

Then microbiological flora of hydrocarbon oxidizing type in water wells is usually evidence of hydrocarbon deposits. Then radioactive isotopic exchange of carbon with rock deposits gives lower C_{14} assay where gaseous hydrocarbons are seeping. Like different geological methods may be there. We are just listing them, we cannot go into the details of all the methods because not part of the course.

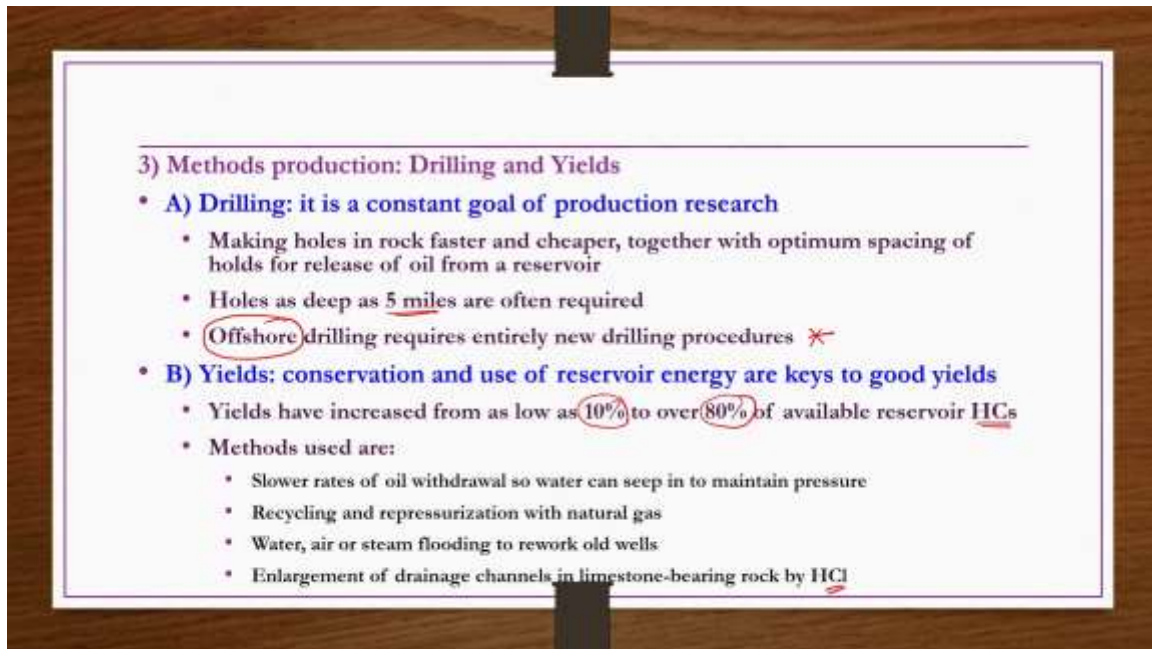
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Second exploration method is geophysical method which is again extensive and intensive. Under the extensive we have seismic survey measures the shock wave patterns and then analyze the strata that is available and accordingly they decide how much reserves are present.

That is one method. Then air surveys from 250 to 300 kilometers per hour low flying planes with magnetometers for magnetic survey also used. Scintillation counter for radioactivity survey that is another method. Under the intensive methods sonic and ultrasonic probing during core sampling to measure porosity is one method. Then neutron reflecting measures with scintillation detector which increase in the vicinity of hydrocarbons is the other ones.

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Finally, methods of production where we have the drilling and yields.

Drilling is the most important part of the petroleum production industry or petroleum industry. Petroleum production industry the terminology we are using that is production of the crude or you know from the reserve taking out the crude whatever the process is that all that we are including under the petroleum industry category whereas the refining and then getting other products we are calling petrochemicals industry. So, in the petroleum industry drilling is very much essential. It is a constant goal of the production research. Making holes in rock faster and cheaper together with optimum spacing of holes for release of oil from a reservoir that is what in general we do in drilling.

Holes as deep as 5 miles are often required. If you have offshore drilling entirely different processes may be needed to apply to find out or to do the required production. Under the yields conservation and use of reservoir energy are keys to good yields. Yields have increased from as low as 10 percent to over 80 percent of available reservoir hydrocarbons thanks to the newer technologies being developed and then still being developed. Methods used are slower rates of oil withdrawal so water can seep in to maintain the pressure. Recycling and repressurization with natural gas, water, air or steam flooding to rework old wells, enlargement of drainage channels in limestone bearing rock by acids like you know hydrochloric acid.

There may be many other methods and then approaches are possible but you know we are not going into the details individual details of these methods. We are going to have a summary of petroleum industry then we are going to talk in detail about the pyrolysis and

then alkylation hydrodealkylation processes with flowcharts etc. But under this class we are looking only at the basics of petroleum production only. Otherwise, whatever the topics that we discussed in today's lecture if you wanted to take you can take this entire as a one particular semester course that much details are present under each of the heading that we have discussed today.

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References for this lecture are presented here. Thank you.